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One Step Catalytic Conversion of Polysaccharides in *Ulva prolifera* to Lactic Acid and Value-Added Chemicals

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Abstract: The production of lactic acid and value-added chemicals (such as hydroxypropanone, glycolic acid, and formic acid) directly from *Ulva prolifera* via one-step catalytic process was studied. The effect of different amounts of YCl_3-derived catalysts on the hydrothermal conversion of carbohydrates in *Ulva prolifera* was explored, and the reaction conditions were optimized. In this catalytic system, rhamnose could be extracted from *Ulva prolifera* and converted in situ into lactic acid and hydroxypropanone at 160 °C, while all the glucose, xylose, and rhamnose were fractionated and completely converted to lactic acid at 220 °C or at a higher temperature, via several consecutive and/or parallel catalytic processes. The highest yield of lactic acid obtained was 31.4 wt% under the optimized conditions. The hydrothermal conversion of *Ulva prolifera* occurred rapidly (within 10 min) and showed promise to valorize *Ulva prolifera*.

Keywords: *Ulva prolifera*; lactic acid; hydrothermal conversion; catalyst; YCl_3

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1. Introduction

Nowadays, fossil resources are increasingly depleting, and their excessive use also brings many environmental problems [1–6]. As a renewable resource, biomass has been widely concerned for and studied by researchers [7–11]. The conversion of biomass resources to valuable products attracted more and more attention due to its ability to reduce carbon dioxide emission [12–14]. Algae is one of the primary raw ingredients of the third-generation biomass, which has a great development potential and advantages in the field of green and sustainable energy [15,16]. Algal biomass has advantages such as no competition with land crops, a short growth cycle, and the impact to reduce carbon dioxide emissions [17]. In recent years, algae disasters in several seas and lakes in China have become more serious [18]. A large number of algae have grown crazily, consuming oxygen, releasing toxins, causing the death of many aquatic organisms, endangering people's health, and seriously affecting the local economic development and ecological balance [19]. In addition, the traditional treatment method of algae focuses on catching, and some of the algae collected are directly discarded, which pollutes the environment and wastes considerable biomass resources [20]. Therefore, it is of great research significance to utilize the abundant natural algae in the "water bloom" phenomenon caused by water pollution and eutrophication as biomass resources, which not only alleviates the environmental pressure but also obtains fuels or valuable chemicals [21,22]. Similar to other algae, carbohydrates, lipids, and proteins are the main components of *Ulva prolifera* [23]. Niyam et al. [24] assessed the monthly variation and optimized the yield of reducing sugar from *U. prolifera* by the thermochemical method and obtained high reducing sugar (0.152 ± 0.009 g/gdw) and fermentative bioethanol yield (6.275 ± 0.161 g/L). Li et al. [25] used an environment-friendly pretreatment method by hydrogen peroxide and improved the efficiency of enzymatic hydrolysis, where the maximum reducing sugar yield (0.42 g/g UPR) and the rate of conversion of reducing sugar in the concentrated hydrolysates to bioethanol (31.4%) were obtained. Niyam et al. [26] also established the modelling of fermentative bioethanol production from *U. prolifera* biomass by an integrated ANN-GA approach, and obtained the maximum experimental bioethanol yield (0.242 ± 0.002 g/g RS) by applying ANN-GA which was very close to the predicted value (0.239 g/g RS). In addition, *U. prolifera* could be used to produce rhamnose with a mixture of furfurals by using homogeneous and heterogeneous catalysts with hydrothermal conditions [21,27].

As an important industrial product, lactic acid (LaA) is considered to have a large and rapidly growing market due to its attractive and value-added multifunctional properties, particularly in the polylactic acid (PLA) industry [28–32]. Recently, PLA has shown great potential for replacing petroleum-based plastics in medical and clinical applications due to its exceptional mechanical properties, biocompatibility, and biodegradability [33]. For example, polylactic acid (PLA) is obtained from polymerization of lactic acid, which can be spun into threads by drawing silk [34]. This kind of thread is a good surgical suture, which can automatically degrade into lactic acid and later could be absorbed by the human body without removing stitches after the stitches are healed, without adverse consequences [35]. With regards to in vivo operation suture, it is especially free from the trouble of second operation suture [36]. The polymer compound could also be used as an adhesive in bone grafting and organ transplantation [37]. However, due to the high price of precursor materials (LaA), PLA has a high production cost, which hindered its large-scale development, resulting in a big gap between the actual output and production capacity [38]. Therefore, it is necessary to find innovative strategies for developing LaA production, particularly from renewable biomass feedstock [34]. Currently, edible crops and pure sugars (glucose, starch, sucrose, etc.) are mainly used for LaA production [39]. However, the use of them as ingredients leads to competition with human food inevitably [40]. Lactic acid can also be synthesized by the traditional chemical synthesis method, but this method requires strong acid, which has great influence on the environment and equipment [31]. In previous work, considerable efforts had been made to find methods to produce LaA from biomass feedstocks, and the advantages and disadvantages of typical methods reported are shown in Table S1 [37,41–43]. Most studies in the literature use solid catalysts to catalyze the conversion of biomass to produce lactic acid. Although solid catalysts can produce a relatively high yield of lactic acid, and the separation is facilitated, there are also some intensive mass transfer resistances due to the fact that actual biomass is usually in a solid state, thus the process efficiency is reduced. The carbohydrates in *Ulva prolifera* are mainly the mixed polymer of rhamnose, glucose, and xylose [44,45]. In our previous study, Xu et al. developed a comprehensive catalytic strategy using YCl_3 as the catalyst precursor to convert cellulose and hemicellulose components in terrestrial corn stover, which consisted of hemicellulose, cellulose and lignin as the main components at the same time, and selectively generate LaA with a yield of 66.3% [41]. *U. prolifera* is rich in carbohydrates, which are suitable to produce valuable chemicals [46]. However, at present, there are no studies available on the direct one-step hydrothermal conversion of *U. prolifera* into lactic acid. This method of producing lactic acid might be suitable for sustainable development and environment protection, and has great research potential. Based on the previous findings, this work explored the effect of the YCl_3-derived catalysts on the extraction and transformation of polysaccharides in aquatic *U. prolifera* to LaA and value-added chemicals, such as hydroxypropanone, glycolic acid, and formic acid, over the temperature range of 160−280 °C. The impact of different parameters on the transformation of *Ulva prolifera* were studied.

2. Materials and Methods

2.1. Materials

Yttrium (III) chloride hexahydrate (99.99%) was purchased from Shanghai Adamas-Beta and used as received. The *Ulva prolifera* was obtained from Shandong Province (China). The sample was dried in an oven for 24 h at 80 °C and ground into powder (<40 mesh). The elemental and biochemical composition analyses of *U. prolifera* were performed based on our previous work [27].

2.2. Hydrothermal Experiments of *Ulva prolifera*

For a typical experiment, the dried *U. prolifera* sample (1 g) and 100 mL of deionized water were placed in a 250-mL stainless-steel autoclave reactor. Then nitrogen was purged in the reactor to replace air for 3 min at 2.0 MPa. The experiments were performed at 160–280 °C with stirring (400 rpm) and maintained for 1 h. The reaction mixture was poured out from the reactor after the reaction and was filtered to separate the solid residue from the liquid phase. Each experiment was repeated 3 times and the results were averaged. The average and standard deviation of the data in Figures 1–4 and Figures S1–S3 are listed in Tables S6–S12.

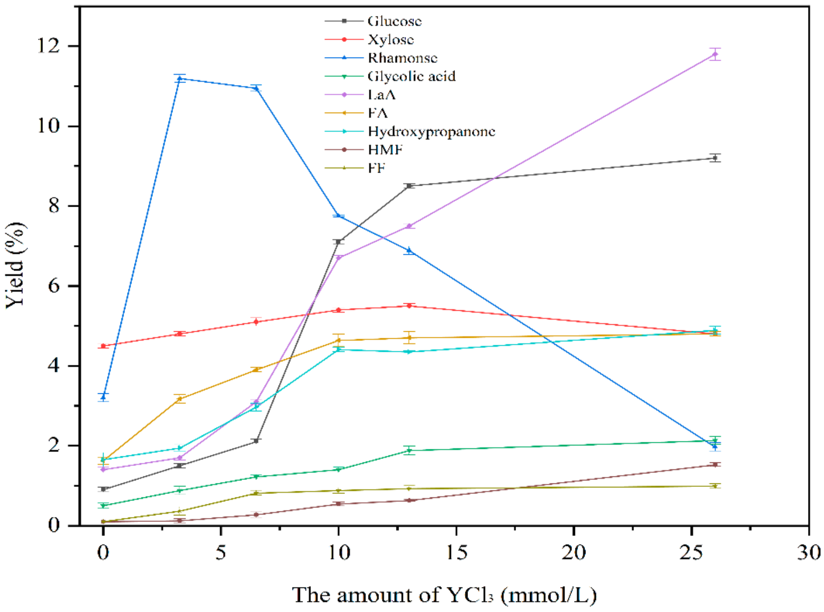

Figure 1. Yields of small molecular products from hydrothermal conversion of *U. prolifera* with different amount of YCl_3. Reaction conditions: 1.0 g of *U. prolifera*, 100 mL water, 160 °C, 2 MPa N_2, 1 h.

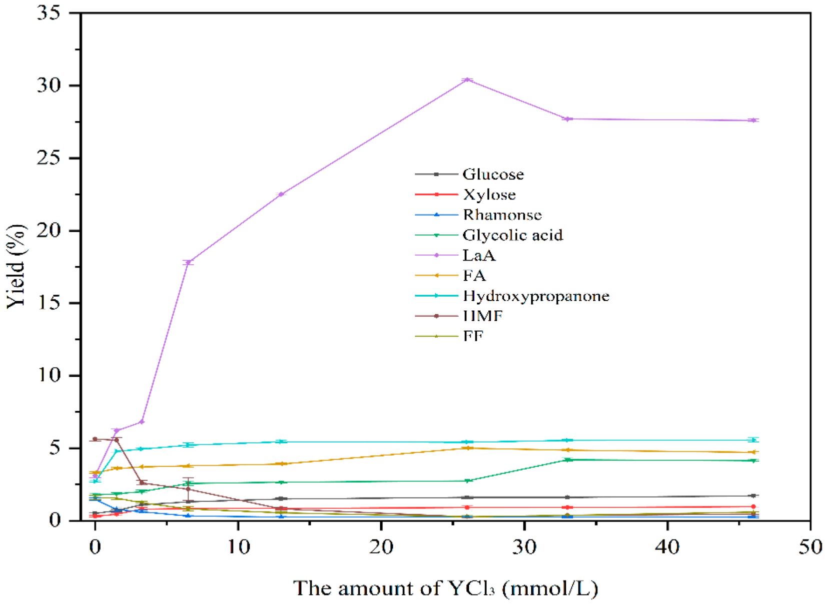

Figure 2. Yields of small molecular products from hydrothermal conversion of *U. prolifera* with different amount of YCl_3. Reaction conditions: 1.0 g of *U. prolifera*, 100 mL water, 200 °C, 2 MPa N_2, 1 h.

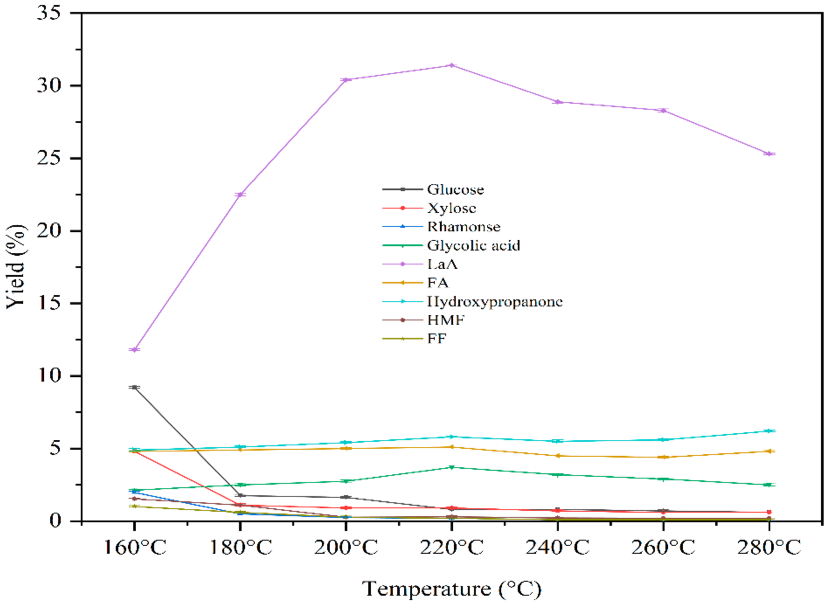

Figure 3. Yields of small molecular products from hydrothermal conversion of *U. prolifera* at different temperatures with YCl_3. Reaction conditions: 1.0 g of *U. prolifera*, 100 mL water, 26 mmol/L YCl_3 if used, 2 MPa N_2, 1 h.

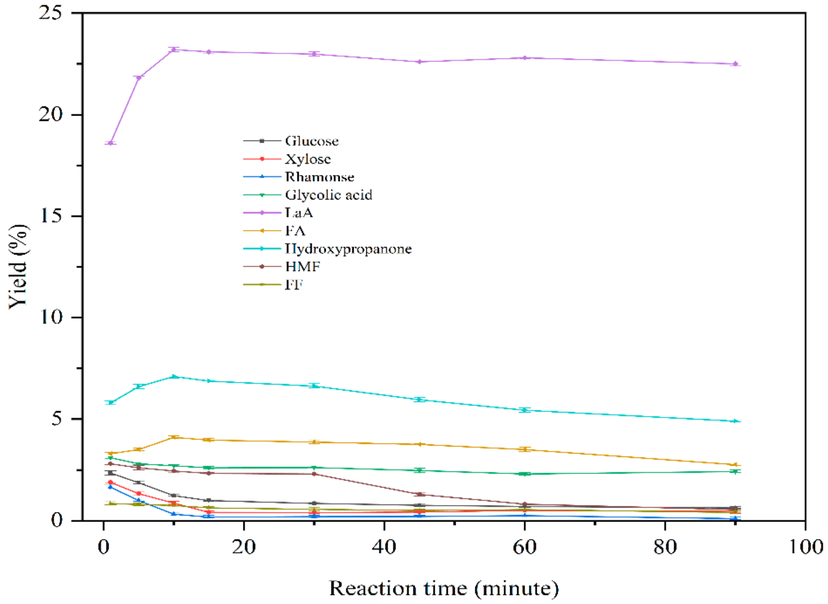

Figure 4. Yields of small molecular products from hydrothermal conversion of *U. prolifera* at different reaction time with YCl_3. Reaction conditions: 1.0 g of *U. prolifera*, 100 mL water, 13 mmol/L YCl_3 used, 2 MPa N_2, 200 °C.

2.3. Liquid Products Analysis

The liquid products were quantitatively analyzed by an HPLC (waters e2695), a gel permeation chromatography (GPC, 1260 Infinity, Agilent), and ESI-MS (LCMS-IT-TOF, Shimadzu). The details of the instrument parameters are provided in Supplementary Materials.

2.4. Characterization of Solid Samples

The solid samples (the raw material and treated residues) were analyzed on a Nicolet 6700 Fourier Transform Infrared spectroscopy (FTIR) spectrometer with a resolution of 4 cm^{-1} and a FLASH 1112SERIES (Thermo Finnigan, Santa Clara, CA, USA) Element

Analyzer to determine the contents of elements. An ICP-OES (Inductively coupled plasma optical emission spectrometer) was used to measure the contents of several metals in the solid samples by Optima 8000 PerkinElmer equipment.

3. Results and Discussion

3.1. Composition of *Ulva prolifera*

The composition of the *Ulva prolifera* feedstock is shown in Table 1. The determined results of different elements were as follows: 41.1 wt% of carbon, 1.6 wt% of nitrogen, 3.4 wt% of sulfur, 7.6 wt% of hydrogen, and 46.3 wt% of oxygen. In this part of elemental analysis and calculation, the ash content was removed and the relative content of the elements was calculated based on organic components of the feedstock. Due to its natural growth, the *Ulva prolifera* contained as high as 26.8 wt% of ash and only 68.9 wt% of combustible. As shown in Table S2, the main metal element contained in the ash composed of 7.8 wt% of calcium, 3.0 wt% of potassium, 4.1 wt% of sodium, 1.9 wt% of magnesium, and 0.7 wt% of iron. Moreover, it was found that the *U. prolifera* feedstock had a low content of proteins (8.1 wt%), a low content of lipids (1.5 wt%) with high carbohydrates content (44.5 wt%). The remaining 14.8% was composed mainly of cell wall components and cytochrome. The carbohydrates included 8.4 wt% of xylose, 18.1 wt% of rhamnose, 13.5 wt% of glucose, and 4.5 wt% of others, which were measured by acid hydrolysis of *Ulva prolifera* feedstock [27]. Therefore, further work was carried out for the transformation of the carbohydrates in *Ulva prolifera* to lactic acid (LaA) and valuable chemicals. All the yields of products were based on the polysaccharides contained in *Ulva prolifera.* The yield in this manuscript was calculated by dividing the mass of product by the mass of carbohydrates contained in the raw material added.

Table 1. The composition of *Ulva prolifera.*

Algae Characterization	Content	Test Methods
Proximate (wt%)		
Moisture	4.3	Drying at 80 °C according to [27]
Combustible	68.9	Burning at 800 °C in air
Ash	26.8	Burning at 800 °C in air
Elemental (wt%)		
C	41.1	FLASH 1112SERIES Element Analyzer
H	7.6	FLASH 1112SERIES Element Analyzer
N	1.6	FLASH 1112SERIES Element Analyzer
S	3.4	FLASH 1112SERIES Element Analyzer
O	46.3	Calculated by difference (O=100-C-H-N-S)
Biochemical (wt%)		
Carbohydrates	44.5	DNS colorimetric analysis
Proteins	8.1	N (wt%) multiplied by conversion factor of 6.25
Lipids	1.5	Bligh and Dyer method
Carbohydrates (wt%)		
Glucose	13.5	Hydrolyzing of polysaccharides in feedstock
Xylose	8.4	Hydrolyzing of polysaccharides in feedstock
Rhamnose	18.1	Hydrolyzing of polysaccharides in feedstock
Others	4.5	Calculated by difference

3.2. Hydrothermal Conversion of *Ulva prolifera*

3.2.1. The Effect of Different Amounts of Y(III) Catalyst

It has been reported that the hydrothermal conversion of *U. prolifera* could obtain high yield monosaccharides at 160 °C [21]. Firstly, the impact of different amounts of YCl_3

(3.25 mmol/L, 6.5 mmol/L, 10 mmol/L, 13 mmol/L, 26 mmol/L) on the hydrothermal conversion of polysaccharides was also explored at 160 °C. As shown in Figure 1, it was interesting to note that the highest amount of rhamnose was obtained when 3.25 mmol/L YCl_3 was added, and the yield of rhamnose decreased continuously with the amount of YCl_3, whereas the yield of LaA increased monotonically with the amount of YCl_3. The yield of xylose climbed up and then declined with the increasing amount of YCl_3, and when 10 mmol/L YCl_3 was added, the maximum yield of xylose could be obtained. Additionally, the yield of glucose increased firstly with the rise in the amount of YCl_3, and upon adding 13 mmol/L YCl_3, the highest amount of glucose could be obtained, which remained almost unchanged with an increase in the amount of YCl_3, suggesting that glucose and xylose could be extracted from the raw material but were hardly converted to LaA at 160 °C under the roles of YCl_3 derived catalysts. This may be caused by the difficulty of C-C bond cleavage in glucose and xylose. The yield of HMF and FF was low and increased slightly with the amount of YCl_3 increased, showing that small amounts of glucose and xylose could be converted to HMF and FF, respectively, at 160 °C. The above data implied that the increased LaA, FA, and hydroxypropanone were mainly originated from the conversion of rhamnose at 160 °C, catalyzed by YCl_3-derived catalysts under the present conditions, whereas glucose and xylose could only be extracted, but not converted to LaA.

Secondly, we explored the effect of the amount of YCl_3 on the conversion of *Ulva prolifera* at 200 °C. The amount of YCl_3 used was (0.0, 1.5 mmol/L, 3.25 mmol/L, 6.5 mmol/L, 13 mmol/L, 26 mmol/L, 33 mmol/L, and 46 mmol/L). As shown in Figure 2, the same as the yield at 160 °C, the yield of LaA was at a low level without a catalyst. The yields of glucose, xylose, and rhamnose were also low, and the polysaccharides in *U. prolifera* were hard to be converted and dissolved. With the addition of 1.5 mmol/L YCl_3, the yields of glucose, xylose, and rhamnose were 0.9 wt%, 0.8 wt%, and 0.9 wt%, respectively. However, the yields of LaA, formic acid (FA), and hydroxypropanone increased with the rise of the amount of YCl_3 from 1.5 mmol/L to 26 mmol/L, proving that most of the dissolved sugars were transformed at 200 °C. In addition, the yield of xylose and rhamnose decreased with the rise of the amount of YCl_3, and their final amount in the liquid product was very low, which revealed that xylose and rhamnose could be completely converted to lactic acid at 200 °C. However, there was still a certain amount of glucose in the liquid product that could not be completely converted to LaA at 200 °C. When adding 26 mmol/L YCl_3, the yield of LaA (30.4 wt%) was the highest, while the amount of YCl_3 increased to 33 mmol/L, the yield of LaA decreased and the yield of glycolic acid increased. The yields of hydroxymethyl furfural (HMF) and furfural (FF) were low and decreased slightly with the increase in the amount of YCl_3.

3.2.2. The Effect of Temperature on Catalytic Reaction

The effect of different temperatures (160 °C, 180 °C, 200 °C, 220 °C, 240 °C, 260 °C, 280 °C) on the conversion of *U. prolifera* without YCl_3 was explored. As shown in Figure S1, the yield of the main products was low without YCl_3 added. After increasing the temperature from 160 °C to 280 °C, the yield of glucose, rhamnose, and xylose rose up and then declined, and the yield of LaA increased with the rise of temperature. It is shown that the rise of temperature could promote the dissolution of polysaccharides in *Ulva prolifera*, and higher temperature can facilitate the conversion of dissolved saccharides to LaA. Meanwhile, rhamnose could be mainly converted at 180 °C, whereas glucose and xylose were mainly transformed at 200 °C. The yield of HMF increased significantly to 4.4 wt%, and the yield of FA (4.2 wt%), glycolic acid (1.8 wt%), and FF (1.6 wt%) were the highest as the temperature raised from 180 °C to 200 °C.

The effect of temperature (160 °C, 180 °C, 200 °C, 220 °C, 240 °C, 260 °C, 280 °C) on the transformation of *Ulva prolifera* with 26 mmol/L YCl_3 added was also explored. As shown in Figure 3, when adding YCl_3, the yield of the main product was significantly improved, compared with that without a catalyst. It confirmed that YCl_3-derived catalysts in this system could promote the transformation of polysaccharides in *U. prolifera* to

LaA and value-added chemicals. More sugars were dissolved and converted when the temperature increased from 160 °C to 180 °C. The xylose, rhamnose, and most of the glucose could be also transformed to LaA with YCl_3 added at 200 °C. Further increasing the reaction temperature to 220 °C, the dissolved glucose, rhamnose, and xylose could be fully converted, and the yield of LaA (31.4 wt%) and glycolic acid (3.7 wt%) were the highest. With a further increase in temperature to 280 °C, the yield of LaA and glycolic acid decreased gradually. It is indicated that at above 220°C, more monosaccharides, intermediates and/or products may condensate to form oligomers or even humins, thus reducing the yield. In addition, the yields of HMF and FF were little and changed little with the increase in temperature in this catalytic system.

Next, we investigated the conditions with relatively good catalytic effect but low YCl_3 dosage (13 mmol/L). The effect of temperature (160 °C, 180 °C, 200 °C, 220 °C, 240 °C, 260 °C, 280 °C) on the transformation of *Ulva prolifera* was also explored with 13 mmol/L YCl_3 added. As shown in Figure S2, the yield of LaA remarkably increased with the rise in reaction temperature. When the temperature rose to 260 °C, the yield of LaA (31.3 wt%) was the highest and it was similar to the yield of LaA (31.4 wt%) at 220 °C with 26 mmol/L YCl_3 added, the yield of LaA decreased as the temperature increased to 280 °C. The yield of FA decreased as the temperature increased. In addition, the yields of HMF (2.9 wt%) and hydroxypropanone (6.0 wt%) were the highest at 180 °C. Compared with adding 26 mmol/L YCl_3, the experiment with 13 mmol/L YCl_3 added needed a higher temperature to achieve the same yield of LaA.

3.2.3. The Impact of Different Reaction Time

The impact of reaction time (1 min, 5 min, 10 min, 15 min, 30 min, 45 min, 60 min, and 90 min) on the conversion of *U. prolifera* was researched at 200 °C (at this temperature, glucose, xylose, and rhamnose can be converted, and the lower temperature is more conducive to studying the process changes of the reaction) when adding 13 mmol/L YCl_3 (with this amount of YCl_3 added, the derived catalysts also exhibit a good catalytic effect, and relatively few catalysts can better study the effect of reaction time). As shown in the Figure 4, the yield of LaA increased from 18.6 wt% to 23.2 wt% when the reaction lasted from 1 min to 10 min at the set temperature. As the reaction time raised to 90 min, the yield of LaA was essentially unchanged and there was a slight reduction, which may just be due to the fact that, with elongated reaction times, the lactic acid decomposed to other reaction products. It proved that the conversion rate was high and it took only 10 min to get a complete yield in the presence of 13 mmol/L YCl_3 as catalyst precursor at 200 °C. The yields of hydroxypropanone and FA climbed up and then declined with prolonging reaction time, which also reached the maximum after 10 min of reaction. The yields of glucose, xylose, rhamnose, and glycolic acid decreased with the increase in the reaction time. It indicated that the dissolved glucose, xylose, and rhamnose could be further converted to LaA under this condition. The effect of reaction time (1 min, 5 min, 10 min, 15 min, 30 min, 45 min, 60 min, 90 min) on the transformation of *Ulva prolifera* at 240 °C in the presence of 13 mmol/L YCl_3 catalyst precursor was also explored. As shown in Figure S3, the conversion of *U. prolifera* at 240 °C was similar to that at 200 °C. When the reaction lasted from 1 min to 10 min at the set temperature, the yield of LaA increased from 25.4 wt% to 27.4 wt%, and was basically unchanged with the reaction time increased to 90 min. It also proved that the reactions occurred quickly at 240 °C. The yields of glucose, rhamnose, and xylose were low, indicating that the dissolved glucose, xylose, and rhamnose could be converted under this reaction condition. The average and standard deviation of the data in Figures 1–4 and Figures S1–S3 are listed in Tables S6–S12.

3.2.4. The GPC and ESI-MS Analysis of Liquid Products

The molecular weight distribution of liquid products from the transformation of *Ulva prolifera* was analyzed by GPC (Figure S4). Figure S4A showed the impact of reaction temperatures on the molecular weight distribution in the presence of 13 mmol/L YCl_3. The component of macromolecules (Mw > 2000 Da) was 75% at 160 °C, and the component of compounds with a molecular weight of less than 200 Da was 7%. With the temperature rising to 240 °C, the component of macromolecules (Mw > 2000 Da) increased to 93% and the component of compounds with molecular weight of less than 200 Da decreased to 2%. Therefore, it proved that more saccharides could be dissolved at a higher temperature and small molecules could be polymerized at higher temperatures, which is why the percentage of small molecules decreased. The compounds with a molecular weight of 200 Da to 400 Da decreased from 9% to 2%, and the compounds with a molecular weight of 400–1000 Da decreased from 6% to 2% when the temperature rose from 160 °C to 240 °C. As the temperature increased from 240 °C to 260 °C, the component of macromolecules (Mw > 2000 Da) decreased to 83% and the component of compounds with a molecular weight of less than 200 Da increased to 4%, and this was consistent with the highest yield of LaA at this temperature. At 280 °C, the component of macromolecules (Mw > 2000 Da) increased and the component of compounds with a molecular weight of less than 200 Da decreased, and it may have been caused by the fact that the amount of macromolecules in solution increased with temperature, and high temperature could promote the formation of oligomers [27].

As shown in Figure S4B, we also explored the effect of temperature on the molecular weight distribution without YCl_3 added. At 160 °C, 69% of the compounds in liquid products were macromolecules (Mw > 2000 Da), and the component of compounds with a molecular weight of less than 200 Da was 11%, because saccharides were hard to dissolve without YCl_3 added. With the rise of temperature, the component of macromolecules (Mw > 2000 Da) increased to 89% at 280 °C, while the component of compounds with a molecular weight of less than 200 Da decreased to 3%. This proved that a high temperature increased the yield of liquid products and made small molecules polymerize. It also indicated that YCl_3-derived catalysts have good catalytic effects on the extraction and conversion of carbohydrates in *U. prolifera*.

The formation of oligomers was the primary cause of the carbon loss during the transformation of *Ulva prolifera*. The formed oligomeric and monomeric products were confirmed by ESI-MS. As shown in Figure S5, the peaks with *m/z* at 97, 113, 149, 165, and 203 were assigned to $[\text{monomer} + \text{H/Na}]^+$ species (monomer = hydroxypropanone, FF, LaA, HMF, glucose or rhamnose). The peak with *m/z* at 163 was assigned to $[2\text{LaA} - \text{H}_2\text{O} + \text{H}]^+$. The peak with *m/z* at 225 was assigned to $[2\text{Rha} - 5\text{H}_2\text{O} + \text{Na}]^+$, and the peaks with *m/z* at 425, 433, 469, 543, and 569 were assigned to $[3\text{monosaccharides} - n\text{H}_2\text{O} + \text{H/Na}]^+$ species (monosaccharide = Glu, Rha, Xyl, or their mixture), which were the trimers formed by the degradation of polysaccharides or etherification of monosaccharides and subsequent dehydration [47]. Additionally, the peak with *m/z* at 499 could be assigned to $[2\text{Glu} - \text{FA} - \text{H}_2\text{O} + \text{H}]^+$. The peaks with *m/z* at 243, 459, and 513 could be assigned to the dimer, trimer, and tetramer formed by partial degradation of polysaccharides, as well as the tetramer formed by the condensation of monosaccharides with LaA and water generated (e.g., $[2\text{Rha} - \text{LaA} - \text{H}_2\text{O} + \text{Na}]^+$).

3.3. The FT-IR Spectra of Solid Samples

The FT-IR spectra of the solid residues and *U. prolifera* feedstock are shown in Figure S6, and the assignment of FT-IR peaks are listed in Table S3. The peak at about 1706 cm^{-1} was attributed to the C=O vibration of amino bonds in the protein, and the absorption bands at 1452 cm^{-1} and 1630 cm^{-1} could be ascribed to the vibration of C–O and C=O of the carboxyl group in uronic acid. Moreover, the absorption bands at about 850 cm^{-1} and 1262 cm^{-1} were corresponded to the C–O–S and S=O of the sulfate ester group in sulfated polysaccharides. The solid residues obtained from the hydrothermal conversion showed different degrees of variation compared with the *U. prolifera* feedstock. It showed that the YCl_3-derived catalysts had a good catalytic conversion effect on *U. prolifera* raw materials. When the temperature was kept at 160 °C, the intensity at 1706 cm^{-1} rose with the amount of YCl_3 added compared with the reaction without YCl_3. This was caused by the dissolution of carbohydrates rather than proteins with YCl_3-derived catalysts, leading to the rise of the relative component of proteins in solid residues. Meanwhile, with the increase in the amount of YCl_3 added from 3.25 mmol/L to 26 mmol/L, the intensity of the peaks at 1630, 1452, and 1262 cm^{-1} remained.

At 200 °C, the intensity at 1452 cm^{-1} decreased with the amount of YCl_3 added compared with the reaction without YCl_3, because YCl_3-derived species promoted the dissolution and conversion of polysaccharide in *U. prolifera* into lactic acid and reduced the composition of sulfate polysaccharide in solid residues, which corresponded to the increase in lactic acid yield in HPLC analysis of liquid products. The intensity at 1706 cm^{-1} decreased with adding YCl_3 as a catalyst precursor compared with the reaction without YCl_3. This was caused by the fact that YCl_3-derived species could promote also the dissolution of proteins. The intensity of the peaks at 1630, 1452, 1262, and 850 cm^{-1} decreased, suggesting the promotion impact of YCl_3-derived catalysts on the dissolution of sulfated polysaccharides. It can also be seen that adding YCl_3 can promote the dissolution and conversion of polysaccharides in *U. prolifera* into monosaccharide and lactic acid. These results were confirmed by an HPLC analysis of liquid products.

The FT-IR spectra of solid residues treated at different temperatures with 13 mmol/L YCl_3 added are displayed in Figure S7. The solid residues obtained from the hydrothermal conversion showed different degrees of variation compared with *U. prolifera* feedstock. As shown in Figure S2, the intensity at 1706 cm^{-1} increased with the increase in temperature from 160 °C to 280 °C. It could have been caused by the fact that higher temperatures promoted the dissolution of carbohydrates, which let the relative component of proteins in solid residues rise. This corresponds to the increased content of macromolecules in the liquid products as shown in the GPC analysis (which will be discussed later). In addition, with the increase in temperature in the presence of YCl_3, the intensity of the peaks at 1630, 1452, and 1262 cm^{-1} decreased, and it indicated the promotion impact of temperature on the dissolution of sulfated polysaccharides. This also indicated that a higher temperature was more conducive to the dissolution and transformation of polysaccharides in *U. prolifera.*

3.4. Catalytic Reaction Pathways of Hydrothermal Experiments

The saccharides in *Ulva prolifera* are linked by β-(1→4) glycosidic bonds and the O-sulfate esters are connected at the C-3 position of rhamnose [48]. According to the obtained results, Figure 5 summarized schematically the corresponding route for *Ulva prolifera* transformation. At first, YCl_3 will generate hydrochloric acid in water, as a strong Bronsted acid, hydrochloric acid will contribute to the dissolution of sulfated polysaccharides in *U. prolifera* and whereafter degrade into the monosaccharides (glucose, xylose, and rhamnose). This is in agreement with the results of the hydrothermal reaction at 160 °C, where the presence of a certain amount of monosaccharide was detected by HPLC. The sulfate group in the sulfated Rha was replaced by the hydroxyl group to form calcium sulfate, as shown in Table S4. Calcium was detected in both *Ulva prolifera* raw material and the solid residue, confirming this result. This corresponds to the reduction of the intensity of the peaks at 1630, 1452, 1262, and 850 cm^{-1} in FT-IR spectra analysis of the solid residue. The hydrolysis of YCl_3 added could also form catalytic species [41], which promote the further conversion of monosaccharide selectively to lactic acid, and related chemicals. Considering the fact that the original *Ulva prolifera* we added is a solid powder, there will be a heterogeneous solid-liquid interaction, homogeneous catalytic processes, and also heterogeneous catalytic reaction process, to achieve the above mentioned transformation. At a lower temperature (160 °C), when adding 3.25 mmol/L YCl_3 as catalyst precursor, glucose, xylose, and rhamnose could be obtained from the degradation of *Ulva prolifera*. However, as we continued to increase the amount of YCl_3 to 26 mmol/L, the yield of glucose increased and maintained at a high level, and the yield of xylose remained unchanged. It demonstrated that glucose and xylose could be extracted from *Ulva prolifera*, but not be converted to LaA at this low temperature. On the contrary, the yield of rhamnose decreased and the yield of LaA increased with the increase in YCl_3 added, and it indicated that the obtained rhamnose dissolved in the solution could be readily transformed to LaA (11.8 wt%) and hydroxypropanone by the catalysis of YCl_3-derived species. In addition, glucose, xylose, and rhamnose were converted to LaA when the reaction temperature reached 180 °C or higher. At 200 °C, the yield of LaA (30.4 wt%) was high with adding 26 mmol/L YCl_3, and this proved that xylose, rhamnose, and most of the glucose could be also transformed to LaA with a YCl_3-derived catalyst. At a higher temperature (220 °C), the glucose, xylose, and rhamnose were completely converted. According to our previous work using glucose as a starting material, temperatures of 220 °C or higher are required for it to be fully converted to LaA [41], and the results of the present work is consistent with those reported previously. We also conducted the separate experiments on the conversion of xylose and rhamnose with YCl_3, and the experimental results are shown in Table S5. Most of xylose could be converted into LaA at 200 °C and xylose can be basically completely converted to lactic acid at 220 ° C, whereas rhamnose can be basically completely converted into lactic acid at 160 ° C, which confirmed the above deduction. When carrying out the reaction at 240 °C with 13 mmol/L YCl_3 added to optimize reaction time, glucose, xylose, and rhamnose could be detected with a short reaction time (only 10 min), and their contents decreased with prolonging reaction time whereas the content of LaA increased when the reaction proceeded from 0 to 10 min. The hydrolysis of YCl_3 can provide simultaneously Bronsted acid, which promotes the extraction and hydrolysis of polysaccharides in *Ulva prolifera* into monosaccharides, and a Y-derived catalyst which is active for the conversion of monosaccharides into lactic acid simultaneously, enhancing greatly the process efficiency. Thus, the space time lactic acid yield is higher compared to the literature results (Table S1). The saccharides in *Ulva prolifera* were transformed into LaA by hydrothermal reaction in the presence of YCl_3. These data indicated that the polysaccharides in *U. prolifera* were firstly decomposed into glucose, xylose, and rhamnose, and then converted into LaA. The effects of different temperatures (160 to 280 °C) on the transformation of *U. prolifera* were explored with 13 and 26 mmol/L YCl_3 added. When adding 26 mmol/L YCl_3, the yield of LaA (31.4 wt%) at 220 °C was the highest. The yield of LaA (31.3 wt%) was at the highest with 13 mmol/L YCl_3 added at 260 °C. The experiment of adding 13 mmol/L YCl_3 needed a higher temperature to achieve the same degree of result with 26 mmol/L YCl_3. It indicated that the reaction temperature and the amount of YCl_3-derived catalyst used co-contributed to the conversion of carbohydrates in *U. prolifera* to LaA.

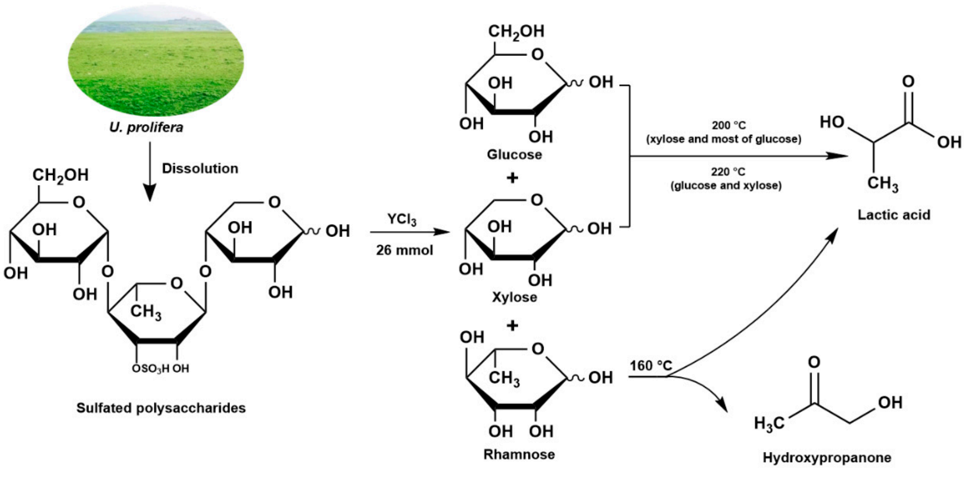

Figure 5. Proposed schematic reaction pathway for the conversion of polysaccharides in *U. prolifera.*

4. Conclusions

In summary, the presence of YCl_3 could promote the transformation of the saccharides in *U. prolifera* to LaA and valuable chemicals. The optimal temperature and amount of Ycl_3 needed for the decomposition-dissolution of saccharides in *U. prolifera* and further conversion of glucose, xylose, and rhamnose to LaA depended on each other. At 160 °C, glucose and xylose could be obtained but could not be converted, whereas LaA and hydroxypropanone mainly came from the transformation of rhamnose. At 200 °C, xylose and most of the glucose could be converted to LaA (30.4 wt%) with 26 mmol/L YCl_3 added. The dissolved glucose, xylose, and rhamnose could be completely converted to LaA at 220 °C. Under the optimized condition, the highest yield of LaA obtained was 31.4 wt% (26 mmol/L, 220 °C). The hydrothermal conversion of *U. prolifera* (HC) was found to occur rapidly in the presence of a YCl_3-derived catalyst with only 10 min.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13020262/s1, Figure S1: Yields of small molecular products from hydrothermal conversion of *U. prolifera* at different temperatures without YCl_3; Figure S2: Yields of small molecular products from hydrothermal conversion of *U. prolifera* at different temperatures with YCl_3; Figure S3: Yields of small molecular products from hydrothermal conversion of *U. prolifera* at different reaction time with YCl_3; Figure S4: (A) Molecular weight distribution of liquid products from the conversion of *U. prolifera* at different temperatures with YCl_3,(B) Molecular weight distribution of liquid products from the conversion of *U. prolifera* at different temperatures without YCl_3; Figure S5: ESI-MS spectra (cation positive mode) of liquid products phase from the conversion of *U. prolifera* in the presence of 13mmol/L YCl_3 at 240 °C; Figure S6: FT-IR spectra of *U. prolifera* feedstock and solid residue; Figure S7: FT-IR spectra of *U. prolifera* feedstock and solid residue at different temperatures with 13 mmol/L YCl_3; Table S1: Comparison of advantages and disadvantages of lactic acid prepared by different hydrothermal catalytic methods; Table S2: The content of main metallic elements in ash; Table S3: The assignment of FT-IR peaks of *U. prolifera*; Table S4: The content of main metallic elements in *Ulva prolifera* and Solid residue; Table S5: Yields of LaA (wt%) from separate hydrothermal conversion of xylose or rhamnose at different temperature with YCl_3; Table S6: S6-1 The average of the data in Figure 1, S6-2 The standard deviation of the data in Figure 1; Table S7: S7-1 The average of the data in Figure 2, S7-2 The standard deviation of the data in Figure 2; Table S8: S8-1 The average of the data in Figure 3, S8-2 The standard deviation of the data in Figure 3; Table S9: S9-1 The average of the data in Figure 4, S9-2 The standard deviation of the data in Figure 4; Table S10: S10-1 The average of the data in Figure S1, S10-2 The standard deviation of the data in Figure S1; Table S11: S11-1 The average of the data in Figure S2, S11-2 The standard deviation of the data in Figure S2; Table S12: S12-1 The average of the data in Figure S3, S12-2 The standard deviation of the data in Figure S3.

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