Acidic seawater improved 5-hydroxymethylfurfural yield from sugarcane bagasse under microwave hydrothermal liquefaction

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ABSTRACT

5-Hydroxymethylfurfural (HMF) as value-added platform chemical can be derived from biomass. This study used microwave hydrothermal liquefaction (MHTL) to obtain HMF from sugarcane bagasse in acidic seawater conditions. The key processing parameters including temperature, reaction time, and liquid-to-solid ratio (L/S) were evaluated and optimized. The highest HMF yield of 8.1 wt% was obtained at 149 °C with a reaction time of 4 min and a L/S value of 12:1, respectively. This yield is considerable and even higher than the yield derived from sugarcane molasses under similar microwave conditions in the absence of seawater. Hence, acidic seawater was found to promote the hydrolysis of sugarcane bagasse to give HMF precursor (i.e. fructose and glucose), while simultaneously inhibiting the conversion of HMF to levulinic acid under MHTL conditions, possibly explaining the high HMF yield. This method presents a new and sustainable means of transforming waste biomass to valuable substances using seawater or brine wastewater.

1. Introduction

The 5-hydroxymethylfurfural (HMF) is a value-added platform chemical and a versatile building block for a diverse range of commodity chemicals with a relatively high market value that can be derived from biomass (Bozell and Petersen, 2010; Chen et al., 2017; Xiong et al., 2017; Yu et al., 2017). At present, the industrial synthesis of HMF primarily uses sugar syrup extracted from energy crops as the feedstock (Kläusli, 2014), which will lead to unsustainable development. Using low-value biomass wastes, such as food waste (Lam et al., 2018; Long et al., 2018; Lucas-Torres et al., 2016; Ren et al., 2018; Shao et al., 2019c; Yu et al., 2018), agricultural waste (Mirzaei and Karimi, 2016; Wang et al., 2014), and forestry residues (Nizamuddin et al., 2016; Peleteiro et al., 2014; Seemala et al., 2016; Shao et al., 2020), instead of virgin sugar from energy crops, is worth considering for the sake of sustainable biorefinery. Biomass having higher glucose and/or fructose concentrations, or with a greater conversion potential for these monosaccharides, is preferred for the production of HMF.

Sugarcane accounts for approximately 80% of global sugar production (Payá et al., 2018), and approximately 640 million tons of sugarcane were produced in 2018, generating about 160 million tons of sugarcane bagasse (Carvalho et al., 2019). Iryani et al. found that the highest HMF yield of 3.09 wt% was obtained from bagasse via a 10 min extraction with 270 °C water which was higher than that of derived from other materials such as coconut husk and rice husk (Iryani et al., 2013; Nakason et al., 2018). Gomes et al. obtained the highest HMF yield of 26.5% (molar basis) from cane bagasse in a tetrahydrofuran/NaCl$_{(aq)}$ biphasic system with AlCl$_3$/HCl at 180 °C for 90 min (Gomes et al., 2018). However, those process mentioned above are complex with significant energy consumption.

In recent years, microwave-based hydrothermal techniques have gained widespread attention as innovative approaches (Afolabi et al., 2015; Elaigwu and Greenway, 2016; Guiotoku et al., 2009; Shao et al., 2019a). Microwave radiation acts on water molecules is that the dipoles of the water molecules align with the electric field of the microwave and rotate at high speed to generate heat (Foong et al., 2020).

And the carbon-rich biomass as a microwave absorber will be rapidly and uniformly heated and begin to decompose when it was exposed to microwave energy (Liew et al., 2018). Microwave heating in water can also help to break hydrogen bonds in cellulose for reducing the crystallinity and increasing the specific surface area, all of which can improve the hydrolysis efficiency. Compared with conventional

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heating, microwave heating presents easy control to the process in terms of rapid initialization and termination and requires a shower time to heat up or cool down (Yek et al., 2019). In addition, microwave radiation has been reported to enhance the efficiency of acidic extractions, increase the rate of saccharification, and shorten the reaction time (Li et al., 2007). Recent studies have attempted to utilize the microwave hydrothermal liquefaction (MHTL), whose main function is that converting solid waste into useful liquid products, to produce the HMF, especially under acidic circumstances (Shao et al., 2019b; Sweygers et al., 2018; Wu et al., 2019; Yi et al., 2013; Yu and Tsang, 2017). Besides, seawater has been employed as the reaction medium for enzymatic and fermentative applications in biorefineries (Domínguez de María, 2013; Grande et al., 2012; Lehmann et al., 2012; Li et al., 2018; Lin et al., 2011), which may also has the potential for HMF production under the microwave-assisted catalytic conversion. Seawater is plentiful and contains a high salt concentration, rendering it to some extent similar to an ionic liquid although it still has a certain gap with the concentration and function of ionic liquids. The penetration of sodium and chloride ions in seawater into cellulose can assist to disrupt the hydrogen bond network. Research indicated that a combination of salt water and acid catalysis resulted in a powerful reaction medium in which polysaccharide hydrolysis proceeds efficiently to produce glucose (vom Stein et al., 2010). This may suggest that acidic seawater has the great advantage for conversion of biomass waste to HMF. Nevertheless, to the best of our knowledge, there has been no research exploring the synergy of acidic seawater in conjunction with MHTL for increasing the yield of HMF production.

In the present work, the generation of HMF from sugarcane bagasse in acidic seawater under different MHTL conditions was assessed, with the aim of developing a viable and sustainable synthesis method. During these trials, the HMF yield was optimized by employing response surface methodology (RSM), and a possible HMF production mechanism is proposed.

2. Materials and methods

2.1. Materials

Fresh sugarcane was obtained from a fruit market in Hangzhou, China. Sugarcane bagasse, with a moisture content of 68.9 ± 1.2 wt% which was calculated in supplementary material, was oven-dried at 105 °C (GZX-9076 MBE, Shanghai, China) to constant weight. Then, it was broken to less than 0.1 mm. The fine bagasse was constantly quartered into parts until it was homogenized before use. Artificial seawater was simulated according to ASTM D1141 (Donatello et al., 2013).

The reagents including HMF (99%) and levulinic acid (LA, 99%) were purchased from Sigma-Aldrich (USA). Glucose (98%) and fructose (99%) were purchased from Shanghai Yuanye (China). All reagents used were analytical grade.

2.2. MHTL processing

2.2.1. Test conditions

The MHTL test conditions consisting of 13 groups were designed by Design-Expert software package (Stat-Ease, Inc., USA). The microwave oven (MarsXpress, CEM, USA) was used to evaluate the effects of MHTL conditions under the maximum power of 1600 W set directly by the instrument and the heating rate of 15 °C min^{-1} based on the calculation of holding temperature and heating up time, which was similar as the previous work (Shao et al., 2019b). 0.5 g bagasse was blended with HCl, artificial seawater, or acidic artificial seawater (Table 1) in each digestion tube. After MHTL reaction, the product was separated by filtration through 0.45 μm filter paper. The liquid fraction was first transferred to a volumetric flask and then diluted to a constant volume with deionized water, finally passed through a 0.22 μm filter paper and

Table 1
Initial sugar content of bagasse under different treatment solvents.

Solvents	pH	Fructose content (wt %)	Glucose content (wt %)
Seawater	7.74 ± 0.03	1.72 ± 0.04	1.80 ± 0.11
Hydrochloric acid	1.00 ± 0.01	7.20 ± 0.07	7.28 ± 0.08
Acidic seawater	1.00 ± 0.01	8.22 ± 0.04	8.84 ± 0.08

Treatment: Mix 1 g of bagasse (dry basis) with 30 mL of the above solvent in 100 mL Erlenmeyer flask, and shake at room temperature for 24 h.

analyzed. All experiments in each MHTL condition were performed in triplicate.

The effects of reaction temperature (°C), reaction time (min), and liquid-to-solid ratio (L/S), the most important parameters associated with the thermochemical conversion, were studied for the HMF yield (Nizamuddin et al., 2017). Namely, the temperatures (130 °C–190 °C), reaction time (1 min–60 min), and L/S (8:1 to 20:1) were tested with reference to previous findings (Shao et al., 2019b). Trials were also performed in HCl and seawater under the same MHTL conditions for comparison. The yields of glucose, fructose, LA and mass yields were all analyzed under different tested scenarios.

2.2.2. MHTL optimization

Based on the conditioning test results, the Box-Behnken design (BBD) and RSM method were further introduced to optimize the combined effects of MHTL parameters. The tested reaction temperature, reaction time, and L/S are summarized in Table 2. Each experiment was performed in triplicate to ensure the data reproducibility. The design of experiments contained 17 trials with the condition of the center point performing five times (Table S1).

2.3. Analytical methods

The concentrations of HMF and LA obtained in each trial were determined by high pressure liquid chromatography (HPLC; Alliance system; Waters, USA) employing a Waters 2489 UV–visible detector operating at 210 nm. An XBridge™ C18 analytical column (4.6 × 250 mm, Waters, USA) was used with a column temperature of 30 °C, together with a mobile phase consisting of a 15:85 (v/v) mixture of acetonitrile (chromatography grade) and a phosphoric acid-sodium dihydrogen phosphate buffer solution at 1.0 mL min^{-1}. Glucose and fructose were analyzed by liquid chromatography-mass spectrometry (LC-MS; UPLC/Xevo TQD, Waters, USA) with an ACQUITY UPLC BEH Amide column (1.7 μm, 3 × 100 mm) held at 30 °C. The mobile phase consisted of acetonitrile (phase A) and 0.1% ammonium hydroxide (phase B) and was applied at a flow rate of 0.2 mL min^{-1}. These two phases were combined in conjunction with gradient program as follows: 0–1 min, 25% B; 1–7 min, 25–55% B; 7–8 min, 55% B. A post-analysis run time of 2 min was used to return the mobile phase to the initial composition (75%:25% B/A). The optimal MS conditions was based on the findings of Wan and Yu (2007). The surface morphologies of the specimens were assessed using scanning electron microscopy (SEM; Phenom G2 Pro, Phenom, Netherlands) at a magnification of 3000 × .

Table 2
The levels of variables in BBD design.

Variables	Symbols	Low	Center point	high
		-1	0	1
Holding temperature (ºC)	A	130	150	170
Holding time (min)	B	0	5	10
L/S	C	8	12	16

Note: The holding time of 0 means the heating procedure will stop when the temperature reach the predetermined value.
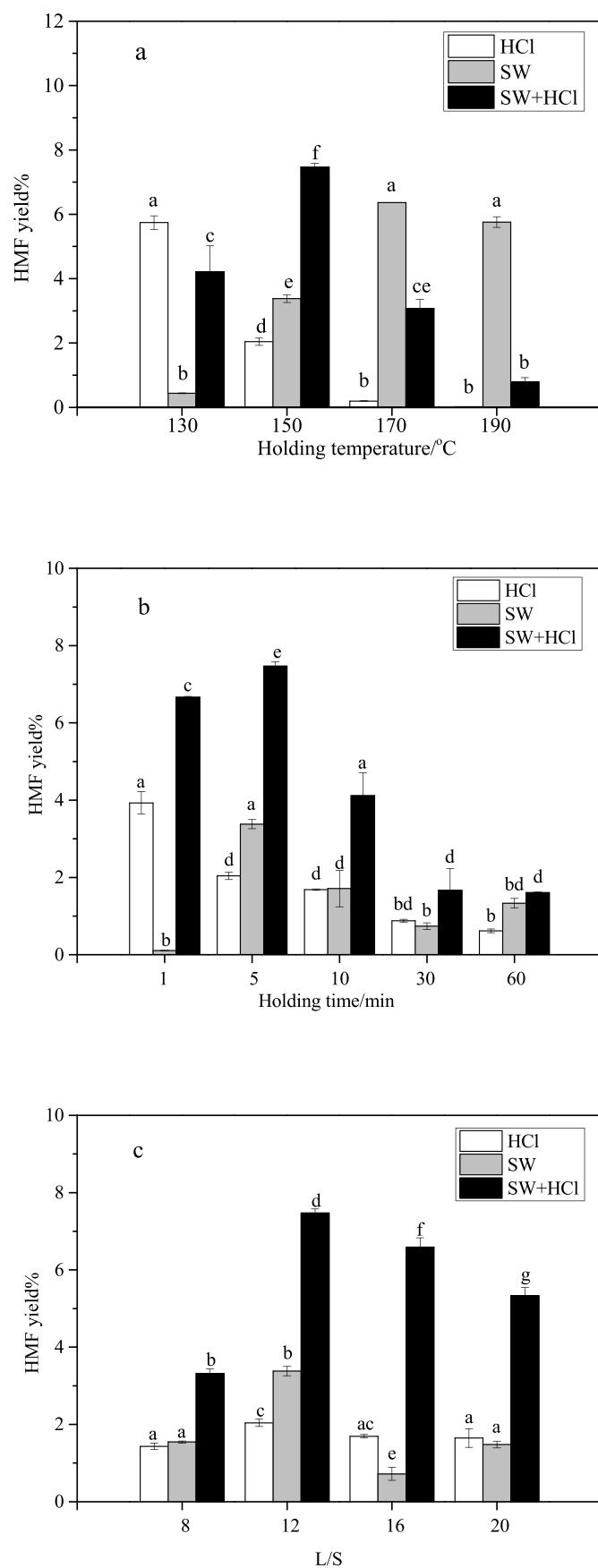
Fig. 1. Effects of (a) holding temperature (° C), (b) holding time (min), and (c) L/S on the HMF yield under different hydrothermal circumstances.

All analyses were performed in triplicate. The yields of HMF, LA, glucose and fructose were calculated using the equation

$$Y = 100 \times CV/M \qquad (2)$$

where Y (wt%) is the yield of the compound, C (mg/L) is the concentration of the compound in the post-reaction medium as determined by HPLC or LC-MS, V (L) is the volume of the post-reaction medium, and M (mg) is the original bagasse mass (on a dry basis), respectively.

3. Results and discussion

### 3.1. Effects of MHTL conditions

The effects of MHTL condition on the HMF yields obtained in HCl, seawater, and acidic seawater were evaluated, respectively. Fig. 1a shows the effect of the reaction temperature on the HMF yields in different reaction media. In HCl with a reaction time of 5 min and a L/S value of 12:1, the HMF yield was significantly decreased from 5.6 ± 0.9 wt% at 130 °C (with even higher yields at 120 °C) to 0 wt% at 190 °C. In contrast, when using seawater, the HMF yield significantly increased from 0.4 ± 0.0 to 6.4 ± 0.0 wt% as the reaction temperature was raised from 130 to 170 °C, then slightly decreased with further increase in the reaction temperature. The same basic trend was observed in the trials in acidic seawater. These results indicate that there is a suitable reaction temperature for the HMF production under acidic conditions, which is consistent with our previous findings (Shao et al., 2019b) and other results (Cao et al., 2018; Yemiş and Mazza, 2012). A significance analysis determined that the highest HMF yield (7.5 ± 0.1 wt%) was obtained in acidic seawater, indicating that the synergistic effect of combining seawater and HCl effectively improved the conversion of sugarcane bagasse to HMF. The scientific reasons for this phenomenon are discussed in detail in Section 3.3.

Fig. 1b summarizes the effect of varying the reaction time at 150 °C and a L/S value of 12:1 on the HMF yields in different solvents. In HCl, the HMF yield significantly decreased from 3.9 ± 0.3 to 0.6 ± 0.0 wt% as the reaction time was prolonged from 1 to 60 min. However, in seawater, the HMF yield immediately increased from 0.1 ± 0.0 to 3.4 ± 0.1 wt% as the reaction time went from 1 to 5 min, then slightly decreased with further increase in the reaction time. The same trend was also observed in the trials in acidic seawater. In addition, comparing the HMF yields derived from different solvents after the 1-min reaction, the highest HMF yield was again obtained in acidic seawater, reinforcing that the synergistic effect of seawater and HCl can improve the conversion of sugarcane bagasse to HMF over short time spans.

Fig. 1c presents the effect of the L/S ratio on HMF yields in different solvents. Because the highest HMF yield was observed in acidic seawater (Fig. 1a &b), a temperature of 150 °C and a reaction time of 5 min were chosen. Low HMF yields were obtained in HCl, and these yields did not vary significantly over the range of L/S ratios from 8:1 to 20:1. Higher HMF yields were apparent when using acidic seawater, which increased from 3.3 ± 0.1 to 7.5 ± 0.1 wt% as the L/S ratio was increased from 8:1 to 12:1, then significantly decreased with further increase in the L/S ratio. These data revealed the significance of these MHTL parameters that should be required to optimize the HMF yield from the sugarcane bagasse conversion performed in acidic seawater.

3.2. MHTL optimization

Based on the results of MHTL conditions testing, the various combination effects of reaction temperature (a), reaction time (b) and L/S (c) on the HMF yield at varying operating conditions are shown in Fig. 2. In Fig. 2a, the HMF yield increased with the increasing of both reaction temperature and reaction time till the highest value of 7.5 wt %. Then, it decreased obviously. It illustrated that the HMF production needs suitable reaction temperature and reaction time under acidic seawater circumstance. This trend was consistent with the MHTL
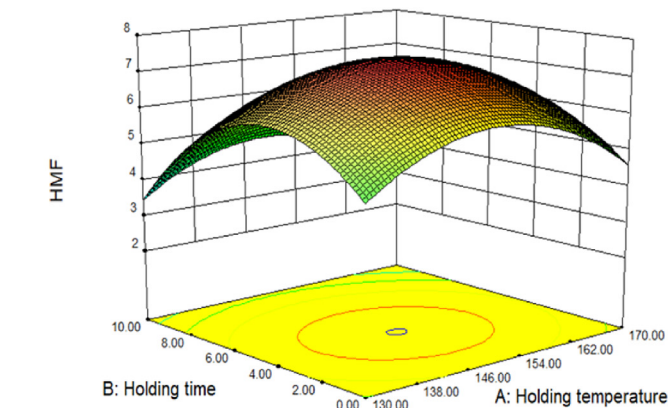
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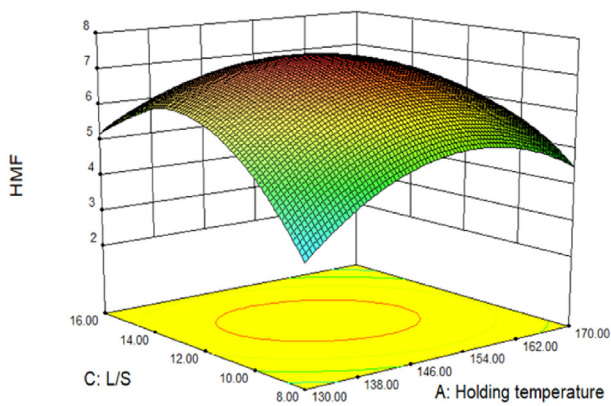
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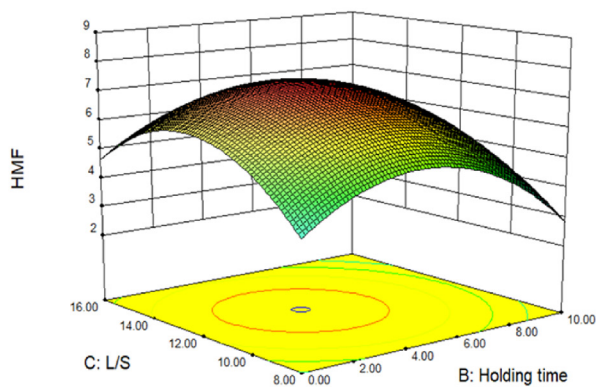
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Fig. 2. Surface plot showing the effect of (a) holding temperature (°C), (b) holding time (min) and (c) L/S on the HMF yield at varying operating conditions.
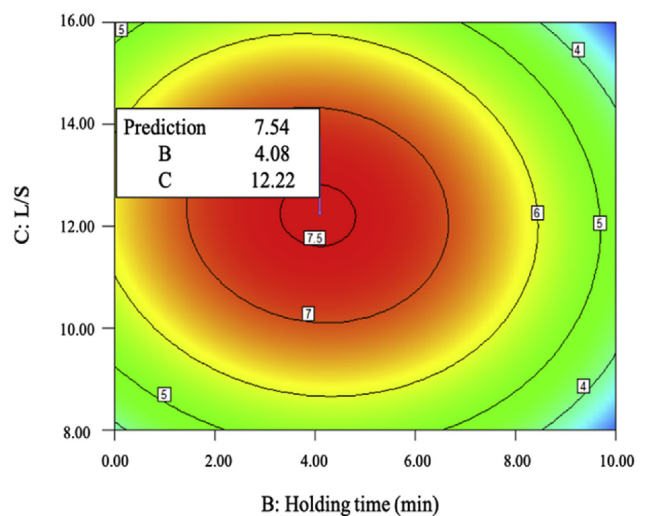
Table 3
ANOVA results of model.

Source	Sum of Squares	df	Mean Square	F Value	Prob > F
Model	55.14	9	6.13	6.12	0.0121
A	0.26	1	0.26	0.26	0.6283
B	4.50	1	4.50	4.49	0.0719
C	0.20	1	0.20	0.20	0.6663
AB	6.60E-03	1	6.60E-03	6.58E-03	0.9376
AC	2.63	1	2.63	2.62	0.1495
BC	0.25	1	0.25	0.25	0.6299
A^2	9.18	1	9.18	9.17	0.0192
B^2	17.03	1	17.03	17.00	0.0044
C^2	16.22	1	16.22	16.19	0.0050
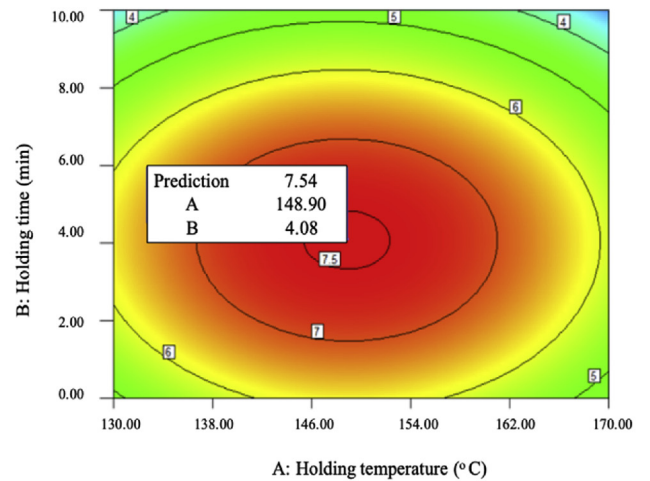
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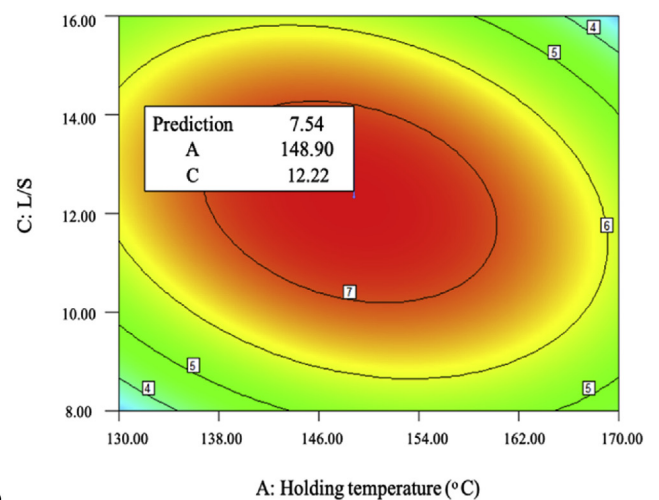
b

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Fig. 3. MHTL conditions under optimal HMF yield.

condition mentioned above. Similar results are observed for the other parameters combination (Fig. 2b&c). The surface p-value data in Table 3 indicate that the model used in this study was adequate. These phenomena are same as the other researches, indicating the optimization work was successful (Maiti et al., 2018; Seo and Han, 2014). Therefore, arbitrary HMF yield can be obtained from sugarcane bagasse in acidic seawater at the reaction temperatures ranging from 130 to

170 °C, reaction times from 0 to 10 min, and L/S ratios from 8:1 to 16:1. Same trend of the plots is also displayed in Fig. S1 indicating that the highest glucose yield could be obtained and the acidic seawater could promote the conversion of bagasse into glucose.

Fig. 3 shows the predicted HMF yield and the corresponding reaction temperature, reaction time and L/S for the model. Compared to the contour plots in Fig. 3a&c, the contour in Fig. 3b is closer to an elliptical shape, indicating the presence of significant interaction between the reaction temperature and L/S value. Based on these plots, the highest HMF yield of 7.5 wt% can be achieved at a reaction temperature of 148.9 °C, reaction time of 4.1 min, and L/S value of 12.2, which is same as the actual value obtained in previous condition testing.

A quadratic fit to the data gave the following equation:

$$\text{HMF yield (wt\%)} = -112.95 + 1.22\,A + 0.87\,B + 4.57\,C - 4.06 \times 10^{-4}\,AB - 0.01\,AC - 0.01\,BCE - 3.69 \times 10^{-3}\,A^2 - 0.08\,B^2 - 0.12\,C^2, \tag{3}$$

where A is reaction temperature, B is reaction time, and C is the L/S ratio, respectively.

Based on this equation, an HMF yield of 8.1 wt% with 8% deviation is predicted under the optimal conditions, and theoretical yields for other conditions can also be predicted. For other materials with using MHTL, this yield is considerable. For example, Carrión-Prieto et al. reported that the HMF yields for the E. arborea and C. ladanifer lignocellulosic biomass hydrolysates after MW-assisted extraction were lower than 1% (Carrión-Prieto et al., 2018). Maiti et al. obtained several HMF yields from brewery industry spent grains, brewery liquid waste, starch industry wastewater, apple pomace solid waste and apple pomace ultrafiltration sludge by microwave heating, which was also lower than that of presented in this study (Maiti et al., 2018). And the highest yield in this study is even higher than the yield (7.6 mol%) derived from sugarcane molasses under similar microwave condition (i.e. reaction temperature at 150 °C, reaction time at 30 min and microwave power for 300 W) (Howard et al., 2018). Furthermore, seawater as a cheap and common solvent is even superior than some ionic liquids. Mamo et al. used [BMIM]Br as the ionic liquid and various mordenites as the catalysts to conversion of glucose into 5-HMF, but the final HMF yield was mostly lower than this study (Mamo et al., 2016). Zhang and Zhao obtained the HMF yield of 6.4% (this value was based on the hexose content and was equal to 3.5 wt%) derived from the pine wood in [C4mim]Cl under oil-bath temperature of 100 °C (Zhang and Zhao, 2010). In addition to the HMF yield, the price of the ionic liquids is very expensive, for example, [BMIM]Br needs $1–100 per kg depended on its quality according to the website (Alibaba, 2019). Therefore, this study presents a new and sustainable means of transforming biomass waste to HMF using seawater and the possible mechanisms for HMF production is worthwhile to investigating.

3.3. Possible mechanisms for HMF production in acidic seawater

The concentrations of LA in the reaction solutions derived from HMF rehydration (Deng et al., 2015; Mukherjee et al., 2015) were determined, and Fig. 4 summarizes the effects of the various MHTL conditions on the LA yields in HCl, seawater, and acidic seawater. These data demonstrate that the LA yield significantly increased as the reaction temperature was raised and the reaction time was increased, except for the increase of L/S ratio. Overall, the increases in the LA yields were consistent with the decreases of its precursor, HMF. Moreover, under certain MHTL conditions in seawater, no LA were produced, suggesting that seawater inhibited the dehydration of HMF to LA. Possible reason is that alkali and alkaline earth metal chlorides (NaCl, CaCl$_2$ and MgCl$_2$) in seawater lead to fewer byproducts and higher 5-HMF selectivity (Yan et al., 2013). Further research is required to determine the specific reason for this positive effect.

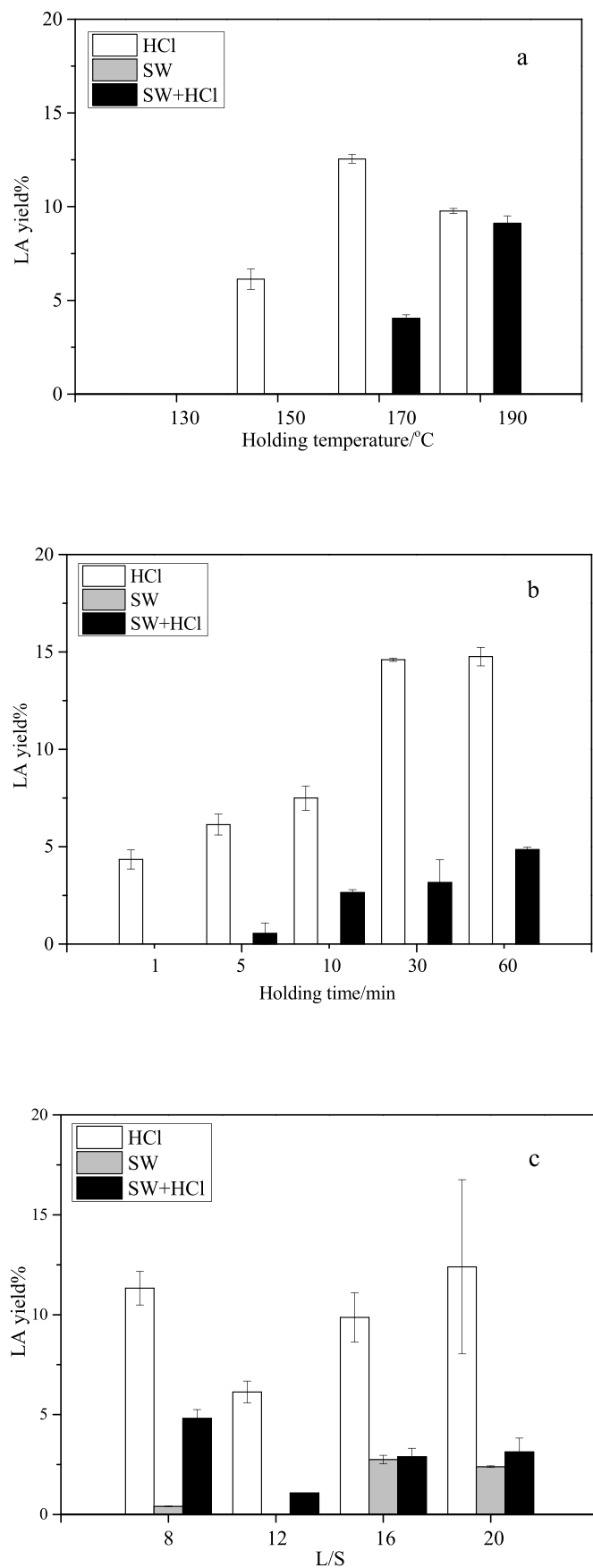The relationships between LA yield (in mol per g dry bagasse) and

Fig. 4. Effects of (a) holding temperature (°C), (b) holding time (min), and (c) L/S on the LA yield under different hydrothermal circumstances.
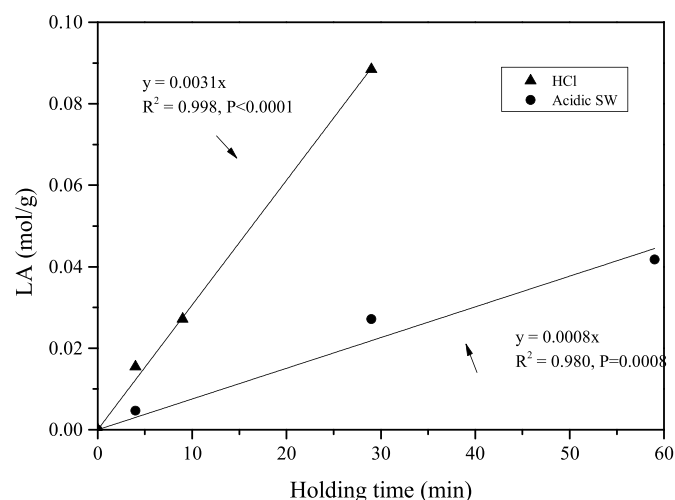
Fig. 5. Relationship between LA yield and holding time in HCl and acidic SW circumstances.

Fig. 6. Reaction pathway for bagasse under acidic SW circumstance.

reaction time in HCl as well as in acidic seawater are plotted in Fig. 5, in which positive correlations are evident between the LA yield and reaction time in both cases. An interesting result was that the degradation rate of HMF to LA in HCl was four times higher than that in acidic seawater, which corroborated the synergistic effect of acidity and seawater. These promising results warrant detailed investigations in the future.

Table 4 summarizes the yields of fructose and glucose derived from the sugarcane bagasse in HCl, seawater, and acidic seawater. Compared to the initial fructose and glucose yields obtained using various solvents (Table 1), the yields of these sugars were significantly changed after the MHTL process. Especially high fructose and glucose yields were obtained in seawater, indicating that the high salt contents in this medium promoted the hydrolysis of the biomass. This function of seawater has been proved by the research published (vom Stein et al., 2010). However, the results of this study also revealed that the minimal HMF yields from biomass conversion were observed in seawater. This may suggest that the conversions of glucose and fructose in seawater were inhibited in the absence of additional acidity and at low MHTL temperatures. Therefore, the use of acidic seawater appears to promote the conversion of fructose and glucose to HMF in conjunction with the catalysis by HCl (Yu et al., 2017), while preventing the dehydration of the newly formed HMF into LA under the MHTL conditions.

Insoluble materials were also obtained under the MHTL conditions

(Table 4). As shown in Fig. S2, a large number of microspheres were present on the solid residues after the reaction at a high temperature or after a long reaction time. These complex and polymeric materials are thought to be solid humins (Ren et al., 2015). Therefore, the increased production of solid residues (e.g., humins) under some experimental MHTL conditions (Table 4) may account for the observed decrease of HMF yield.

Finally, we illustrate the mechanisms by which HMF is produced in acidic seawater (Fig. 6). Bagasse is a typical waste biomass, which will undergo a series of complex and simultaneous reactions such as depolymerization, hydrolysis, dehydration, isomerization, rehydration, and polyermerization during the MHTL process (Liu et al., 2019; Yu et al., 2019a, 2019b). The conversion of sugarcane bagasse to HMF in acidic seawater can be considered to proceed primarily via several steps. The sugarcane bagasse initially undergoes rapid depolymerization and hydrolysis to form glucose and fructose, as reflected in the high yields of these sugar compounds obtained over the short reaction time. These monosaccharides are then efficiently converted to HMF by isomerization or direct dehydration, especially in the case of fructose which has a lower energy barrier towards conversion, because the acid-catalyzed reaction rate of fructose is 30–40 times that of glucose (Moreau et al., 1996). Only a small quantity of HMF is rehydrated to LA, as indicated by the red arrow in Fig. 6, while humins are simultaneously produced by undesirable polymerization.

4. Conclusions and perspectives

The results of this study demonstrate that a combination of HCl and seawater can synergistically promote the conversion of sugarcane

Table 4
Product yield under different MHTL conditions.

Conditions	HCl circumstance			SW circumstance			Acidic SW circumstance		
	Fructose (wt%)	Glucose (wt%)	Solid residues (wt %)	Fructose (wt%)	Glucose (wt%)	Solid residues (wt %)	Fructose (wt%)	Glucose (wt%)	Solid residues (wt %)
130 °C	4.3 ± 1.7	20.9 ± 4.3	33.2 ± 0.3	10.1 ± 0.9	11.5 ± 1.4	63.3 ± 1.4	3.6 ± 1.5	20.4 ± 4.0	36.1 ± 0.5
150 °C	ND	18.9 ± 2.0	25.7 ± 0.4	8.1 ± 1.4	15.9 ± 0.6	38.1 ± 1.1	1.2 ± 0.1	18.2 ± 0.3	33.4 ± 0.2
170 °C	ND	1.4 ± 0.0	18.1 ± 0.3	0.6 ± 0.0	12.8 ± 0.4	28.6 ± 0.0	ND	17.1 ± 1.4	34.0 ± 0.5
190 °C	ND	ND	21.1 ± 0.2	ND	3.7 ± 0.9	37.2 ± 0.2	ND	5.3 ± 0.0	21.3 ± 1.3
1 min	ND	14.2 ± 0.6	26.8 ± 0.5	4.7 ± 0.2	5.2 ± 0.4	62.7 ± 2.4	2.2 ± 0.0	9.8 ± 0.1	34.0 ± 0.2
5 min	ND	18.5 ± 2.0	25.7 ± 0.4	8.1 ± 1.4	15.9 ± 0.6	38.1 ± 1.1	1.2 ± 0.1	18.2 ± 0.4	33.4 ± 0.2
10 min	ND	23.5 ± 3.2	24.3 ± 1.1	7.4 ± 0.3	10.4 ± 0.2	43.8 ± 1.7	ND	10.6 ± 0.4	31.1 ± 0.3
30 min	ND	8.0 ± 0.5	17.6 ± 0.8	7.8 ± 0.2	9.7 ± 0.2	53.3 ± 2.6	ND	10.4 ± 0.0	29.7 ± 0.2
60 min	ND	6.6 ± 0.1	19.1 ± 0.2	4.7 ± 0.2	5.2 ± 0.4	58.5 ± 8.3	ND	9.1 ± 0.0	31.1 ± 0.0
8:1	ND	10.3 ± 0.3	30.7 ± 2.2	5.1 ± 0.8	9.1 ± 0.9	54.5 ± 1.2	ND	15.1 ± 1.9	37.8 ± 1.7
12:1	ND	18.8 ± 2.9	25.7 ± 0.4	8.1 ± 1.4	15.9 ± 0.6	38.1 ± 1.1	1.2 ± 0.1	18.2 ± 0.4	33.4 ± 0.1
16:1	ND	12.9 ± 1.2	23.6 ± 1.9	10.9 ± 1.2	14.6 ± 0.2	54.8 ± 2.6	0.5 ± 0.1	17.0 ± 1.4	33.9 ± 0.0
20:1	ND	15.5 ± 0.6	16.9 ± 1.7	14.3 ± 1.5	16.4 ± 1.7	42.1 ± 0.2	0.2 ± 0.0	23.5 ± 0.6	30.4 ± 1.3

The MHTL conditions for these products are same as that of HMF. ND: Not detected.
The calculation of solid residue yield was same as the reference (Shao et al., 2019a).
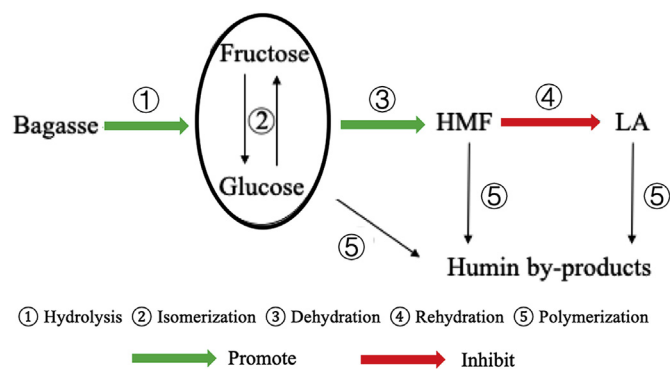
bagasse to generate glucose, fructose, and HMF under MHTL conditions. The highest HMF yield of 8.1 wt% was obtained using the MHTL process in acidic seawater at 149 °C in association with a reaction time of 4 min and a L/S ratio of 12:1. Seawater can effectively inhibit the dehydration of HMF to LA, i.e., the rate at which HMF is transformed to LA in HCl is four times higher than that in acidic seawater. This study indicates that the proposed application of acidic seawater in the MHTL process can efficiently transform waste biomass into value-added chemicals.

Future research can further explore the effects and mechanisms of various ions in seawater on the conversion of biomass waste into HMF under microwave and acidic conditions. More parameters such as microwave power, reaction pressure, pH, etc. can also be used as factors to optimize HMF yield. All these works aim to provide references for the HMF production by seawater instead of pure water in future biorefining industry.

CRediT authorship contribution statement

Yuchao Shao: Conceptualization, Methodology, Software, Validation, Investigation, Data curation, Writing - original draft. **Daniel C.W. Tsang:** Writing - review & editing. **Dongsheng Shen:** Validation, Formal analysis, Visualization. **Ying Zhou:** Resources, Writing - review & editing, Supervision, Data curation. **Zhiyuan Jin:** Resources, Writing - review & editing, Supervision, Data curation. **Dan Zhou:** Writing - review & editing. **Wenjing Lu:** Writing - review & editing. **Yuyang Long:** Writing - original draft, Conceptualization, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2020.109340.

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