CONVERSION OF SUGARCANE BAGASSE INTO LEVULINIC ACID BY ACID-CATALYZED HYDROTHERMAL METHOD*

Shunn Lei Nandar[1], Soe Soe Than[2]

Abstract

Lignocellulosic biomass is a long-term alternative carbon source and could be used as raw material to prepare liquid fuels and valuable chemicals. Among these chemicals, levulinic acid is a valuable platform compound, which is intermediate for preparing alternative petroleum-based chemicals such as plasticizer, coating, and fuel additives. This research work focused on the extraction of levulinic acid from lignocellulosic biomass such as sugarcane bagasse by acid-catalyzed hydrothermal method. The physico-chemical characteristics of sugarcane bagasse such as cellulose, hemicellulose, lignin, extractives, and ash content were analyzed by using TAPPI and AOAC methods. Dilute sulfuric acid pretreatment of sugarcane bagasse was firstly carried out with different variables such as solid to liquid ratio and reaction time for the optimum extraction of cellulose content. Acid-catalyzed hydrothermal treatment of pretreated sugarcane bagasse was performed by controlling reaction temperature, reaction time, concentration of hydrochloric acid (Bronsted acid) and concentration of aluminium chloride (Lewis acid). Central composite design was used to arrange experimental runs to optimize the cellulose content of sugarcane bagasse during dilute sulfuric acid pretreatment and the yield percent of levulinic acid based on concentration during acid-catalyzed hydrothermal method. For calculating the yield percent of levulinic acid based on concentration, the absorbance of levulinic acid was measured by UV-visible spectroscopy at 266 nm (λ_{max}). The maximum yield percent of levulinic acid based on concentration from sugarcane bagasse (89.64 ± 3.14 %) with the 6.78 % composition of levulinic acid was obtained by synergistic use of 6.4 % (v/v) HCl and 2.3 % (w/v) $AlCl_3$ at 171 ºC for 3 hr and 6 min. The levulinic acid under optimum conditions from pretreated sugarcane bagasse was identified by UV-Visible Spectroscopy for λ_{max}, FTIR Spectroscopy for functional groups and Gas Chromatography-Mass Spectroscopy (GC-MS) for the presence of levulinic acid.

Keywords: levulinic acid, sugarcane bagasse, bronsted acid, lewis acid

Introduction

Bioenergy and biomass-derived green chemicals have been attracting attention in recent years due to growing concerns about fossil fuel depletion and climate change (Kang *et al*., 2018). Low-value agro-residues, grasses and energy crops are preferred biomass sources from both a technical and socio-economic point of view, as biomass feedstock does not compete with the food chain (Rackemann & Doherty, 2011).

Due to their complex and specialized structures, biomass such as lignin, cellulose and hemicellulose are difficult to convert directly into desired fuels and chemicals. Therefore, converting biomass to specific platform chemicals and using the platform chemicals to produce various fuels and chemicals would be a viable strategy for biomass utilization (Yang *et al*., 2013). According to the US Department of Energy, one of the top 12 most promising building materials is levulinic acid, commonly known as 4-oxopentanoic acid or γ-kevaleric acid. It is also known as a promising organic intermediate for synthesizing a wide range of chemicals used in

---

* Special Award (2023)

[1] Part-time Demonstrator, Department of Industrial Chemistry, University of Yangon

[2] Professor, Department of Industrial Chemistry, University of Yangon

[*] Best Paper Award Winning Paper in Industrial Chemistry (2024)

products such as solvents, fragrances, oil additives, pharmaceuticals, and fuel additives (Pileidis & Titirici, 2016).

Significant research is currently underway worldwide to identify attractive pathways for the chemical conversion of lignocellulosic biomass to functional intermediates or platform chemicals. The most widely used method is the hydrolysis of biomass at high temperatures (100-250 °C) using acids as catalysts (Girisuta *et al*., 2013). In a Chromium (III) Chloride – Hydrochloric acid ($CrCl_3$-HCl) environment, Choudhary *et al*. (2013) presented a synergistic catalytic method for converting glucose to 5-HMF and LA. Due to their increased activity, Lewis acids are favored over Bronsted acids as isomerization catalysts. A combination of Lewis and Bronsted acids selectively catalyzes the hydrolysis of cellulose, isomerization of glucose, dehydration of fructose, and degradation of 5-hydroxymethyl furfural (5-HMF), ultimately leading to the yield of LA. It may improve the rate and selectivity (Yang *et al*., 2013).

More studies have been done using Bronsted acids alone than using a combination of Lewis and Bronsted acids to convert lignocellulosic biomass to levulinic acid. Zhang *et al*. (2016) reported the kinetic study of the conversion of levulinic acid from glucose, but not from lignocellulosic biomass, by a combination of HCl and $AlCl_3$. Therefore, the aim of this study is to apply the synergistic effect of combined Bronsted HCl and Lewis acids $AlCl_3$ on the conversion of sugarcane bagasse to levulinic acid.

Materials and Methods

Materials

Sugarcane bagasse was collected from Hledan Market, Yangon Region. The analytical grade of hydrochloric acid, aluminium chloride, sodium hydroxide, sulfuric acid, and acetone were purchased from Supershell Store, Pabedan Township, Yangon. **Methods**

Analysis of Composition of Sugarcane Bagasse

Determination of Moisture Content

Moisture content was determined by AOAC 925.09 method (AOAC, 2000).

Determination of Extractives Content

Extractives content was determined following the method (TAPPI T204 cm-97). 2.5 g of dried sample were loaded into the cellulose thimble. With a dry and clean Soxhlet extractor set up, 150 mL of acetone was used as solvent for extraction for 4 hr. After extraction, the sample was air-dried at room temperature for few minutes. Constant weight of the extracted sample was achieved in a hot air oven at 105 ^{o}C. Drying, cooling and weighing were repeated until the constant weight was obtained. Then, the extractive content was calculated with the following equation.

Extractives Content, % (w/w) = [Weight of raw extractive-laden sample – Weight of extractive-free sample] × 100

Determination of Hemicellulose Content

Hemicellulose content was determined following (Sluiter *et al*., 2012). 1 g of extractive-free sample was transferred into a 250 mL Erlenmeyer flask and 150 mL of 0.5 M NaOH was added. The mixture was boiled for 3.5 hr. It was filtered after cooling through vacuum filtration and washed until neutral pH. The residue was dried to constant weight in a hot air oven at 105 ^{o}C. Then, the hemicellulose content was calculated with the following equation.

Hemicellulose Content, % (w/w) = [Weight of sample before treatment – Weight of sample after treatment] × 100

Determination of Lignin Content

Lignin content was determined following the method (TAPPI T222 om-11). 0.3 g of extractive-free sample was transferred into a 250 mL Erlenmeyer flask and 3 mL of 72 % H_2SO_4 was added. The sample was kept at room temperature for 2 hr with careful shaking at 30 min intervals in order to allow complete hydrolysis. After initial hydrolysis, 84 mL of distilled water was added. The second step of hydrolysis was made to occur in an autoclave for 1 hr at 121 ^{o}C. Then, the slurry was cooled at room temperature and was filtered through vacuum filtration. The residue was dried to constant weight in a hot air oven at 105 ^{o}C. Then, the lignin content was calculated with the following equation.

$$\text{Lignin Content, \% (w/w)} = \frac{\text{Weight of sample after treatment}}{\text{Weight of sample before treatment}} \times 100$$

Determination of Cellulose Content

The cellulose content % (w/w) was calculated by difference, assuming that extractives, hemicellulose, lignin, ash, and cellulose are the only components of the entire biomass.

Cellulose Content, % (w/w) = 100 – [Hemicellulose + Lignin + Ash + Extractives]

Determination of Ash Content

Ash content was determined by AOAC 923 method (AOAC, 2000).

Conversion of Sugarcane Bagasse into Levulinic Acid

The sugarcane bagasse was sun-dried until its moisture content reached below 10 % (w/w). Then, the dried sugarcane bagasse was ground and screened to get suitable particle sizes (- 20 + 40 mesh size). The prepared sugarcane bagasse powder was treated with dilute sulfuric acid 3 % (v/v) at 121 ^{o}C to enhance the rupture of biomass. 18 experimental runs were conducted with different process variables such as solid to liquid ratio [1:10 (g : mL) - 1:20 (g : mL)] and reaction time (10 min – 30 min) for the maximum yield of cellulose content. About 3 g of prepared sample were added in a cylindrical stainless steel reactor with polytetrafluoroethylene line inside to resist corrosion by the acid catalyst. The acid catalyzed hydrothermal method was carried out under various process conditions such as acid concentration of Bronsted acid (HCl) and Lewis acid ($AlCl_3$), reaction temperature and reaction time with a fixed acid ratio (1 ($AlCl_3$) : 2 (HCl)) and solid to liquid ratio [1:15 (g : mL)] (Chang *et al*., 2007) in order to optimize the yield of levulinic acid. A preheated air oven was used for heating the reactor to the desired temperature. The reaction was quenched by immersing the reactor in a cool water bath after the desired reaction time. The reaction product was collected and separated from the unreacted residual biomass by filtration. The filtrate was partially neutralized to pH 5 with 1 M NaOH to stabilize levulinic acid and others possibly separated by centrifuge machine with 500 rpm for 5

min. The supernatant was separated by rotary evaporator under vacuum at 120 ºC. The distillate residue was detected by UV-visible spectrophotometer at 266 nm for the presence of levulinic acid.

Optimization of Process Variables by Response Surface Methodology

Central Composite Design was chosen for experimental arrangements. Stat-Ease Design-Expert 13 was used. The levels of variables with duplicated samples during dilute sulfuric acid pretreatment are shown in Table 1. The levels of variables for optimization of yield percent of levulinic acid from sugarcane bagasse during acid-catalyzed hydrothermal method are shown in Table 2.

Table 1: Levels of Variables during Dilute Sulfuric Acid Pretreatment of Sugarcane Bagasse

Parameters	Lower Level	Upper Level
Solid to Liquid ratio, g : mL	1 : 10	1 : 20
Reaction Time, min	10	30

Table 2: Levels of Variables during Acid-Catalyzed Hydrothermal Method of Sugarcane Bagasse

Parameters	Lower Level	Upper Level
Temperature, ºC	160	180
Reaction Time, hr	2	4
Concentration of HCl, % (v/v)	4	8
Concentration of $AlCl_3$, % (w/v)	1	3

Determination of Yield Percent of Levulinic Acid Produced from Sugarcane Bagasse Based on Concentration

The absorbance of levulinic acid at 266 nm was measured by UV-visible Spectrophotometer (Thermo Fisher Scientific Evolution 201/202 UV-Visible Spectrophotometer). The standard calibration curve for HMF (0 − 0.093 mmol/L) and LA (0 – 64.66 mmol/L) of (Zhang *et al*., 2013) was applied to calculate the concentration of levulinic acid and yield percent of levulinic acid based on concentration by using the equation; $A_{LA,\,266} = 0.0096 + 0.023C$.

$$\text{Yield percent of Levulinic Acid Based on Concentration} = \frac{\text{Concentration of Levulinic Acid } \left(\frac{\text{g}}{\text{L}}\right) \times \text{Dilution Factor} \times \text{Volume of Acid Catalyst (L)} \times 100}{\text{Amount of Biomass Used (g)}}$$

Where, $A_{LA,266}$ = Absorbance of Levulinic Acid at 266 nm, C = Concentration of Levulinic Acid

Identification of Levulinic Acid Produced from Sugarcane Bagasse by UV-Visible Spectroscopy, FTIR Spectroscopy and Gas Chromatography-Mass Spectroscopy (GC-MS)

The λ_{max} of levulinic acid was identified by UV-visible Spectrophotometer (Thermo Fisher Scientific GENESYS 10S UV-Visible Spectrophotometer) at the Department of Chemistry, University of Yangon.

The functional groups of levulinic acid were identified by FTIR Spectrometer (PerkinElmer Spectrum Two FT-IR spectrometer) at the Department of Chemistry, University of Yangon.

The levulinic acid produced from sugarcane bagasse was identified by Gas chromatography-mass spectroscopy (GC-MS), (Shimadzu GC-MS QP2010 Ultra) at the Department of Chemistry, University of Mandalay.

Results and Discussion

The chemical composition of sugarcane bagasse powder was presented in Table 3.The cellulose content of sugarcane bagasse was 46.7 % (w/w). Sugarcane bagasse had 24.79 % (w/w) of hemicellulose. The lignin content of sugarcane bagasse was 21.25 % (w/w). Below 10 % (w/w) moisture content gave suitable condition for further processing. Neureiter *et al*. (2002) reported that sugarcane bagasse is composed of 40.2 % (w/w) cellulose, 26.4 % (w/w) hemicellulose, 25.5 % (w/w) lignin and 8.2 % (w/w) others.

Table 3: Composition of Sugarcane Bagasse

Sr. No.	Components of Sugarcane Bagasse	Percent Composition, % (w/w)
1	Moisture content	8.0
2	Extractives	2.2
3	Hemicellulose content	24.79
4	Lignin content	21.25
5	Cellulose content	46.7
6	Ash content	5.06

Dilute sulfuric acid pretreatment was performed to enhance the rupture of sugarcane bagasse for the maximum yield of cellulose content. The 3D surface plots of the effect of solid to liquid ratio and reaction time on the yield percent of cellulose content, hemicellulose content and lignin content are shown in Figure 1 (a, b, c) respectively. The maximum cellulose content 56.15 ± 0.35, % (w/w), the minimum hemicellulose content 8.63 ± 0.35, % (w/w) and lignin content 28.76 ± 0.35, % (w/w) for sugarcane bagasse has resulted by 3 % (v/v) dilute sulfuric acid pretreatment with 1:14 (g:mL) solid to liquid ratio and 24 min reaction time at 121 ^{o}C. It was indicated that dilute acid pretreatment of sugarcane bagasse was related to produce maximum cellulose content. According to Mosier *et al*. (2005) and according to Zheng *et al*. (2009), a pretreatment procedure using dilute acid can dissolve virtually all hemicellulose and disrupt lignin-cellulose bonds, thus increasing the digestibility of enzymes/catalysts in the hydrolysis process. During dilute acid pretreatment, increasing solid to liquid ratio and increasing reaction

time resulted increasing in cellulose and lignin and decreasing in hemicellulose content. After increasing the reaction time beyond the optimum conditions, it was found that the slight decrease in cellulose content because of the further degradation products such as furfural and 5-HMF. A dilute sulfuric acid pretreatment is used, which can practically fully dissolve the hemicellulose component (80-90 %), increase the sensitivity of the cellulose, but only marginally break down the lignin component (Yang & Wyman, 2008). Almost all hemicellulose can be dissolved during the pretreatment process using dilute acid, but the lignin component cannot be dissolved. The process can be performed at a temperature range from 120-180 °C and residence times ranging from 15-60 min (Zheng *et al*., 2009).

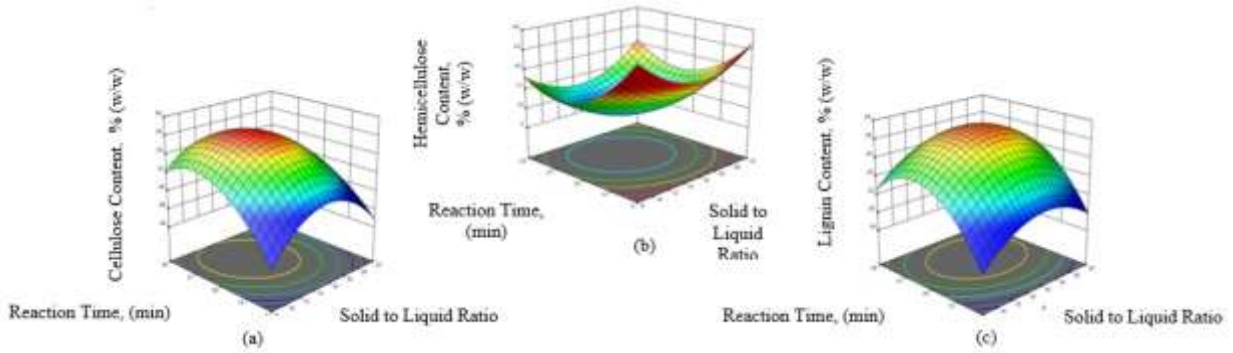


Figure 1: 3D Surface Plots of the Effect of Solid to Liquid Ratio and Reaction Time on the Yield Percent of (a) Cellulose Content (b) Hemicellulose Content (c) Lignin Content during Dilute Sulfuric Acid Pretreatment

The observed yield percent of levulinic acid produced from sugarcane bagasse due to the effect of temperature, reaction time, concentration of HCl and concentration of $AlCl_3$ are presented with three-dimensional surface plots for plotting to explore the interactions between variables and determine the optimum conditions for each factor for maximum yield percent of levulinic acid from sugarcane bagasse are shown in Figure 2. The coded equation for the quadratic model describing responses such as yield percent of levulinic acid from sugarcane bagasse based on concentration as a function of temperature, reaction time, concentration of HCl and concentration of $AlCl_3$ are shown in equation 1.

Yield Percent of Levulinic Acid Produced from Sugarcane Bagasse =

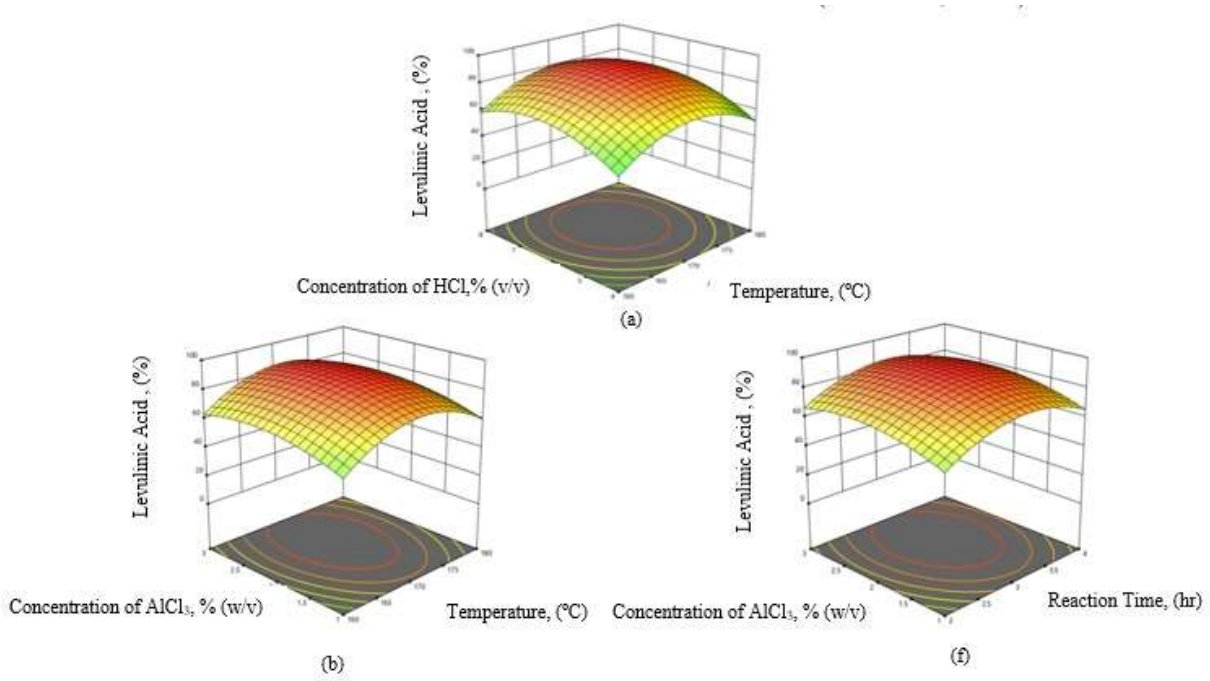
$$+88.55+3.13A+3.81B+5.94C+4.3D+0.2325AB+0.3313AC-0.0387AD+1.19BC$$

$$-0.0837BD+0.6275CD-19.32A^2-14.37B^2-14.17C^2-8.08D^2 \text{ ----------(1)}$$

By solving equation in Microsoft Excel, the predicted value for the optimum variables and yield percent of levulinic acid from sugarcane bagasse are obtained. The maximum yield percent of levulinic acid from sugarcane bagasse (89.64 ± 3.14 %) has resulted with optimum variables such as 171 ºC of temperature, 3 hr and 6 min of reaction time, 6.4 % (v/v) of concentration of HCl and 2.3 % (w/v) of concentration of $AlCl_3$. It was observed that as HCl and $AlCl_3$ concentrations increased, the production of levulinic acid increased significantly. However, increasing the concentrations of HCl and $AlCl_3$ above the optimum conditions resulted in no further increase in levulinic acid yield. Kuznetsov *et al*. (2013) noted that the following activity order might be used to categorize inorganic acids capacity to hydrolyze carbohydrate into LA: HCl > H_2SO_4 > H_3PO_4. Higher concentrations of mineral acid also severely corroded the

reactor (Chang *et al*., 2007). According to Signoretto *et al*. (2019), Lewis acid catalysts are used in this procedure because not all Lewis acid sites are active for glucose isomerization, but they also act as a catalyst for side reactions involving soluble polymers and insoluble humins. In this study, the more $AlCl_3$ was utilized in levulinic acid production from biomass beyond the optimum condition, the lower the percentage of levulinic acid produced due to the formation of undesirable side reactions. One undesirable side reaction is the formation of humins as a result of polymerization processes from a number of intermediate products. The synthesis of humins during the conversion of C6 carbohydrates to levulinic acid is also said to be more evident under harsh reaction circumstances (Sevilla & Fuertes, 2009a, 2009b; Sweygers *et al*., 2018; Van Zandvoort *et al*., 2013). The effect of reaction temperature on levulinic acid yield from sugarcane bagasse was investigated in the temperature range of 160–180 °C. Regarding the temperature, it can be seen that the yield of levulinic acid was sufficiently improved as the reaction temperature increased. This clearly indicates that the conversion of biomass to levulinic acid is endothermic in nature, so high temperatures are advantageous for effective conversion (Liu *et al*., 2017). However, the production of levulinic acid decreased above 180 °C. High temperatures can accelerate the conversion of carbohydrates to levulinic acid, but also cause undesirable side effects (Chang *et al*., 2007). The effect of reaction time on levulinic acid yield from sugarcane bagasse was investigated in the range of 2 hr to 4 hr. Regarding the reaction time; a decrease in the yield of levulinic acid was observed when the reaction was performed beyond the optimal conditions. This decrease in levulinic acid yield is due to the fact that the dehydrated product is unstable and can undergo decomposition upon prolonged exposure to high temperatures. In addition, prolonged hydrolysis of biomass may promote side reactions and generate chars and humins (Joshi *et al*., 2014; Patil & Lund, 2011).

Furthermore, if the reaction is prolonged, decomposition of levulinic acid may occur, resulting in a decrease in the yield of levulinic acid (Liu *et al*., 2017).



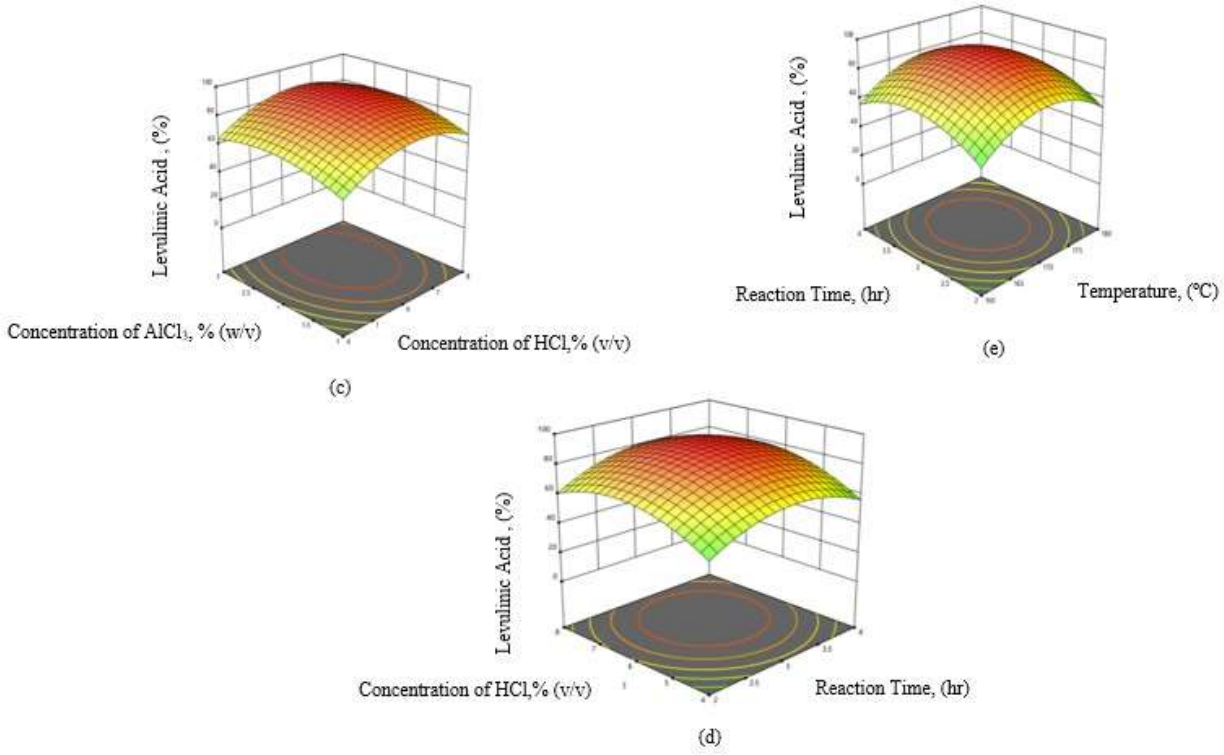


Figure 2: 3D Surface Plots of the Effect of (a) Temperature and Concentration of HCl(b) Temperature and Concentration of $AlCl_3$ (c) Concentration of HCl and Concentration of $AlCl_3$ (d) Reaction Time and Concentration of HCl (e) Temperature and Reaction Time (f) Reaction Time and Concentration of $AlCl_3$ on the Yield of Levulinic Acid Produced from Pretreated Sugarcane Bagasse

Identification of Levulinic Acid Produced from Sugarcane Bagasse

UV-Vis Spectrum of levulinic acid from sugarcane bagasse was shown in Figure 3. For interpretation of UV-Vis spectrum, the more easily an electron can be excited, the greater the wavelength that is absorbed, and the more electrons will be excited, the higher the absorbance. Compounds such as ketones, acids, esters, amides, and other compounds that contain the system π and lone pair shows two absorption: the transition n → π* at wavelengths longer (> 300 nm, low intensity) and the transition π → π* at wavelengths lower (< 250 nm high intensity with their conjugations), λ_{max} ribbon π → π* shifted to wavelengths greater and predictable with the Rules of Woodward (Pratiwi & Nandiyanto, 2022). Levulinic acid is keto-carboxylic acid containing keto carbonyl group and carboxylic acid group. Based on the observation of the absorption bands and the identification of the possible chromophore, it can be inferred that the chromophore absorption band at 266 nm appearing in Figure 3 is levulinic acid.

To identify the functional groups of levulinic acid produced from sugarcane bagasse, FTIR analysis was conducted. Figure 4 show the results of the FTIR spectrum of levulinic acid produced from sugarcane bagasse. Mthembu (2016) reported that the O-H (3300-2500 cm^{-1}) stretching of carboxyl groups, the C=O (1715 cm^{-1}) stretching of ketone and carboxyl groups, and the C-H (3000-2850 cm^{-1}) stretching of alkanes groups are essential vibrations of levulinic acid. For sugarcane bagasse, the FTIR spectrum contains all of the important vibrations of LA,

including O-H (3289 cm^{-1}) stretching for the carboxylic group, a very strong absorption of C=O at 1698 cm^{-1} stretching for the carboxylic ketone group, C-H (2928 cm^{-1}) stretching for alkane and the sp^2 hybridized C-O vibration stretching for carboxylic groups at 1209 cm^{-1}.

Levulinic acid was detected using the Gas chromatography-mass spectroscopy (GC-MS), as indicated in Figure 5. The GC chromatogram for sugarcane bagasse revealed the presence of two main products in the sample taken from the reaction mixture. The components were identified by comparing with the GC libraries (NIST14.lib) and literature. 4-oxo-pentanoic acid, methyl ester (levulinic acid, methyl ester) is present in the sample at a concentration of 0.62 peak area % with the similarity index 94 %, as indicated by the peak that emerged at 4.854 retention time. Levulinic acid, with a 6 .16 peak area % with the similarity index 98 %, is the primary component of the second peak with a retention time of 7.663. For sugarcane bagasse, the mass spectrum of levulinic acid, methyl ester is depicted in Figure 5a. The first bar found has an m/z ratio of 130, which is identical to the relative molecular mass of methyl ester of levulinic acid. The subsequent fragmented isotopes found are 115, 99, 88, 71, 57, 43, and so on. This particular fragment or ion may be the most abundant and have the highest intensity among all the observed ions because m/z 43 is the base peak in this mass spectrum. For sugarcane bagasse, there is another peak for confirmation of the presence of levulinic acid. Figure 5b shows the mass spectrum of levulinic acid. The first bar found has an m/z ratio of 116, which is identical to the relative molecular mass of levulinic acid. Following that, fragmented isotopes 96, 73, 56, 43, and so on are discovered. The pattern is extremely similar to the data retrieved from the NIST library, as illustrated in Figure 5. The fact that m/z 43 is the base peak in this mass spectrum indicates that this particular fragment or ion is the most abundant and has the highest intensity of all the observed ions. According to the peak area %, the composition of levulinic acid was 6.78 % with similarity index 98 % from sugarcane bagasse. The yield percent of 6.78 % composition of levulinic acid from sugarcane bagasse based on concentration (89.64 ± 3.14 %) was obtained.

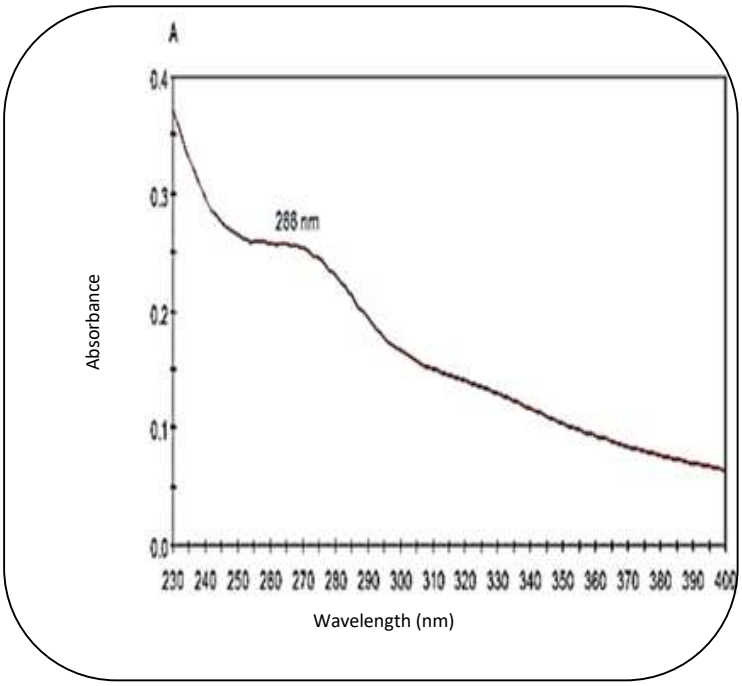


Figure 3: UV-Visible Spectrum of Levulinic Acid from Sugarcane Bagasse

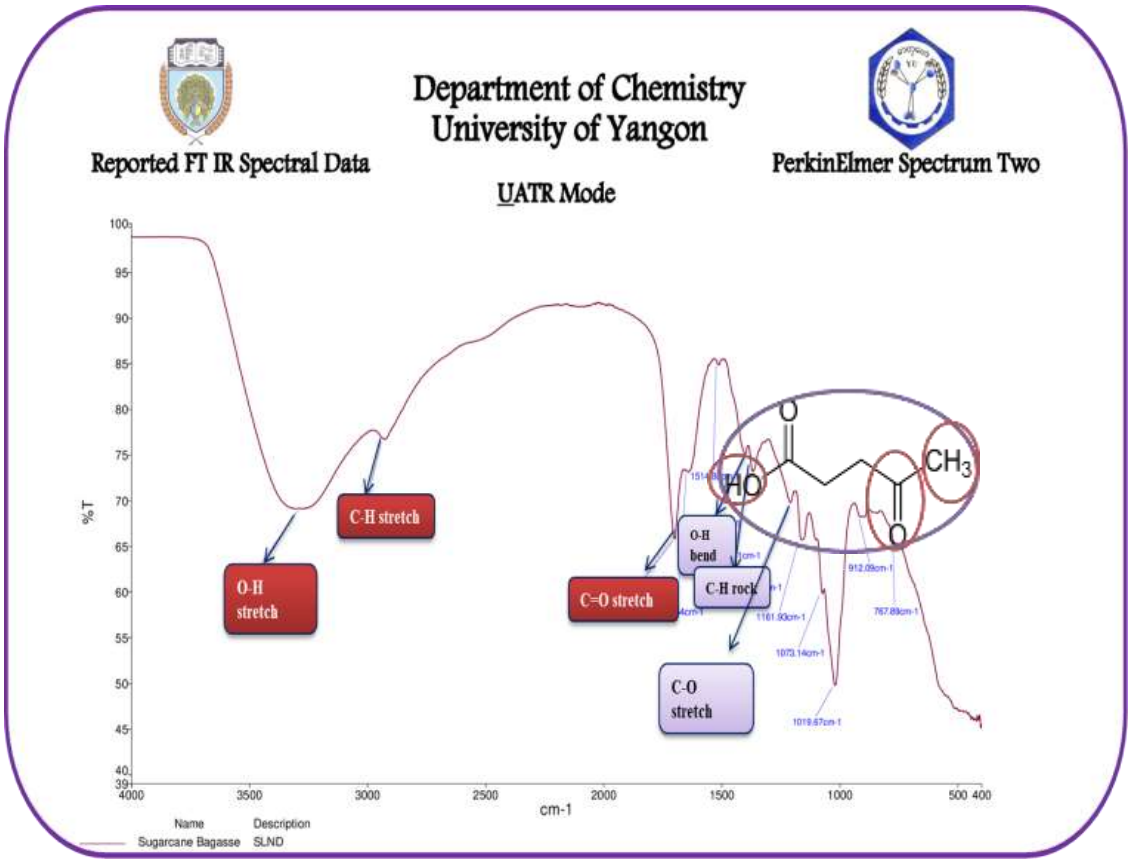
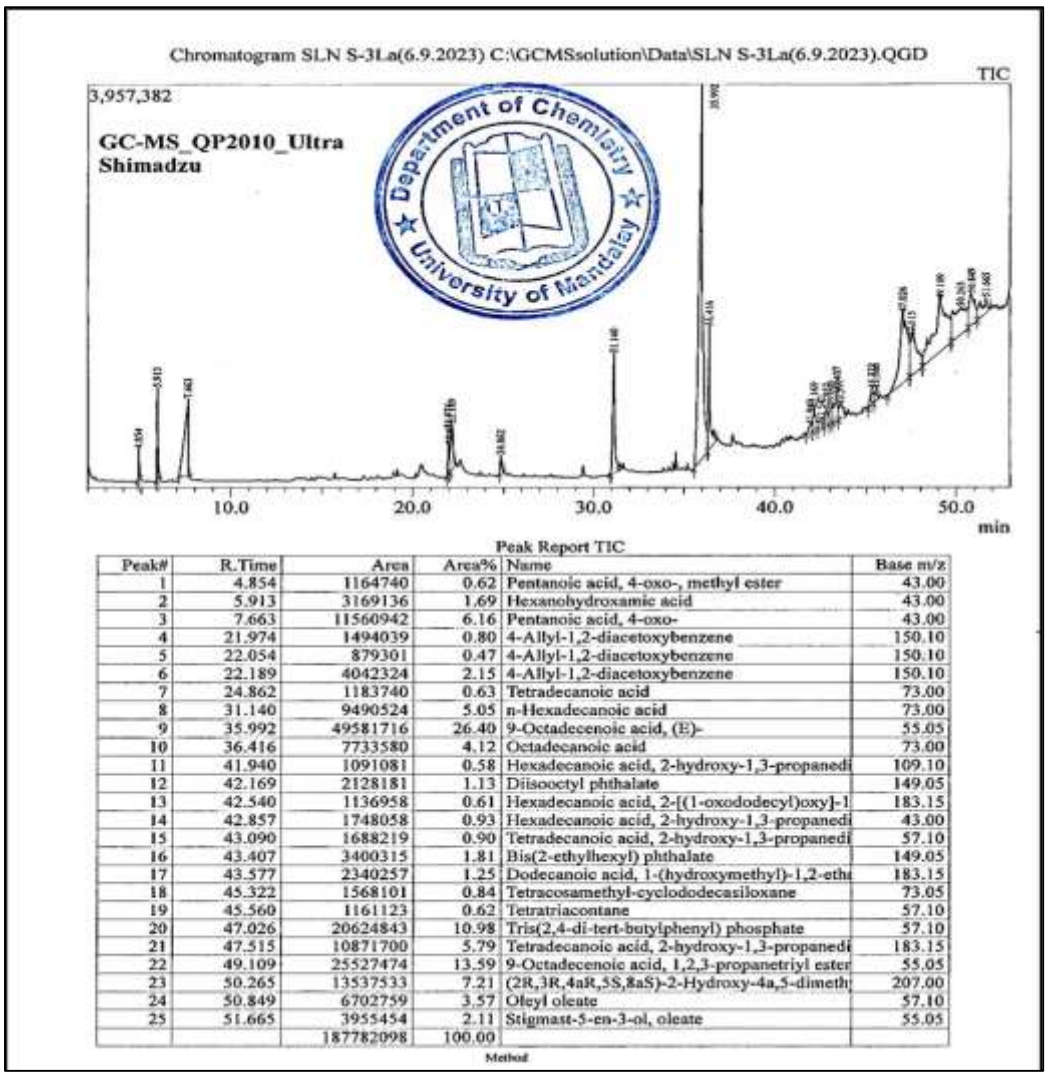


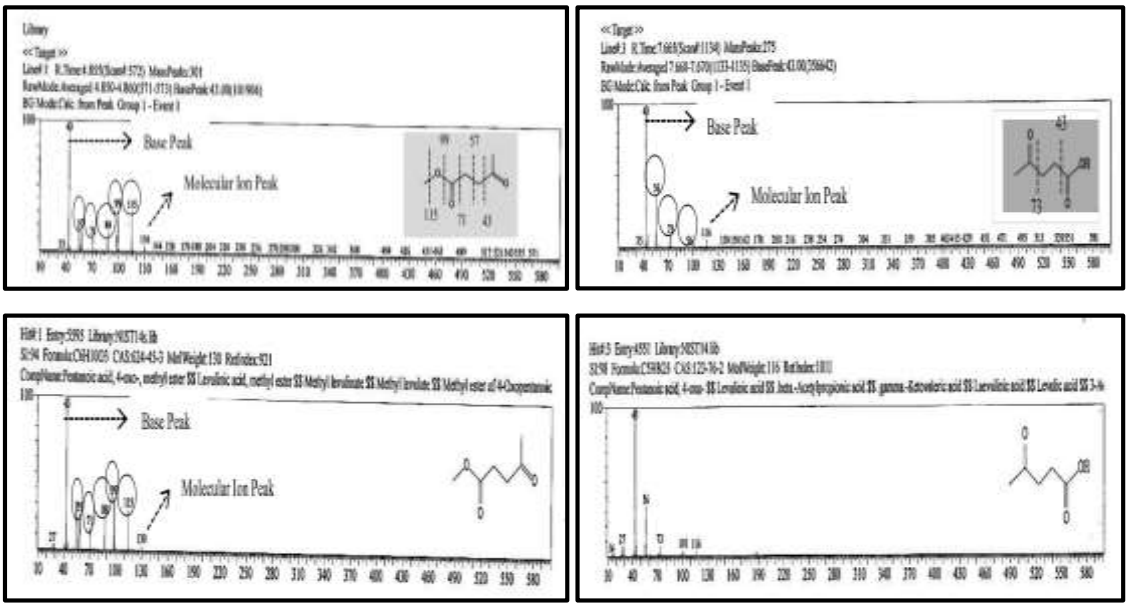
Figure 4: FTIR Spectrum of Levulinic Acid from Sugarcane Bagasse



Peak Report TIC

Peak#	R.Time	Area	Area%	Name	Base m/z
1	4.854	1164740	0.62	Pentanoic acid, 4-oxo-, methyl ester	43.00
2	5.913	3169136	1.69	Hexanohydroxamic acid	43.00
3	7.663	11560942	6.16	Pentanoic acid, 4-oxo-	43.00
4	21.974	1494039	0.80	4-Allyl-1,2-diacetoxybenzene	150.10
5	22.054	879301	0.47	4-Allyl-1,2-diacetoxybenzene	150.10
6	22.189	4042324	2.15	4-Allyl-1,2-diacetoxybenzene	150.10
7	24.862	1183740	0.63	Tetradecanoic acid	73.00
8	31.140	9490524	5.05	n-Hexadecanoic acid	73.00
9	35.992	49581716	26.40	9-Octadecenoic acid, (E)-	55.05
10	36.416	7733580	4.12	Octadecanoic acid	73.00
11	41.940	1091081	0.58	Hexadecanoic acid, 2-hydroxy-1,3-propanedi	109.10
12	42.169	2128181	1.13	Diisooctyl phthalate	149.05
13	42.540	1136958	0.61	Hexadecanoic acid, 2-[(1-oxododecyl)oxy]-1	183.15
14	42.857	1748058	0.93	Hexadecanoic acid, 2-hydroxy-1,3-propanedi	43.00
15	43.090	1688219	0.90	Tetradecanoic acid, 2-hydroxy-1,3-propanedi	57.10
16	43.407	3400315	1.81	Bis(2-ethylhexyl) phthalate	149.05
17	43.577	2340257	1.25	Dodecanoic acid, 1-(hydroxymethyl)-1,2-eth	183.15
18	45.322	1568101	0.84	Tetracosamethyl-cyclododecasiloxane	73.05
19	45.560	1161123	0.62	Tetratriacontane	57.10
20	47.026	20624843	10.98	Tris(2,4-di-tert-butylphenyl) phosphate	57.10
21	47.515	10871700	5.79	Tetradecanoic acid, 2-hydroxy-1,3-propanedi	183.15
22	49.109	25527474	13.59	9-Octadecenoic acid, 1,2,3-propanetriyl ester	55.05
23	50.265	13537533	7.21	(2R,3R,4aR,5S,8aS)-2-Hydroxy-4a,5-dimeth	207.00
24	50.849	6702759	3.57	Oleyl oleate	57.10
25	51.665	3955454	2.11	Stigmast-5-en-3-ol, oleate	55.05
		187782098	100.00		

Method



(a) **(b)**

Figure 5: Gas Chromatogram and Mass Spectra of (a) Levulinic Acid, Methyl Ester and (b) Levulinic Acid from Sugarcane Bagasse

Conclusion

This research work aimed to undertake the conversion of sugarcane bagasse into levulinic acid by acid-catalyzed hydrothermal method. The reaction pathways for conversion of sugarcane bagasse into levulinic acid are (1) hydrolysis of cellulose to glucose, (2) isomerization of glucose to fructose, (3) dehydration of fructose to 5-hydroxy methyl furfural and (4) rehydration of 5-hydroxy methyl furfural to levulinic acid. Only the isomerization process is catalyzed with Lewis acid $AlCl_3$. The Lewis acid was used in this research because the direct conversion of glucose to 5-HMF is slow and fructose is high selectivity to form levulinic acid. In this research, the purity of levulinic acid from sugarcane bagasse was low because of complex structure of sugarcane bagasse, the necessary for pretreatment process of sugarcane bagasse to achieve pure cellulose and the necessary for further purification process to achieve high purity levulinic acid.

Acknowledgements

I would like to express my gratitude to Dr Soe Soe Than, Professor and Head, Department of Industrial Chemistry, University of Yangon, for allowing me to conduct this research at the department and to submit this article.

References

Chang, C., Chen, P., & Ma, X. (2007). Levulinic acid production from wheat straw. *Bioresource Technology*, *98*(7), 1448–1453.

Choudhary, V., Mushrif, S. H., Ho, C. R., Anderko, A., Nikolakis, V., Marinkovic, N., Frenkel, A. I., Sandler, S. I., & Vlachos, D. G. (2013). Insights into the Interplay of Lewis and Brønsted Acid Catalysts in Glucose and Fructose Conversion to 5-(Hydroxymethyl)furfural and Levulinic Acid in Aqueous Media. *Journal of the American Chemical Society*, *135*(10), 3997–4006.

Girisuta, B., Dussan, K., Haverty, D., Leahy, J. P., & Hayes, M. G. (2013). A kinetic study of acid catalysed hydrolysis of sugar cane bagasse to levulinic acid. *Chemical Engineering Journal*, *217*, 61–70.

Joshi, S. S., Zodge, A., Pandare, K., & Kulkarni, B. D. (2014). Efficient conversion of cellulose to levulinic acid by hydrothermal treatment using zirconium dioxide as a recyclable solid acid catalyst. *Industrial & Engineering Chemistry Research*, *53*(49), 18796–18805.

Kang, S., Fu, J., & Zhang, G. (2018). From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis. *Renewable & Sustainable Energy Reviews*, *94*, 340–362.

Kuznetsov, B. N., Sharypov, V. I., Grishechko, L. I., & Celzard, A. (2013). Integrated catalytic process for obtaining liquid fuels from renewable lignocellulosic biomass. *Kinetics and Catalysis*, *54*(3), 344–352.

Liu, Y., Li, H., He, J., Zhao, W., Yang, T., & Yang, S. (2017). Catalytic conversion of carbohydrates to levulinic acid with mesoporous niobium-containing oxides. *Catalysis Communications*, *93*, 20–24.

Mosier, N. S., Wyman, C. E., Dale, B. E., Elander, R. T., Lee, Y., Holtzapple, M. T., & Ladisch, M. R. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, *96*(6), 673–686.

Mthembu, L. D. (2016). *Production of levulinic acid from sugarcane bagasse*.

Neureiter, M., Danner, H., Thomasser, C., Saidi, B., & Braun, R. (2002). Dilute-Acid hydrolysis of sugarcane bagasse at varying conditions. *Applied Biochemistry and Biotechnology*, *98–100*(1–9), 49–58.

Patil, S. K. R., & Lund, C. (2011). Formation and Growth of Humins via Aldol Addition and Condensation during Acid-Catalyzed Conversion of 5-Hydroxymethylfurfural. *Energy & Fuels*, *25*(10), 4745–4755.

Pileidis, F. D., & Titirici, M. (2016). Levulinic Acid Biorefineries: New Challenges for Efficient Utilization of Biomass. *Chemsuschem*, *9*(6), 562–582.

Pratiwi, R. A., & Nandiyanto, A. B. D. (2022). How to read and interpret UV-VIS spectrophotometric results in determining the structure of chemical compounds. *Indonesian Journal of Educational Research and Technology*, *2*(1), 1–20.

Rackemann, D. W., & Doherty, W. J. (2011). The conversion of lignocellulosics to levulinic acid. *Biofuels, Bioproducts and Biorefining*, *5*(2), 198–214.

Sevilla, M., & Fuertes, A. B. (2009a). Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. *Chemistry: A European Journal*, *15*(16), 4195–4203.

Sevilla, M., & Fuertes, A. B. (2009b). The production of carbon materials by hydrothermal carbonization of cellulose. *Carbon*, *47*(9), 2281–2289.

Signoretto, M., Taghavi, S. S., Ghedini, E., & Menegazzo, F. (2019). Catalytic Production of Levulinic Acid (LA) from Actual Biomass. *Molecules*, *24*(15), 2760.

Sluiter, A., Hames, B. R., Ruiz, R., Scarlata, C. J., Sluiter, J., Templeton, D. W., & Crocker, D. P. (2012). Determination of Structural Carbohydrates and Lignin in Biomass. *NREL Laboratory Analytical Procedures for Standard Biomass Analysis*.

Sweygers, N., Harrer, J., Dewil, R., & Appels, L. (2018). A microwave-assisted process for the in-situ production of 5-hydroxymethylfurfural and furfural from lignocellulosic polysaccharides in a biphasic reaction system. *Journal of Cleaner Production*, *187*, 1014–1024.

Van Zandvoort, I., Wang, Y., Rasrendra, C. B., Van Eck, E. R. H., Bruijnincx, P. C. A., Heeres, H. J., & Weckhuysen, B. M. (2013). Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions. *Chemsuschem*, *6*(9), 1745–1758.

Yang, B., & Wyman, C. E. (2008). Pretreatment: the key to unlocking low-cost cellulosic ethanol. *Biofuels, Bioproducts and Biorefining*, *2*(1), 26–40.

Yang, F., Fu, J., Mo, J., & Lu, X. (2013). Synergy of Lewis and Brønsted Acids on Catalytic Hydrothermal Decomposition of Hexose to Levulinic Acid. *Energy & Fuels*, *27*(11), 6973–6978.

Zhang, J., Li, J., Tang, Y., & Xue, G. (2013). Rapid method for the determination of 5-Hydroxymethylfurfural and levulinic acid using a Double-Wavelength UV spectroscopy. *The Scientific World Journal*, *2013*, 1–6.

Zhang, X., Murria, P., Jiang, Y., Xiao, W., Kenttämaa, H. I., Abu-Omar, M. M., & Mosier, N. S. (2016). Maleic acid and aluminum chloride catalyzed conversion of glucose to 5-(hydroxymethyl) furfural and levulinic acid in aqueous media. *Green Chemistry*, *18*(19), 5219–5229.

Zheng, Y., Pan, Z., & Zhang, R. (2009). Overview of biomass pretreatment for cellulosic ethanol production. *International Journal of Agricultural and Biological Engineering*, *2*(3), 51–68.