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ORIGINAL ARTICLE

Microwave synthesis of alkyl levulinates using a Keggin heteropolyacid from the cellulose of *Eichhornia crassipes*

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Abstract
Alkyl levulinates were synthesized directly from cellulose derived from water hyacinth (*Eichhornia crassipes*) using a Keggin heteropolyacid under microwave-assisted hydrolysis. The pretreatment method to obtain cellulose was identified as a key factor to achieve higher yields of butyl levulinate. Hydrothermal pretreatment with H_2SO_4 resulted in the highest cellulose yield, with minimal hemicellulose and lignin content, the highest crystallinity index, and reduced water adsorption, all contributing to an increased yield of butyl levulinate. Additionally, the use of longer-chain alcohols, such as pentanol, further enhanced the yield, indicating that solvent polarity significantly impacts on alkyl levulinate production.

Keywords Cellulose · Water hyacinth · Pretreatment · Keggin heteropolyacid · Butyl-levulinate

1 Introduction

Lignocellulosic biomass is a renewable carbon-based feedstock that can be used to obtain fuels and chemicals that would otherwise come from fossilized carbon sources such as petroleum [1, 2]. One of the little explored sources of lignocellulosic biomass is the biomass obtained from water hyacinth, a free-floating aquatic plant native to the Amazon River basin in South America that has spread to more than 50 countries on five continents, has an extremely high growth rate of between 100 and 140 tons of dry material each year, depending on location and time of year. This growth rate is among the highest reported for a wide range of biomass sources [3]. Therefore, the chemical-catalytic route for the valorization of this type of biomass has been at the forefront of biorefinery research, since it is fast, selective, and relatively less energy-intensive [4, 5].

In this regard, among all possible derivatives of lignocellulosic biomass to be used as raw materials for the potential substitution of fuels and petroleum derivatives, levulinic acid (LA) and alkyl levulinates (AL) are the most promising products [1]. Multiple routes exist for producing AL [4, 6–9], from simple biomass-derived products such as LA via esterification in alcoholic medium [4], or furfuryl alcohol (characterized by high yield and selectivity) [5], or 5-hydroxymethylfurfural (HMF) and HMF ether intermediate in alcoholic medium [10, 11], or directly from lignocellulosic biomass, but with limited yield [6].

Table 1 summarizes some works using various substrates and their derivatives resulting from acid hydrolysis using Brönsted catalysts to obtain different types of alkyl levulinates, specifically ethyl and butyl levulinates (EL and BL, respectively) [12, 13]. As can be seen, the use of pure monomeric sugars can offer higher yields compared to lignocellulosic raw materials. Other researchers have explored alkyl levulinate production via the hydrolysis of raw biomass. However, reaction yields towards alkyl levulinates remain

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Table 1 Catalysts, conditions, and yield to ethyl levulinate (EL) and butyl levulinate (BL) from lignocellulosic biomass, derivatives, and carbohydrates

Substrate	Catalyst	Substrate (g)	Catalyst (g)	mL ethanol	Time (h)	T (°C)	Yield (%)	Ref.
Glucose	HTC-Glu-S	1	0.05	15	3	60	97% for EL	[16]
Fructose	HPMo supported on mesoporous carbon CMK-8 and CMK-3	0.1	0.05	5	3	180	72% for EL	[15]
Glucose	HPMo supported on mesoporous carbon CMK-8 and CMK-3	0.1	0.05	5	3	180	64% for EL	
Sucrose	HPMo supported on mesoporous carbon CMK-8 and CMK-3	0.1	0.05	5	3	180	53% for EL	
Fructose	HPMo supported on mesoporous carbon CMK-8 and CMK-3	0.1	0.05	5	3	180	66% for EL	
Glucose	HPMo supported on mesoporous carbon CMK-8 and CMK-3	0.1	0.05	5	3	180	42% for EL	
Sucrose	HPMo supported on mesoporous carbon CMK-8 and CMK-3	0.1	0.05	5	3	180	53% for EL	
Commercial cellulose	HSiW	1	0.2	30	4	200	77% for EL	[17]
Biomass-derived levulinic acid substrate	$H_{14}NaP_5W_{30}O_{110}$ immobilized on silica matrix	0.6	0.1	3	24	78	61% for EL	[18]
Biomass-derived levulinic acid substrate	HTC-Cellulose-S	0.116	0.05	3	3	60	89% for EL	[16]
Biomass-derived levulinic acid substrate	HTC-PC-S	0.116	0.05	3	3	60	92% for EL	
Pine needle	Sulfonated coal	2	0.2	10	8	80	96% for EL	[19]
Sugarcane bagasse	C-SO_3H	0.3	0.3	15	9	120	88% for EL	[16]
Sugarcane bagasse	SB-SO_3H	0.3	0.3	15	9	120	68% for EL	
Sugarcane bagasse	AC-SO_3H	0.3	0.3	15	9	120	48% for EL	
Biomass-derived levulinic acid substrate	NS-FCM	1	0.05	4	8	120	72% for EL	[20]
Biomass-derived levulinic acid substrate	S-FCM	1	0.05	4	6	150	69% for EL	
Biomass-derived levulinic acid substrate	SO_4/SnO_2	116	2.5	294	5	70	44% for EL	[21]
Biomass-derived levulinic acid substrate	Se-40WS/D	0.2	0.02	7.5	10	78	76% for EL	[22]
Biomass-derived furfuryl alcohol substrate	SO_4/TiO_2	1	0,1	20	2,5	200	68% for EL	[23]
Biomass-derived furfuryl alcohol substrate	SeAl-TUD-1	0.03	10	1	24	140	80% for EL	[24]
Biomass-derived furfuryl alcohol substrate	S-ZSM-5	0.4	0.1	12.3	6	120	86% for EL	[25]
Biomass-derived furfuryl alcohol substrate	S-GO	0.4	0.1	12.3	6	120	96% for EL	
Wheat straw	H_2SO_4	19.8	19.8	19.8	0,6	183	18% for EL	[26]
Paper pulp	H_2SO_4	50	12.1	319	1,7	190	26% for EL	[27]
Wood chips	H_2SO_4	50	12.1	319	1,7	190	17% for EL	
Switch grass	H_2SO_4	50	12.1	319	1,7	190	14% for EL	
Furfural residues	H_2SO4	1	0.02 + 0.6 zeolite USY	26	1,8	219	19% for EL	
Corn stover	H_2SO4	2	0.84	38	0,5	190	6% for EL	
Corn stover	H_2SO4	2	0.84	38	0,5	190	16% for EL	

Table 1 (continued)

Substrate	Catalyst	Substrate (g)	Catalyst (g)	mL ethanol	Time (h)	T (°C)	Yield (%)	Ref.
Bamboo	H_2SO_4 / Al(OTf)3	20	0.98 g/ 0.95 g	1000	3	180	54% for EL	[28]
Paper pulp	H_2SO_4 / Al(OTf)3	20	0.98 g/ 0.95 g	1000	3	180	65% for EL	
Pine wood	H_2SO_4 / Al(OTf)3	20	0.98 g/ 0.95 g	1000	3	180	54% for EL	
Eucalyptus	H_2SO_4 / Al(OTf)3	20	0.98 g/ 0.95 g	1000	3	180	46% for EL	
Rice straw	H_2SO_4 / Al(OTf)3	20	2.94 g/ 0.95 g	1000	3	180	34% for EL	
Bagasse	H_2SO_4 / Al(OTf)3	20	2.94 g/ 0.95 g	1000	3	180	65% for EL	
Corn stalk	H_2SO_4 / Al(OTf)3	20	2.94 g/ 0.95 g	1000	3	180	45% for EL	
Commercial cellulose	H_2SO_4	0.5	0.126	25	0.5	200	50% for BL	[29]
Commercial cellulose	H_2SO_4 / $Cs_2HPW_{12}O_{40}$	0.5	0.125/0.2	25	0.5	200	13% for BL	
Mesocarp fiber	[BSMim]H_2SO_4	1.62	0.05	20	1.4	130	15% for BL	[30]
Commercial cellulose	$[C_4H_8SO_3Hmim]HSO_4$	1.62	0.05	20	0.75	180	31% for BL	

low, and certain reaction conditions such as temperature and time are excessively high [14–19]. The best yields are obtained with Bronsted acid where the temperature and amount of cellulose are the principal variables for obtaining a higher yield towards alkyl levulinates.

Thus, an important aspect to consider is the dissolution of cellulose, which is inherently insoluble under standard conditions [31]. Processes used for this purpose generally involve either low [32]. or high temperatures [33] high-pressure environments (such as supercritical conditions) [34], aggressive solvents like concentrated mineral acids [35], solvent mixtures [36], or specific techniques like microwave heating [37], intense gravitational fields, or ultrasonic fields [38].

The hydrothermal liquefaction (HTL) process breaks down biomass in hot, pressurized water or organic solvents (such as alcohols, polyols like ethylene glycol [39], or acetone) [40] in the presence of acid catalysts. Temperature plays a crucial role in this process. During liquefaction, cellulose undergoes bond cleavage (C-C and C-O), initiated by solvent radicals generated at high temperatures [41]. Operating temperatures typically range between 250 and 400 °C, with pressures from 5 to 20 MPa. Reaction times can vary from 10 min to 24 h [40].

Microwave-assisted liquefaction of cellulose offers reduced time and energy consumption [42], enabling effective dissolution and depolymerization under milder reaction conditions [43–45]. When microcrystalline cellulose is liquefied in water under acidic conditions, the main products are 5-hydroxymethylfurfural and levulinic acid. At temperatures of 120 °C and 150 °C, nearly complete selectivity is achieved; however, at 180 °C, selectivity decreases, and glucose appears in the product mixture [46].

Thus, to evaluate these two variables in the production of alkyl levulinate from water hyacinth, we studied the effect of different hydrothermal pretreatments on the lignocellulosic biomass to obtain cellulose. Depending on the type of cellulose obtained, it is expected that the yield of alkyl levulinate will be improved. The celluloses were submitted to acid-assisted hydrolysis using a Keggin heteropolyacid and microwave heating.

2 Materials and methods

2.1 Materials

Chemicals such as ethanol, propanol, butanol, pentanol, and Keggin heteropolyacid ($H_3PW_{12}O_{40}$) were purchased commercially. Water hyacinth samples were collected in the north and south cooling pools of the "Termopaipa" thermoelectric plant located in the municipality of Paipa, Boyacá, Colombia (N °5 46' 8.3'' W 73° 08' 40.3''). The drying process of the samples (leaves and stems of water hyacinth) was carried out at room temperature. Once this stage was completed, the particle size of the material was reduced using a high-speed multifunction grinder HC-150, followed by a sieving process with a Tyler # 30 sieve until a particle size of 500 µm was obtained.

2.2 Cellulose obtained using different hydrothermal pretreatments

The samples of *E. crassipes* were submitted to three pretreatments. (i) Hydrothermal at 121 °C, (ii) hydrothermal in the presence of 2% NaOH, and (iii) hydrothermal in the presence of H_2SO_4. The untreated sample was considered as the control.

The hydrothermal pretreatment was performed as described by Rabemanolontsoa in 2016 [47]. In a 250 mL Erlenmeyer, 5 g of the sample free of extractable products of pulverized water hyacinth was added along with 100 mL

of distilled water. Then, it was brought to a temperature of 121 °C in an autoclave for 1 h. Filtration was carried out with a filter of known weight using distilled water. The hydrothermal procedure was similar to the one described earlier, but it included 2% NaOH solution at a 1:20 ratio [48] or 2% H_2SO_4 acid solution at a 1:20 ratio. The samples were washed with distilled water until pH = 7.0. All the pretreated samples of *E. crassipes* were dried in a Memmert UN75 universal oven at 105 °C for 48 h and weighed again to determine their final weight. The process was carried out in triplicate.

To obtain bleached cellulose, an additional treatment with a 1.5% w/v glacial $NaClO_2/CH_3COOH$ solution was applied to the samples obtained with each of the pretreatments. The ratio of the treated water hyacinth biomass mass solution to the $NaClO_2/CH_3COOH$ solution was 1:20. The mixture was heated in a water bath at 75 ◦C for 2 h. During the 2-h period, the pH was maintained at around 4.0. The samples were washed abundantly until a neutral pH was reached. If the sludge obtained was not pure white, the addition of the $NaClO_2$ and glacial CH_3COOH mixture was repeated. The final white samples were dried in a Memmert oven at 40 °C for 48 h [49].

2.3 Physicochemical properties of *Eichhornia crassipes* cellulose

The procedure for determining the amount of extractable, holocellulose, cellulose, and lignin was developed according to the protocols of the TAPPI T 204 os-46 standard [35–38].

The ATR infrared spectra of cellulose extracted from water hyacinth were obtained using a Nicolet IS50 analytical FTIR spectrometer. XRD patterns were recorded using a Malvern Panalytical Empyrean 2012 X-Ray Diffractometer, with Pixel 3D detector and Cu source (λ = 1.5453) at 45 kV and 40 mA. The step was 0.02° and the time per step was 50 s. The crystallinity index (% ICr) of the obtained cellulosic material was determined by Eq. (1) or Segal method [50].

$$\% IC_r = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

where, I_{002} is the maximum intensity of the grating diffraction peak 002 (I_{002}) and I_{am} is the minimum intensity scattered by the amorphous part of the sample (I_{am}) [50, 51].

Scanning electron microscopy (SEM) samples mounted on conductive tape and coated with palladium gold were run on JEOL JSM-6490LV scanning electron microscope, using a voltage of 20 KV [52]. Finally, thermal analyses of the cellulose samples were performed using a differential scanning calorimeter and a Setaram 1600 thermogravimetric analyzer. Temperature conditions ranged from 0 to 400 °C with a ramp of 5 °C/min and a nitrogen flow of 50 mL/min.

2.4 Synthesis of alkyl levulinates

Butyl levulinate synthesis was used as a test reaction. The reactions were conducted using an Anton Paar Monowave 400 microwave reactor. Briefly, 0.3 g of water hyacinth cellulose, 0.15 g of heteropolyacid, 2 mL of anhydrous butanol, 2 mL of chloroform, and 0.5 mL of octane as internal standard were added to the sealed reactor. The mixture was then heated to 170 °C with agitation at 300 rpm for up to 90 min. After the reaction, the reactor was rapidly cooled under cold water, and the product was collected. Separation of the liquid-solid mixture was achieved using a Power Spin LX Centrifuge. This same procedure was used with ethanol, isopropanol, and pentanol to study the effect of alcohol. Reaction monitoring was conducted via gas chromatography using a Shimadzu 2014 chromatograph with an SPB-1 column (30 m, 32 mm, 1.00 µm), equipped with an FID detector [27]. The moles (n_{AL}), grams (g_{AL}), and yield (% Y_{AL}) of alky levulinates were calculated using Eqs. (2)–(4):

$$n_{AL} = \frac{C_{AL} \times V_s}{1000} \quad (2)$$

$$g_{AL} = n_{AL} \times M_{AL} \quad (3)$$

$$\% Y_{AL} = \frac{g_{AL}}{g_{cell}} \times 100 \quad (4)$$

where C_{AL} is the initial concentration of alky levulinate calculated with a calibration curve with internal octane standard. Vs is the volume of reaction solution in mL. g_{cell} are the grams of cellulose, and M_{AL} is the molar mass of AL.

3 Results and discussion

3.1 Yield and physicochemical properties of cellulose from *water hyacinth*

The chemical composition of water hyacinth on a dry basis for each of the celluloses obtained from three pretreatments is given in Table 2. It can be seen that the hydrothermal treatment only slightly increases the cellulose content compared with untreated samples. However, the pretreatment with H_2SO_4 led to a higher content of cellulose, followed by NaOH pretreatment. It is important to indicate that the effectiveness of each pretreatment will depend on the lignin content [53]. Thus, the lignin content decreased in the 2% H_2SO_4 and 2% NaOH samples, which was not the case in the hydrothermal pretreatment. The cellulose, hemicellulose,

Table 2 Chemical composition on dry basis of water hyacinth pretreated by different methods and crystallinity index (CrI) obtained by XRD with Segal method [50]

Percentage (%)	Untreated	Hydrothermal	2% NaOH	2% H_2SO_4
Moisture	7.79 ± 0.12	7.79 ± 0.12	7.79 ± 0.12	5.69 ± 0.15
Ashes	7.87 ± 0.002	7.87 ± 0.002	7.87 ± 0.12	5.28 ± 0.17
Cellulose	23.73 ± 0.12	31.27 ± 0.91	51.50 ± 0.73	69.77 ± 0.54
Hemicellulose	44.46 ± 0.75	33.49 ± 0.82	23.04 ± 0.98	10.19 ± 0.11
Lignin	14.35 ± 0.87	14.35 ± 0.08	9.81 ± 0.08	9.59 ± 0.07
Extractables	2.39 ± 0.15	4.77 ± 0.30	0.56 ± 0.054	0.41 ± 0.015
CrI	25	26	56	65

and lignin contents of the samples used in the acidic and basic pretreatments are in agreement with those reported by other authors [43–45]. Extractable products [54] were also successfully removed with NaOH or H_2SO_4 pretreatment.

Figure 1 displays the ATR-FTIR spectra of purified cellulose, whose bands for the different pretreatments are similar. However, in the untreated samples a decrease in the broad absorption band in the range of 3500–3000 cm^{-1} with the pretreatment with NaOH, and H_2SO_4 is observed. This band is attributed to OH-stretching vibrations and is related to surface moisture absorption [55], which is associated with a decrease in the band at 1640 cm^{-1} due to the removal of most of the hemicelluloses [56, 57] that were not removed with a hydrothermal pretreatment. Similarly, the band between 1200 and 900 cm^{-1} decreases with the chemical pretreatments. This indicates a surface modification in the cellulose from raw material. The bands at 1367, 1321, and 1246 cm^{-1} are characteristic of type I cellulose [58–62]. Additionally, some characteristic bands of hemicellulose and lignin remain in the sample after the purification process. They are mainly at 1735 cm^{-1} and are associated with the C = O stretching band of residual hemicellulose or the ester linkage of the carboxylic group of ferulic and *p*-coumaric acids in lignin.

The XRD patterns of untreated and treated samples are shown in Fig. 2. It can be seen that in both cases the XRD patterns of celluloses are similar. However, the XRD patterns of cellulose treated with 2% NaOH and 2% H_2SO_4 showed the disappearance of the signal at 14.3° and the peak displacement from 21.9° to 20.8°, which could be associated with the conversion of cellulose I to cellulose II. This fact is due to the rearrangement of natural cellulose chains after alkali treatment [55] or acidic treatment [63]. Besides, these treated samples have a crystallinity index higher than that of the untreated and hydrothermally treated samples, as can be seen in Table 2.

Figure 3 presents the derivative thermogravimetric (DTG) curves of the cellulose obtained from 50 to 400 °C. For all samples, a small initial weight loss at 50–125 °C was attributed to the evaporation of physically adsorbed water [64]. The second region in DTG curves is observed from 225 °C to 335 °C. This region refers to the volatilization and decomposition of other low molecular weight organic compounds, such as extractives, and the decomposition of hemicellulose at 290 °C [65, 66]. The loss between 320 and 330 °C is due to the decomposition of cellulose chains by depolymerization, dehydration, and decomposition reactions [67]. Some differences can be observed in the pretreatments with NaOH and H_2SO_4, indicating that cellulose degradation is faster in these samples.

The differential scanning calorimetry (DSC) thermogram in Fig. 4 exhibits a first endothermic peak before 100 °C

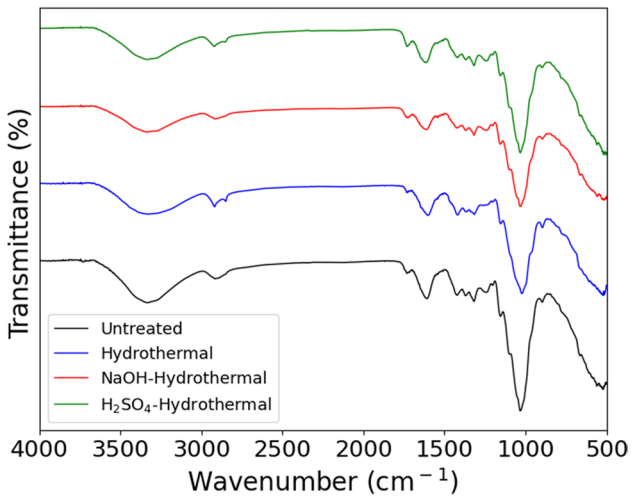


Fig. 1 FTIR spectra of purified cellulose from water hyacinth obtained from hydrothermal pretreatments

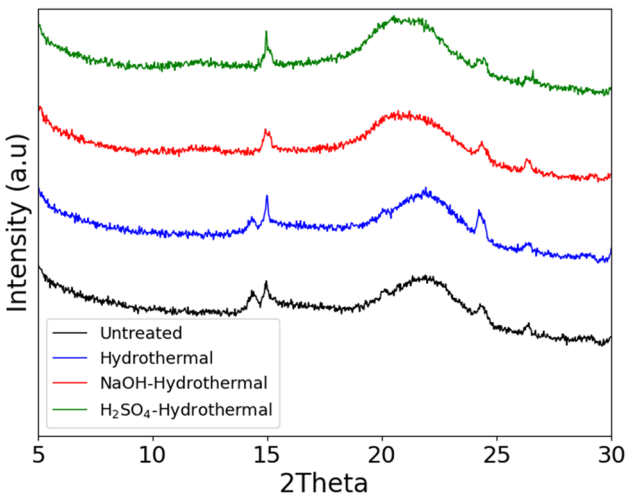


Fig. 2 X-ray diffraction patterns of the cellulose from water hyacinth obtained from hydrothermal pretreatments

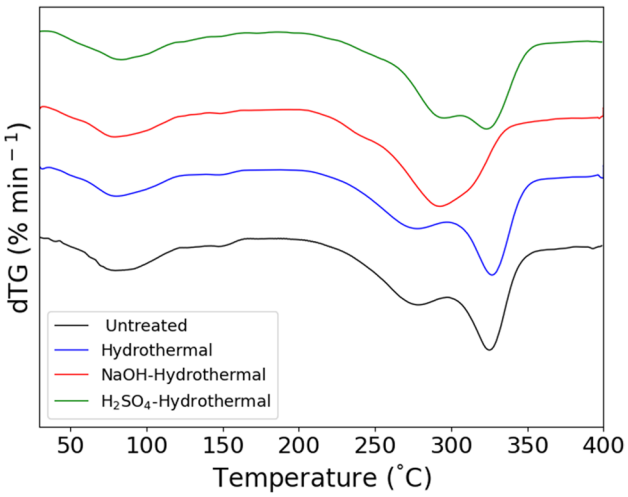


Fig. 3 Derivative thermogravimetric (DTG) curves of the cellulose from water hyacinth obtained from hydrothermal pretreatments

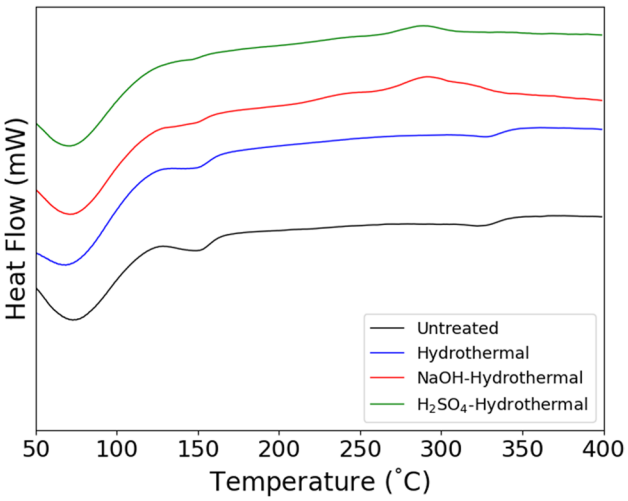


Fig. 4 Differential scanning calorimetry (DSC) thermogram of the cellulose from water hyacinth obtained from hydrothermal pretreatments

in all samples. This change is attributed to water desorption. The pretreatment with H_2SO_4 and NaOH led to water desorption at a lower temperature, confirming that the cellulose structure had been modified with these pretreatments. Besides, the absence of the endothermic peak at 150 °C in these samples could be associated with a smaller presence of crystalline water inside the cellulose structure [68, 69]. This could also be associated with a higher removal of hemicelluloses, which are responsible for higher water adsorption. The broad exothermic peak around 290 °C can be attributed to partial pyrolysis due to the fragmentation of carbonyl and carboxylic bonds from anhydrous glucose units giving carbon or monoxide carbon [69, 70].

The morphological changes in bleached cellulose resulting from various pretreatments applied to water hyacinth biomass are depicted in Fig. 5. Although fiber separation was not achieved in all pretreatments, there is a notable difference among the celluloses obtained from pretreatments with NaOH, distilled water, H_2SO_4, compared with the cellulose obtained with the untreated sample. The fiber appears somewhat smoother, especially in the cellulose resulting from the NaOH pretreatment. However, in the celluloses after acidic pretreatments with H_2SO_4, the fiber structure exhibits a more severe disruption, leading to increased surface roughness. This roughness is caused by the removal of lignin, which covers the outer surface of the water hyacinth (*E. crassipes*) cellulose cell wall, leaving the fiber surface more exposed.

3.2 Alkyl levulinates from cellulose obtained from water hyacinth

Applying microwave heating induced the liquefaction of cellulose to alkyl levulinate. Lignocellulosic materials are converted into low-molecular-weight soluble components. Cellulose is primarily a biopolymer composed of six-carbon sugars, which can be transformed into various organic compounds, including oligosaccharides, monosaccharides, sugar-derived furfurals, furfural degradation products, and acetic acid. Figure 6 summarizes the reactions involving acid- and heat-catalyzed hydrolysis of the cellulose fraction to alkyl levulinate produced from this process through the direct esterification of the acid in the presence of the corresponding alcohol [71].

Figure 7 depicts the yields of butyl levulinate from microwave-assisted reactions of celluloses obtained through different pretreatments up to 90 min using a Keggin-type HPA ($H_3O_{40}PW_{12}$) as an acid catalyst. The Bronsted sites of the heteropolyacid are responsible for effectively promoting the conversion of cellulose to butyl levulinate. The yield trend to BL follows the order of cellulose obtained from the pretreatments with H_2SO_4, NaOH, the hydrothermal one, and the untreated sample. This order is dependent on the cellulose characteristics and suggests that cellulose with the highest ICr, less adsorbed water, lower hemicellulose content, and a smaller proportion of extractives could favor butyl levulinate production, effectively promoting cellulose hydrolysis.

It has been reported that a higher crystallinity of cellulose favors the formation of alkyl levulinates [72, 73]. The acidic and alkaline pretreatments increase crystallinity, but do so differently, influencing the removal of hemicelluloses and lignin [74]. The delignification with H_2SO_4 is because H^+ can preferentially degrade the cellulose of the amorphous fraction [47], while the alkaline treatment increases the % CrI value mainly due to a removal of xylans [67, 75].

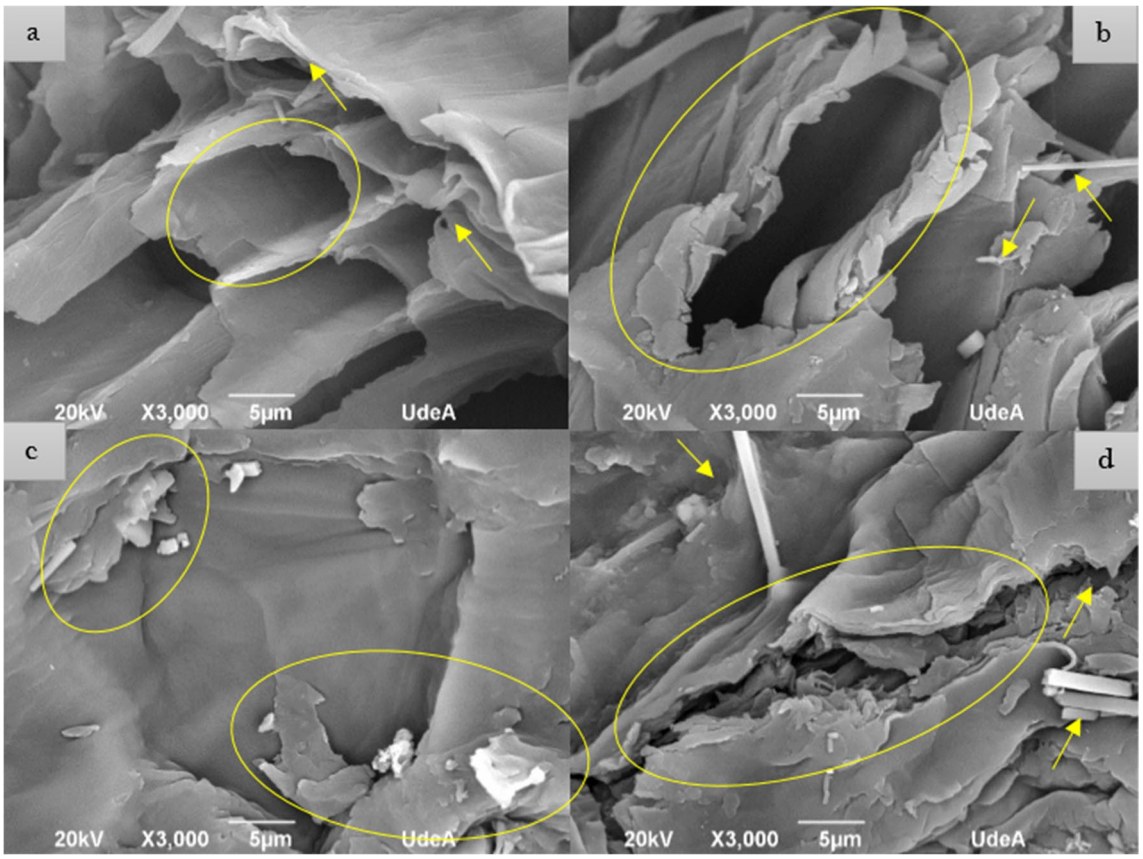


Fig. 5 SEM images of cellulose derived from water hyacinth biomass at 3000X: **(a)** Untreated, **(b)** Hydrothermal, **(c)** NaOH-Hydrothermal, **(d)** H_2SO_4-Hydrothermal

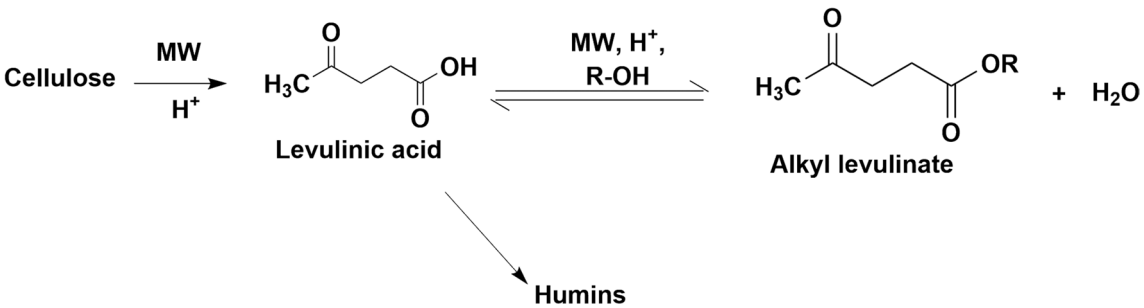


Fig. 6 Scheme of the esterification reaction of water hyacinth cellulose with alcohols

It has been reported that acid pretreatments with H_2SO_4, at an acid concentration generally between 0.5 and 6% w/w, lead to a higher solubilization of hemicellulose [76, 77]. Besides, a decrease in the percentage of extractable compounds, and a lower moisture content in the sample would favor the accessibility of the catalyst to the cellulose and consequently give the highest yield of alkyl levulinates [78, 79].

The hydrothermal pretreatment with NaOH is insufficient to cause an effective removal of hemicellulose and lignin binders from cellulosic surfaces. Therefore, this may be the reason for surface moisture absorption in the celluloses obtained with these pretreatments, as was seen by FTIR and thermal analyses. This characteristic could be responsible for the lower yield to BL.

Figure 8 shows the reaction of cellulose obtained by hydrothermal pretreatment with 2% H_2SO_4 using different alcohols (ethanol, propanol, butanol, pentanol), under the same reaction conditions. This cellulose was chosen due to the highest yield to butyl levulinate. It can be seen that the use of short-chain

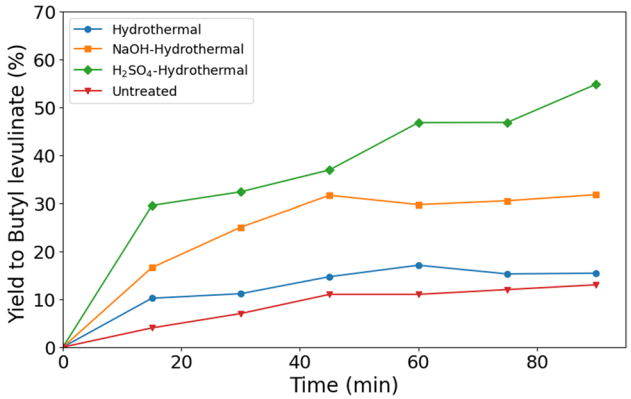


Fig. 7 Yield to butyl levulinate of the cellulose from water hyacinth obtained from hydrothermal pretreatments

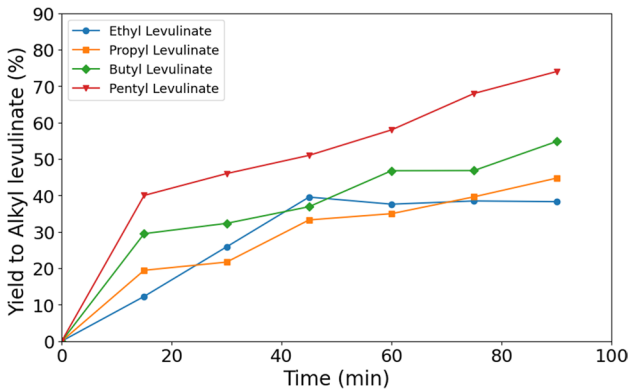


Fig. 8 Yield of alkyl levulinates for water hyacinth cellulose obtained from H_2SO_4-hydrothermal treatment

alcohols results in a lower concentration of their corresponding alkyl levulinates, being higher with pentanol, suggesting that a change in the polarity of the solvent increases the yield to alkyl levulinate. Cellulose is insoluble in H_2O and typical organic solvents [66–68], due to the presence of a highly crystalline structure with extensive intra- and intermolecular hydrogen bonds [80] and can only dissolve if the intra- and intermolecular hydrogen bonds are effectively broken. However, increasing the temperature as well as the acidity of the reaction medium favors both the hydrolysis and dissolution of cellulose [81]. Thus, this process affects the supramolecular structure of cellulose and enhances interfibrillar swelling, weakening the intermolecular hydrogen bonds between cellulose microfibrils and loosening the packing. As a result, the accessibility of chemical reagents to the molecules is improved [82]. This aspect is also essential for the recovery of heteropolyacids, which is currently being studied by us.

To verify the effect of microwave heating, a control experiment was conducted following the methodology of Wang et al. [17]. The reaction was performed in a stainless-steel high-pressure reactor under 0.25 MPa of nitrogen atmosphere, using 0.3 g of water hyacinth cellulose, 0.15 g of heteropolyacid, and 2 mL of anhydrous butanol. The yield of ethyl levulinate obtained at 170 °C after 1 h of reaction was 19%. In contrast, when microwave heating was used without a nitrogen atmosphere, the yield of ethyl levulinate increased to 25% at 170 °C.

Based on a simple calculation, the energy consumption (kWh) per gram of alkyl levulinate produced from cellulose at 170 °C was determined for 1 h of reaction using both microwave and batch reactors. Energy consumption was lower for levulinate production from cellulose using microwaves (0.8 kWh/g_{AL}). However, the energy required per gram of alkyl levulinate produced was significantly higher in the batch reactor (2.94 Kwh/g_{AL}).

4 Conclusions

The study highlights the effectiveness of different pretreatments on *E. crassipes* to obtain cellulose and, by acid hydrolysis, produce butyl levulinate (BL) using a Keggin-type heteropolyacid (HPA) as a catalyst. The results indicate cellulose pretreated with 2% H_2SO_4 yields the highest amount of BL, followed by NaOH, hydrothermal pretreatments, and untreated cellulose. This trend is attributed to the varying characteristics of cellulose obtained through these pretreatments, such as higher crystallinity, lower water content, and a lower amount of hemicellulose and extractives. The findings suggest that enhancing the crystallinity and reducing impurities in cellulose can significantly improve its conversion to alkyl levulinates. Additionally, the study underscores the importance of acid and alkaline pretreatments in modifying cellulose structure to favor hydrolysis and subsequent BL production. Besides, longer-chain alcohols such as pentanol increased the yield to alkyl levulinate, suggesting that solvent polarity plays a crucial role.

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Declarations

Conflict of interest The authors declare no conflicts of interest.

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