Niğde Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi
Niğde Ömer Halisdemir University Journal of Engineering Sciences

Araştırma makalesi / Research article

www.dergipark.org.tr/tr/pub/ngumuh / www.dergipark.org.tr/en/pub/ngumuh

Conversion of chicory to valuable chemical LA and by-products with LABSA and BSA

Hindibanın LABSA ve BSA katalizörleri ile değerli kimyasal LA ve yan ürünlere dönüştürülmesi

Özge Biçer[1,*], Nihal Üremek Cengiz[2]

[1,2] *Ege University, Department of Chemical Engineering, 35040, İzmir, Türkiye*

Abstract

This work examined the hydrothermal breakdown of biomass into platform chemicals, including acetic acid (AA), formic acid (FA), 5-hydroxy methyl furfural (5-HMF), and levulinic acid (LA). Chicory was selected as feedstock because of its high potential to produce valuable chemicals. Reactions were performed with BSA (benzenesulfonic acid) and LABSA (linear alkyl benzene sulfonic acid) as sulfonic acid catalysts. The studies were conducted with different catalyst concentrations (100, 300, and 600 mM) for 110 minutes at 200 °C with a biomass-to-solvent ratio of 1g/25 mL. The variation of product yield and composition on parameters such as time, sulfonic acid concentration, and type of catalyst were investigated. The maximum levulinic acid yields in wt.% achieved through the experiments of this study were 22.65 wt.% (9.05 g/L) for 600 mM BSA and 85.93 wt.% (34.37 g/L) for 600 mM LABSA at 200 °C.

Keywords: Chicory, Levulinic acid, Biomass, Sub-critical water

Öz

Bu çalışmada biyokütlenin levulinik asit, 5-hidroksi metilfurfural, formik asit ve asetik asit gibi değerli kimyasallara hidrotermal dönüşümü araştırılmıştır. Değerli kimyasalların üretimi amacıyla yüksek potansiyeli sebebiyle hindiba biyokütle olarak seçildi. Reaksiyonlar, sülfonik asit katalizörleri olarak BSA (Benzensülfonik asit) ve LABSA (Doğrusal alkil benzen sülfonik asit) varlığında gerçekleştirildi. Deneyler, 110 dakikalık bir reaksiyon süresinde, 200°C sıcaklıkta, 1g/25mL biyokütle/çözücü oranında ve değişen kataliözör konsantrasyonlarında (100, 300 ve 600 mM) yapılmıştır. Ürün verimi ve bileşiminin zaman, sülfonik asit konsantrasyonu ve katalizör türü gibi parametreler ile ilişkisi araştırıldı. Bu çalışmada elde edilen maksimum levulinik asit verimi olarak, 200°'de 600 mM BSA için ağırlıkça %22.65 (9.58 g/L) ve 600 mM LABSA için ağırlıkça %85.93 (34.37 g/L) elde edilmiştir.

Anahtar kelimeler: Hindiba, Levulinik asit, Biyokütle, Kritik altı su

1 Introduction

The decrease in fossil resources and environmental concerns has increased the need to research chemical production from renewable resources. Biomass is considered as a potential feedstock to obtain valuable chemicals from renewable resources, therefore its utilization in chemical synthesis carries importance.

Plant biomass is a complex and diverse material consisting of various components that are of interest for producing platform chemicals such as levulinic acid (LA). These components can be broadly categorized as polysaccharides (such as cellulose, hemicellulose, starch, inulin, chitin, etc.), lignin, protein, and extractives [1] Through the hydrolysis of polysaccharides, monosaccharides like glucose and fructose can be obtained [2]. The initial step in the synthesis of LA involves the acid-catalyzed dehydration of monosaccharides to produce 5-HMF. LA is obtained through the subsequent rehydration of 5-HMF, with formic acid being co-produced as the side product [3]. LA is a highly desirable chemical intermediate for the synthesis of synthetic liquid fuels, valuable chemicals, and polymers. It is considered a promising product derived from biomass by the Biomass Program of the US Department of Energy, owing to its unique chemical structure containing active ketonic and carboxylic functional groups [4].

LA finds extensive applications in the production of resins, solvents, polymers, and chemical intermediates. It is also a crucial ingredient in the manufacturing of spices, cosmetics, pharmaceuticals, pesticides, and fungicides [5]. With its bi-functional group comprising a carboxylic acid and a ketone, both possessing active acidic hydrogens, LA exhibits high reactivity and versatility for various chemical reactions and transformations [6]. It can be involved in esterification, redox, substitution, and condensation reactions which make it a valuable platform chemical [7]. Some compounds that can be synthesized from LA include, gamma-valerolactone, and levulinic esters which are produced through hydrogenation of LA, angelica lactone, diphenolic acid, 2-methyltetrahydrofuran, 1,4-butanediol and, 1,4-pentanediol [7,8]. Furthermore, LA acts as a feedstock for the synthesis of liquid hydrocarbon fuels through various catalytic pathways [8]

---

* Sorumlu yazar / Corresponding author, e-posta / e-mail: nihal.cengiz@ege.edu.tr (N. Üremek Cengiz)

Geliş / Recieved: 23.02.2024 Kabul / Accepted: 01.05.2024 Yayımlanma / Published: 15.07.2024
doi: 10.28948/ngumuh.1442011

Numerous studies have been conducted in the literature regarding the production of LA from various feedstocks and biomass. Signoretti categorized these studies from three different generations of biomass as basically food crops, non-food crops, and algae [2]. Antonetti et al. [9] classified research on this field based on the employed catalyst systems in the catalytic conversion of cellulose and biomass they reviewed four types of catalyst systems, homogeneous mineral acids, and salts in water, heterogeneous catalysts in water which are also employed in C_6 sugars [10]. Homogenous mineral acid catalysts such as HCl, H_2SO_4, HNO_3, and H_3PO_4 are widely used in the oldest methods and the highly efficient catalysts for sugar decomposition into LA [9–12].

Zheng et al. performed a study on LA synthesis from corn stalks using $FeCl_3$ as the catalyst [13]. The highest yield of LA achieved was 48.89% (concentration of 16.14 g/L) at 180 °C with 0.5 mol/L $FeCl_3$. Qing et al. investigated the production of LA from corncobs using tin tetrachloride ($SnCl_4$) as the catalyst. The highest LA yields obtained at temperatures of 170, 180, and 190 °C were 65.81%, 68.34%, and 69.50%, respectively, achieved within 36, 26, and 24 minutes. The results indicated that the reaction time required to achieve maximum yields decreased significantly with increasing temperature [4].

Cheng et al. studied glucose conversion to LA over a solid acid catalyst. They utilized CH_3-SBA-15-SO_3H as a catalyst and γ-valerolactone as the solvent for the conversion. The hydrothermal experiments were conducted at temperatures between 140 and 180°C. The highest yield of LA (60 mol%) was achieved in 150 minutes at 180°C [11]. Weiqi and Shubin [15] investigated the conversion of glucose to LA using various homogeneous Brønsted acids or Lewis acids in a batch reactor system. They explored the synergistic catalytic effect of mixed acid systems consisting of Brønsted and Lewis acids. Among the systems tested, the H_3PO_4-$CrCl_3$ system showed optimal performance. A maximum LA yield of 54.24% was obtained in 100 % glucose conversion at 170 °C for 240 min.

In this study, the aim is to investigate the reaction yields and product composition of the acid-catalyzed hydrolysis process of chicory. Chicory is a promising biomass due to its high content of carbohydrates such as inulin. Inulin is hydrolyzed and decomposed into structural units which are fructose and glucose in an acidic medium. So, it is a significant alternative raw material in LA and HMF production [16,17]

Specifically, the goal of this research is to investigate the potential of BSA and LABSA as a catalyst for biomass conversion to LA and the effects of their different concentrations on the reaction yields. BSA and LABSA are novel catalysts that have comparable catalytic performance with mineral acids and are less corrosive. From an environmental point of view using sulfonic acid catalysts provides an advantage in this manner. The selection of chicory as the biomass type and its interaction with aromatic sulfonic acid catalysts makes this study original, as there are a few studies in the literature that focus on the acidic hydrolysis of real biomass with a sulfonic acid catalyst. Exploring the potential of these catalysts and process configurations can contribute to the development of economically viable and sustainable pathways for the synthesis of LA from biomass. The findings provide valuable insights for further research and development in this field, intending to commercialize LA as a platform chemical for a wide range of applications.

An optimization process was performed by using Response surface methodology (RSM). The analysis of variance (ANOVA) test was conducted to evaluate the influence of independent variables (catalyst type, catalyst concentration, and reaction time) on the LA yield, which is the dependent variable using Minitab software. Optimization of the process is significant to produce LA at higher concentrations and it decreases the cost of the refining process.

2. Material and method

Figure 1. The reactor system

2.1 Materials

In this study, chicory was selected as biomass feedstock. Experimental runs were carried out in the presence of BSA (Benzenesulfonic acid) and LABSA (Linear alkyl benzene sulfonic acid). BSA (>97%) was purchased from Merck, and LABSA) (>95%) was purchased from Sigma-Aldrich. The necessary quantities of catalysts containing sulfonic acid were dissolved in distilled water to produce solutions with predetermined concentrations. Before use, the biomass samples were dried and pulverized into 1 mm particles.

2.2. Methods

2.2.1. Experimental system

In this work, stirring batch autoclave systems were used to perform hydrothermal cracking studies at the reaction temperature of 200 °C. The experiments were conducted in a reactor setup that provided easy sampling at predetermined intervals. The slight internal volume change did not affect the concentration of the solution in the reactor. Eight samples, each with a volume of 0.5 mL, were taken during the reaction time, and one sample at the beginning of the run. Manometers, high-pressure valves, ovens, PID temperature control units, autoclave stirring systems, cooling water circulation lines, and sample lines are all parts of the reactor system's equipment. The reactor system is given in Figure 1. Within the reactor is a vessel with a capacity of 25 mL.

2.2.2 Experimental procedure

A biomass sample and 25 mL of sulfonic acid solution were added to the reactor to start the experiment. The valves were closed after the components were supplied in the proper amounts and the system was flushed with N_2 gas to eliminate any remaining air. After that, the reactor was put in a heater, which raised the system's temperature to the required reaction temperature. Experiments were carried out in sub-critical water due to the high yields obtained at sub-critical conditions. The studies were carried out for 110 minutes, agitating the reaction liquid with a magnetic bar. After the reaction was finished, the reactor was cooled, and the solid residue was removed from the aqueous component by filtration.

2.2.3. Analytical methods

Analytical methods were employed to analyze the products obtained from the experiments using HPLC and GC-MS instruments. These devices facilitated the determination of the existing compounds in the products, as well as the quantification of specific compounds present in the liquid products.

Numerous samples were gathered for the investigation, both before the reaction reached the desired temperature and while the reaction was maintained during the reaction time. Samples were taken at 0, 10, 20, 30, 50, 70, 90, and 110 minutes of reaction. Refractive index (RI) detector-equipped Agilent 1200 HPLC system and Biorad column were used to measure the concentrations of organic acids, 5-HMF, and sugar monomers. The yields of various acids, including levulinic acid (LA), 5-hydroxymethylfurfural (5-HMF), formic acid (FA), and acetic acid (AA), as well as various sugar molecules, including glucose, sucrose, arabinose and the summation of mannose, fructose, galactose, xylose, and rhamnose (M+F+G+X+R) were determined. Aminex HPX-87H Column #1250140 and 0.5 mM H_2SO_4 as mobile phase was used with a flow rate of 0.6 mL/min The column and detector temperature of 30 °C are set in the method. Analysis run time is 50 min and the injection volume is 20 µL.

To determine the various chemical compounds that might have been generated in the aqueous product, GC-MS equipment was used. Agilent Technologies' 7890A GC system and 5975C VL MSD with triple-axis detector make up the GC-MS device. The carrier gas is Helium, and the flow rate is 1.2 mL/min is adjusted. Detector and Injector temperatures are set to 250 °C. The oven is kept at 40°C.

2.2.4. Calculation of product yields and Carbon liquefaction efficiency

Amount of the species “i” in the product [mg], m_i

Carbon ratio in the molecular formula of the species, X_C

Amount of Carbon of the species in the product [mg],

$$C_i = m_i \times X_C \tag{1}$$

$$\text{Carbon-based yield, \%} = \frac{C_i}{C_{feed}} \times 100 \tag{2}$$

$$\text{Weight-based yield, \%} = \frac{m_{product}}{m_{biomass}} \times 100 \tag{3}$$

Carbon Liquefaction Efficiency:

$$CLE_i\ (\%) = \left(\frac{\sum C_i}{C_{feed}}\right) \times 100 \tag{4}$$

3. Results and discussion

Chicory's elemental composition was examined using elemental analysis. The results are given in Table 1.

Table 1. Elemental analysis results of chicory

Elements	(% Weight)
C	40.78
H	6.12
N	1.83
S	-
O	51.27

The composition of the structural components of the biomass, which include cellulose, hemicellulose, lignin, and extractives was determined according to the Van Soest methodology [18]. Table 2 shows the results of this analysis.

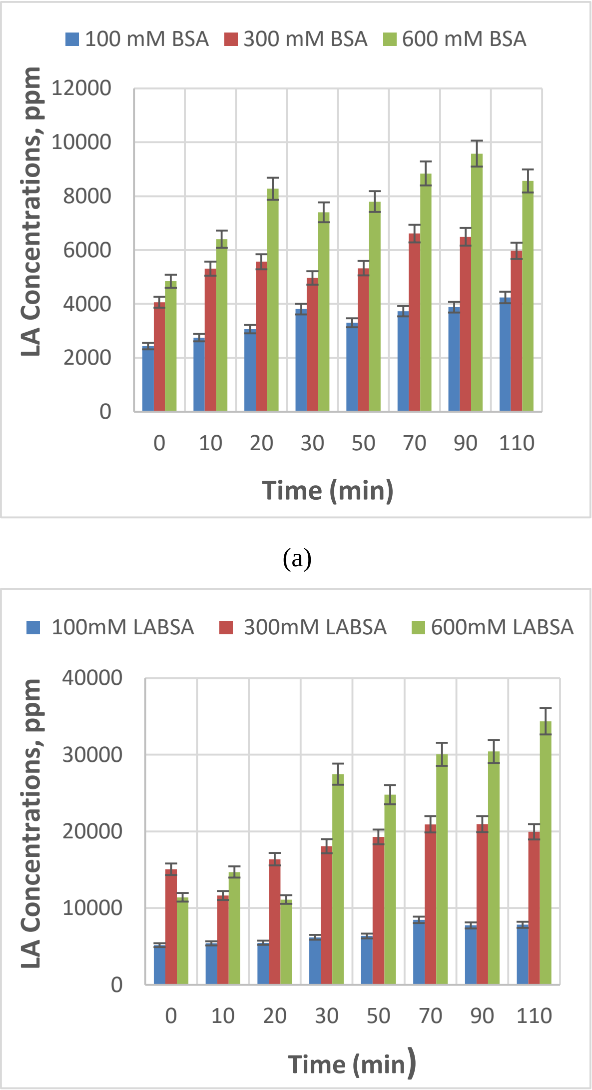
Table 2. The composition of chicory

Components	(% Weight)
Moisture (% weight)	7.05
Ash (%weight)	15.80
Extractive Matter (Water soluble)	14.30
Extractive Matter (In organic solvents) (%weight)	10.26
Total Extractives (%weight)	24.56
Lignin, %	8.0
Cellulose, %	37.54
Hemicellulose, %	10.89

As stated by Signoretto et al. [2] the acid-catalysed hydrolysis process has been recognized as a pivotal stage in chemical production, conducted at a moderately low-temperature range of 100–250°C [2]. To obtain LA from biomass and glucose, Girisuta et al. used sulfuric acid as a catalyst, with concentrations ranging from 0.11 to 0.55 M and 0.05 to 1 M, respectively [19,20]. Based on this literature and our previous works [21], we have selected sulfonic acid concentrations (ranging from 0.1 to 0.6 M) and a reaction temperature of 200 °C for our study. It was planned to work in below-critical conditions of water to obtain higher LA yields. We have found through our experiments that with the sulfonic acid catalysts used in this study, acid formation occurs at temperatures above 180 °C, and our results proved that 200 °C was a suitable temperature for this conversion.

The sulfonic acid catalysts' effects on levulinic acid production are given in sections 3.1 and 3.2, and the other products such as organic acids, 5-HMF, and sugar compounds are given in section 3.3. The performance of LABSA and BSA are compared and evaluated in Section 3.4. The Carbon content of the species in the product stream is found by Equation 1 and the product yields are calculated based on the carbon content of the feed stream and the weight of biomass as shown in Equations 2 and 3, respectively. Carbon liquefaction efficiency shows what percentage of Carbon content in the feed is converted to aqueous products and is shown in Equation 4. 3.1. Effects of BSA Concentration on Levulinic Acid Production.

Experiments employing various BSA concentrations (100, 300, and 600 mM) were carried out to evaluate the effect of BSA concentration on LA yield. For every reaction, the feed content was 1g/25mL and the reaction temperature was kept at 200 °C. To investigate the impact of BSA concentration on LA yield, experiments were conducted using different concentrations of BSA (100, 300, and 600 mM). Figure 2a illustrates the variation in the weight-based yields of LA with varying BSA concentrations.



(a)

(b)

Figure 2. The effect of catalyst concentration on the levulinic acid concentration (T=200 °C, Concentrations: 100, 300, 600mM, b/s:0.04 g/mL) with (a) BSA and (b) with LABSA.

Specifically, when using 100 mM BSA, the highest amount of LA was achieved after 110 minutes of reaction time. The maximum amount of LA was obtained with 300 mM BSA, within 70 minutes while for 600 mM BSA in 90 minutes of reaction time. The highest LA concentrations obtained with 100, 300, and 600 mM BSA are 4.25, 6.61, and 9.58 g/L, respectively. These results indicate that the concentration of BSA plays a significant role in determining the yield of LA. While the concentration of the sulfonic acid is lower, the reaction proceeds slower, and the optimum reaction time was found as 110 min at 100 mM. At higher concentrations, the highest yields were reached in shorter reaction times.

Kang et al. [22] investigated the effects of p-toluene sulfonic acid in varying concentrations of 0.2 mol/L to 0.6 mol/L in the conversion of glucose into LA. They found little increases in yields of LA which are close to yields obtained with H_2SO_4. Yüksel et al. focused on the conversion of safflower with BSA, PTSA, and LABSA in the catalyst concentration range of 30-300 mM. PTSA showed better catalytic activity than other catalysts at the highest concentration [21]. These findings are consistent with our results, and it can be concluded that higher amounts of LA are obtained at higher acid concentrations.

3.2. Effects of LABSA concentration on Levulinic Acid production

Three tests with varying LABSA concentrations (100, 300, and 600 mM) were carried out to investigate the impact of LABSA concentration on LA production. For every reaction, the feed content was 1g/25mL and the reaction temperature was kept at 200 °C. Figure 2b illustrates the variation in the weight-based yields of LA with varying LABSA concentrations.

Among the different LABSA concentrations tested, the experiment with 600 mM LABSA exhibited higher amounts of LA. The maximum concentration of LA, 34,372 ppm was achieved after 110 minutes of reaction time. In comparison, the greatest LA production was observed for 100 mM and 300 mM LABSA as 8,484 ppm and 20,931 ppm respectively, obtained at reaction times of 70 and 90 minutes.

Throughout the reaction duration, the conversion of chicory to LA was more stable with 100 mM and 300 mM LABSA, while at the highest concentration of 600 mM LABSA, the amount of LA was steeply increased especially from 20 min to 30 min of reaction time. This suggests that an optimal LABSA concentration plays a crucial role in achieving higher and more consistent yields of LA. It is worth noting that LABSA generally outperformed BSA in terms of the overall production of LA.

3.3. Variation in product concentrations and yields

The graphs in this section provide information about the C-based yields of these different acids and sugar compounds and their varying proportions in the products of the reactions. Tables 3-4 show the carbon liquefaction efficiency (CLE) values calculated for the samples from these reactions. The carbon liquefaction efficiency (CLE) indicates the conversion of biomass to products (acids and sugars) on a carbon basis.

3.3.1. Effects of BSA on product concentrations and yields.

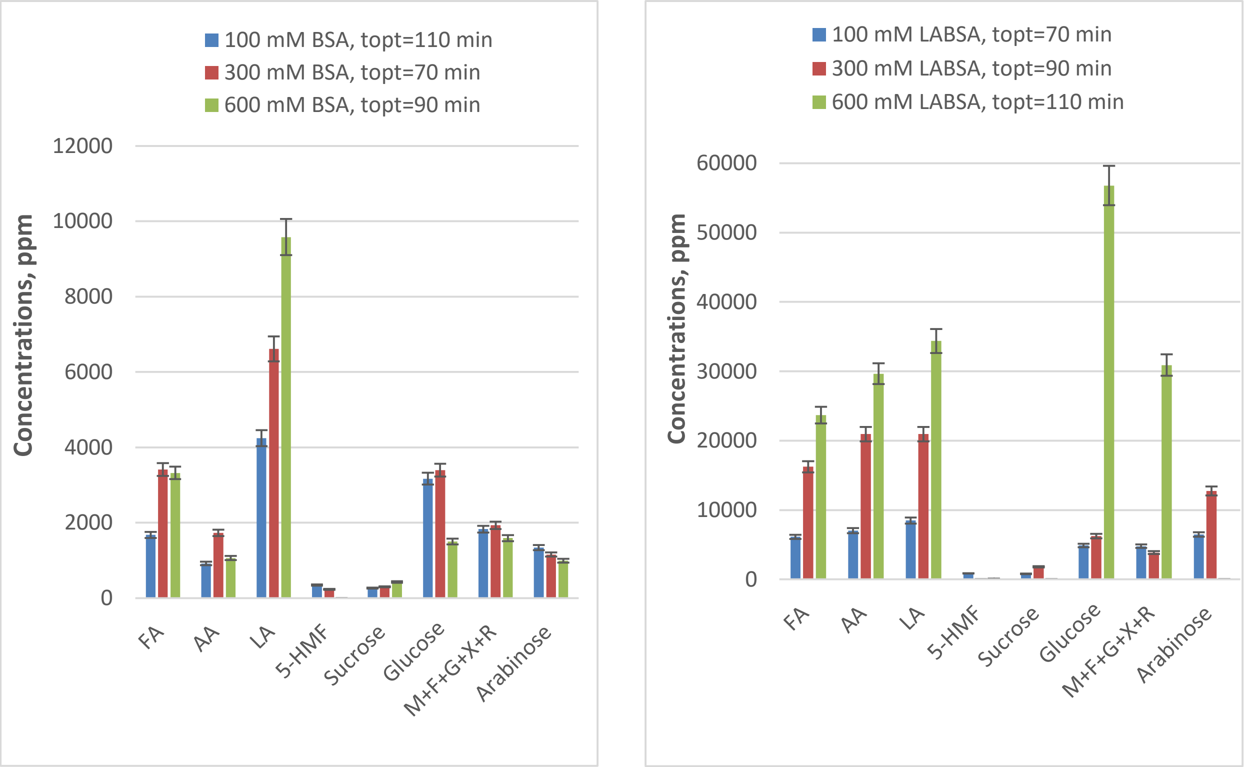
The variation in acid and sugar yields in reactions catalyzed by different concentrations of BSA at 200°C were obtained as a result. The effects of BSA concentration on the product concentrations for the optimum reaction times are illustrated in Figure 3a.

Sugar formation starts to occur at temperatures lower than 200 °C, and sugar levels decrease over time in the runs carried out with both sulfonic acid catalysts. The reason for this trend is that the carbohydrates present in the biomass are hydrolyzed to sugar monomers first; then, they are converted into acids. As the temperature approaches 200 °C acids start to form and with increasing reaction time LA yield peaks and stabilizes towards the end of the reactions at 200 °C.

In terms of sugar monomers, the highest concentration in the products belonged to glucose. This is due to the biomass containing a high percentage of cellulose, which is the polymer of glucose. This result indicates that effective hydrolysis of the cellulose fraction of the biomass was achieved with both catalysts, under these reaction conditions. Acid-catalyzed dehydration of monosaccharides produces 5-HMF, which was efficiently achieved with the acid catalysts in this study. Within the 0–30-minute period, 5-HMF is formed and consumed rapidly as the LA yield increases. This is because 5-HMF is the source of LA production and is converted into LA at a fast rate. The results indicated that the 5-HMF formed during the catalytic reactions is not very stable and can be easily rehydrated into LA and other by-products that support the quick decomposition of HMF found in previous studies [19,23].

LA makes up a high percentage of the final products, which was proved through HPLC and GC-MS analyses. Acetic acid and formic acid were also detected in the product samples in smaller amounts. This indicates that the reaction conditions and catalysts in this study provide a good alternative and selective for the synthesis of the target product LA. The total yield of acids decreased with increasing concentration of BSA as shown in Table 3. 100 mM BSA gave the highest total acid yields for the reaction. A more rapid decrease in sugar yields occurred when using the higher concentrations of the sulfonic acid catalyst.

The highest amounts of LA were obtained at 200°C, 9,580 ppm with 34,373 ppm with 600 mM BSA and 600 mM LABSA, respectively as the highest. LA yields are found as greater while HMF is decreased towards the end of the reaction as expected.



(a) (b)

Figure 3. The concentrations of acids and sugars in the products (weight-based) for the optimum reaction time, t_{opt} (T=200 °C, b/s:0.04 g/mL), (a) with BSA, and (b) with LABSA

Table 3 presents the total acid and sugar yields, as well as the carbon liquefaction efficiencies, resulting from the hydrolysis of chicory using different concentrations of BSA (100, 300, and 600 mM). These reactions were conducted at 200 °C with a biomass/solvent ratio of 0.04. The highest acid yield of 20.4 % was obtained in 30 minutes, while the maximum sugar yield reached 42.6% at the beginning of the reaction with the lowest concentration of BSA. The total sugar yield decreased to 12.3% and 6.3% with 300 mM, and 600 mM, respectively at the start of the reaction since the sugar compounds converted to organic acids in the heating stage before the reaction temperature reached. At a concentration of 300 mM of BSA, the yield for organic acid compounds increased up to 13.6% within 90 min, and at 600 mM BSA, it increased up to 12.3% within 20 minutes, then decreased during the reaction time. These findings suggest that while BSA can catalyze the hydrothermal conversion of chicory, higher concentrations of BSA may be more favorable for achieving higher amounts of acid products in milder reaction conditions as displayed in Figure 3a in terms of concentration.

Table 3. Variation of Total Acid and Sugar Yields (C-based) in the aqueous products and Carbon liquefaction efficiencies at 200 °C, with 0.04 biomass/solvent ratio, in the presence of different concentrations of BSA (TAY: Total Acid yield, TSY: Total Sugar Yield, CLE: Carbon Liquefaction Yield**)**

C (mM)		**Time (min)**			
		0	**10**	**20**	**30**
100	TAY	16.5±1.0	18.5±0.9	17.8±1.0	20.4±1.1
	TSY	42.6±2.2	41.4±2.0	31.5±1.7	34.5±1.9
	CLE	59.1±3.2	59.9±2.9	49.3±2.7	54.9±3.0
		50	**70**	**90**	**110**
	TAY	14.3±0.8	14.8±0.6	13.8±0.7	13.6±0.6
	TSY	15.4±0.8	15.4±0.9	12.0±0.6	11.2±0.8
	CLE	29.9±1.6	30.3±1.5	25.1±1.3	24.8±1.4
		0	**10**	**20**	**30**
300	TAY	12.7±0.7	12.7±0.6	12.5±0.7	12.0±0.5
	TSY	12.3±0.6	9.8±0.6	7.6±0.5	10.3±0.5
	CLE	24.9±1.3	22.6±1.2	20.6±1.2	22.4±1.0
		50	**70**	**90**	**110**
	TAY	10.1±0.6	13.5±0.7	13.6±0.7	11.0±0.6
	TSY	7.4±0.4	7.1±0.4	6.1±0.3	6.4±0.3
	CLE	17.7±1.0	20.7±1.1	19.8±1.0	17.5±0.9
		0	**10**	**20**	**30**
600	TAY	6.3±0.3	8.3±0.5	12.3±0.7	8.6±0.4
	TSY	6.3±0.3	5.5±0.3	4.3±0.3	6.8±0.4
	CLE	12.6±0.6	13.8±0.7	16.6±1.0	15.5±0.8
		50	**70**	**90**	**110**
	TAY	8.5±0.5	9.6±0.6	10.5±0.5	9.4±0.5
	TSY	4.4±0.3	3.4±0.2	3.0±0.2	2.5±0.2
	CLE	12.5±0.8	13.1±0.8	13.5±0.7	12.0±0.7

The CLE values were within the range of 24.8-59.9 % for the reaction catalyzed by 100 mM BSA. The carbon liquefaction efficiencies reflect the conversion of carbon feed into products and indicate that the reactions with 100 mM BSA had higher efficiencies. The higher concentrations of this catalyst gave lower carbon liquefaction efficiencies which may indicate that more unidentified compounds might have formed at these conditions. CLE values showed a decrease with time for all the reactions catalyzed by BSA while at 600 mM concentration, CLE firstly increased up to 16.6 % and then decreased towards to end of the reaction.

3.3.2. Effects of LABSA on the product concentration and yields

The impact of LABSA concentration on the variation in product yields was examined in reactions conducted at 200°C. Figure 3b presents the acid and sugar amounts obtained using different concentrations of LABSA (100, 300, and 600 mM) for the optimum reaction times. Table 4 complements these findings by providing comprehensive data on total acid and sugar yields, as well as the carbon liquefaction efficiencies, obtained from the acidic hydrolysis of chicory using 100, 300, and 600 mM LABSA, at a fixed temperature of 200 °C.

Table 4. Variation of Total Acid and Sugar Yields (C-based) in the aqueous products and Carbon liquefaction efficiencies at 200°C, with 0.04 biomass/solvent ratio, in the presence of different concentrations of LABSA with a given margin of error range (TAY: Total Acid yield, TSY: Total Sugar Yield, CLE: Carbon Liquefaction Yield, C: Concentration)

C (mM)		**Time (min)**			
		0	**10**	**20**	**30**
100	TAY	19.6±1.0	19.4±0.8	17.9±1.0	20.9±0.9
	TSY	29.7±2.1	23.2±1.6	17.5±0.9	19.7±0.6
	CLE	49.3±3.1	42.7±2.4	35.4+1.9	40.7±1.5
		50	**70**	**90**	**110**
	TAY	19.7±1.1	24.5±1.7	21.2±1.4	21.8±1.6
	TSY	18.9±1.4	17.9±0.7	14.3±0.4	14.3±0.5
	CLE	38.6±2.5	42.4±2.4	35.5±1.8	36.1±2.1
		0	**10**	**20**	**30**
300	TAY	23.2±1.1	17.4±0.8	23.7±1.2	25.9±1.0
	TSY	13.3±0.7	8.7±0.4	11.8±0.8	10.9±0.6
	CLE	36.5±1.8	26.2±1.2	35.5±2.0	36.9±1.6
		50	**70**	**90**	**110**
	TAY	27.2±1.5	29.2±1.3	28.9±1.6	28.2±1.5
	TSY	11.7±0.5	13.7±0.8	12.2±0.6	11.4±0.8
	CLE	38.9±2.5	43.0±2.1	41.1±2.2	39.7±2.3
		0	**10**	**20**	**30**
600	TAY	9.4±0.4	12.6±0.5	9.3±0.5	18.6±0.7
	TSY	4.5±0.2	5.5±0.3	3.6±0.2	24.5±1.2
	CLE	14.0±0.6	18.2±0.8	12.9±0.7	43.2±1.9
		50	**70**	**90**	**110**
	TAY	16.3±0.7	21.7±1.1	20.9±1.1	24.5±1.3
	TSY	17.1±0.9	16.3±0.7	12.8±0.6	24.0±1.4
	CLE	33.5±1.6	38.3±1.8	32.7±1.7	48.6±2.7

It was observed that the highest total organic acid compound yields were achieved when the LABSA concentration was 300 mM, indicating the catalytic efficiency of this concentration. On the other hand, the maximum sugar formation occurred with a lower LABSA concentration of 100 mM at the beginning of the reaction. The catalytic decomposition of sugar compounds is observed as time proceeds with 100 mM LABSA.

The carbon liquefaction efficiencies (CLE) for the reactions catalyzed by 100 mM LABSA were found to range between 35.5% and 49.3%. As observed with the BSA, higher concentrations of LABSA led to lower CLE values. However, an interesting trend was observed with the reactions using 300 and 600 mM LABSA. Unlike the reactions with BSA, where CLE values decreased with time, the CLE values for the higher concentrations of LABSA showed an increase over time. This suggests a different reaction mechanism or kinetics associated with LABSA catalysis compared to BSA. Further investigation can be beneficial to understand the underlying factors influencing the CLE values in these reactions.

3.4. Evaluation of LABSA and BSA performance

Chang et al. investigated the kinetics of LA formation through the hydrolysis of wheat straw using dilute sulfuric acid as the catalyst. The experiments were conducted at temperatures ranging from 190 to 230 °C and acid concentrations ranging from 1 to 5 wt. %. A kinetic model consisting of first-order serial reactions was developed and the consumption rate of 5-HMF was found to be the fastest step in the series. The maximum LA concentration obtained was 10.40 g/L, achieved at 210 °C with 3% H_2SO_4 in 42.4 minutes [24]. The results showed that temperature and acid concentration had a significant effect on the yield of LA as found in our study. These findings of the study are consistent with the results previously reported in the literature [4, 10-13].

The evaluation of LABSA and BSA performance in this study focused on comparing different sulfonic acid catalysts for LA production. A comparison was made among the catalysts tested based on the reaction yields presented in Table 5. Maximum LA yields obtained at 200 °C and various concentrations of the catalysts at certain times are given as t_{opt}.

Table 5. Maximum levulinic acid yields obtained with different catalysts at 200 °C

Catalyst	Catalyst concentration (mM)	LA Yield% (wt.%) (g/g biomass)	t_{opt} (min)
BSA	100	10.6±0.6	110
BSA	300	16.5±1.1	70
BSA	600	23.9±2.0	90
LABSA	100	21.2±1.3	70
LABSA	300	52.4±3.1	90
LABSA	600	85.9±4.2	110

Specifically, the highest yield of LA, reaching 85.9 wt.% was obtained at 200 °C with 600 mM LABSA within a reaction time of 110 minutes. Many studies on LA synthesis from biomass, use mineral acid catalysts for this conversion. The most used mineral acid catalyst is H_2SO_4. The product yields obtained with the sulfonic acid catalyst used in this study, are comparable with the results found in the literature. Girisuta et al. conducted a study on the acid-catalyzed hydrolysis of sugar cane bagasse as a real biomass to LA. The experiments were carried out at reaction temperatures ranging between 150 and 200 °C using a homogeneous mineral acid catalyst, sulfuric acid (0.11-0.55 M) in water. The highest yield of LA obtained was 63 mol %, achieved at 150 °C with 0.55 M H_2SO_4 [20]. In this study, LA Yield of 61.5 mol% was obtained with 300 mM BSA at 200 °C which is in close agreement with the yields reported in the study.

Shen and Wyman [26] studied the kinetics of hydrochloric acid-catalyzed hydrolysis of cellulose to levulinic and formic acids. The research focused on the acid-catalyzed hydrolysis of microcrystalline cellulose to levulinic and formic acids using a batch reactor at temperatures ranging from 160 to 200 °C, catalyst concentrations from 0.309 to 0.927 M, cellulose concentrations of 49.8 to 149 mM, and residence times of 0 to 50 minutes. The highest theoretical yield of LA achieved was 60%, obtained with an initial cellulose concentration of 99.6 mM, 0.927 M HCl, and temperatures between 180 and 200 °C. In previous research, the conversion of Jerusalem artichoke to LA was investigated by using an H_2SO_4-catalyzed hydrothermal reaction. A maximum LA yield of 32.3 wt.% (based on biomass weight) was reported under the optimum conditions of 185 °C, 30.8 kg m^{-3} H_2SO_4, and 33.7 min [27]. A different study on the H_2SO_4 catalyzed conversion of wheat straw to LA reported a maximum LA yield of 19.86 wt.% and the optimal conditions were found to be 209.3 °C, 3.5% acid concentration, 15.6 liquid: solid ratio, and 37.6 min of reaction time [28]. In this study, comparable LA yields of 23.9 wt.% were achieved with 600 mM BSA at 200°C, and it reached 85.93 wt.% for 600 mM LABSA, experimentally.

3.5. GC-MS analysis results

Figure 4 provides the GC-MS analysis results of several selected samples from BSA-catalyzed reactions during the acidic hydrolysis of chicory. A total of 7 compounds were found in the sample taken from the reaction catalyzed by 100 mM LABSA, while only 2 compounds were identified in the sample of 300 mM LABSA catalyzed reaction. The common compounds are oxime methoxy phenyl and LA (pentanoic acid, 4-oxo-). 2-Furancarboxaldehyde, 5 hydroxymethyl (5-HMF) made up a high percentage of the sample taken at 10 min from 100 mM LABSA-catalysed reaction. The percentage of LA was greater for the sample taken at 50 min from 300 mM LABSA catalyzed reaction while 5-HMF was not present. It confirmed the conversion of 5-HMF to LA in these reactions over time.

The GC-MS analysis results indicate the formation of compounds that are commonly expected to be produced through the acidic hydrolysis of biomass, such as LA (pentanoic acid, 4-oxo-), furfural, formic acid, and acetic acid. The results show that these compounds make up a high percentage of the product samples. When we examine the graph in terms of formic acid production, it can be concluded that the BSA catalyst promotes the formation of formic acid, while no formic acid formation was observed in the experiments with LABSA. In addition, several other chemicals such as oxime-methoxy phenyl (methyl N-hydroxybenzenecarboximidate), levoglucosenone, diethyl phthalate, and diphenyl sulfone were detected in the samples in lower percentages.

These findings can be attributed to the usage of an aromatic sulfonic acid catalyst and its interaction with the components of the biomass or 5-HMF and LA further converting into different chemicals. A high percentage between 88-98 % of the compounds that make up the product samples were identified by GC-MS.

3.6. Statistical analysis and optimization

The optimization of process conditions was conducted to maximize the LA yield. The optimal combination of processing factors was determined and the highest LA yields that can be achieved with the catalytic systems in this study were predicted. Independent variables (factors) and levels defined in the experimental program are as follows:
Catalyst concentration: 100, 300, and 600 mM
Reaction time: 0,10,20,30,50,70,90, and 110 minutes

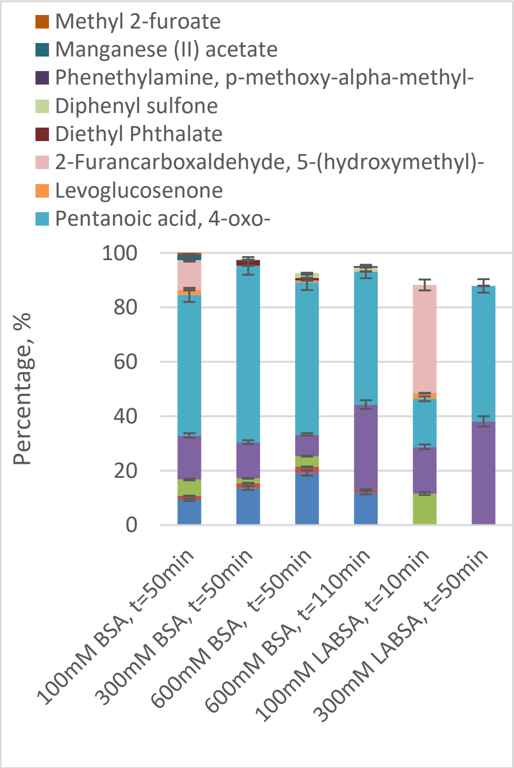


Figure 4. GC-MS analysis results of sample obtained from acidic hydrolysis of chicory (experimental conditions: T=200°, catalyst:100, 300, 600mM BSA, b/s:1g/25 mL, t=50,110min and catalyst:100, 300mM LABSA, b/s:1g/25 mL, t=10,50min)

The impact of these parameters on the yield of LA was investigated, and the optimal conditions were determined using Minitab software. Response surface methodology (RSM) was employed as an efficient approach to determine the optimal combination of variables, where the objective was to maximize the yield of LA, which is the response variable. The following regression equations were obtained for each catalyst:

BSA
LA yield, wt. % $=3.16 + 0.1013\, t + 0.02950\, C - 0.000730\, t*t - 0.000017\, C*C + 0.000085\, t*C$
(S: 1.43, R-sq: 94.0 % , R-sq(adj): 92.33% , R-sq(pred): 87.85%)

LABSA
LA yield, wt. % $= - 4.34 + 0.202\, t + 0.1728\, C - 0.00236\, t*t - 0.000192*C*C + 0.000927\, t*C$
(S: 6.66, R-sq: 92.96 %, R-sq(adj): 91.01% , R-sq(pred): 88.53%)

The R-square values indicate a good fit of the models to the data. The analysis of variance (ANOVA) test was conducted to assess the influence of independent variables on the dependent variable. The P-values obtained from the ANOVA test indicate the significance of the interactions between different factors. The detailed ANOVA results can be found in Table 6 and 7.

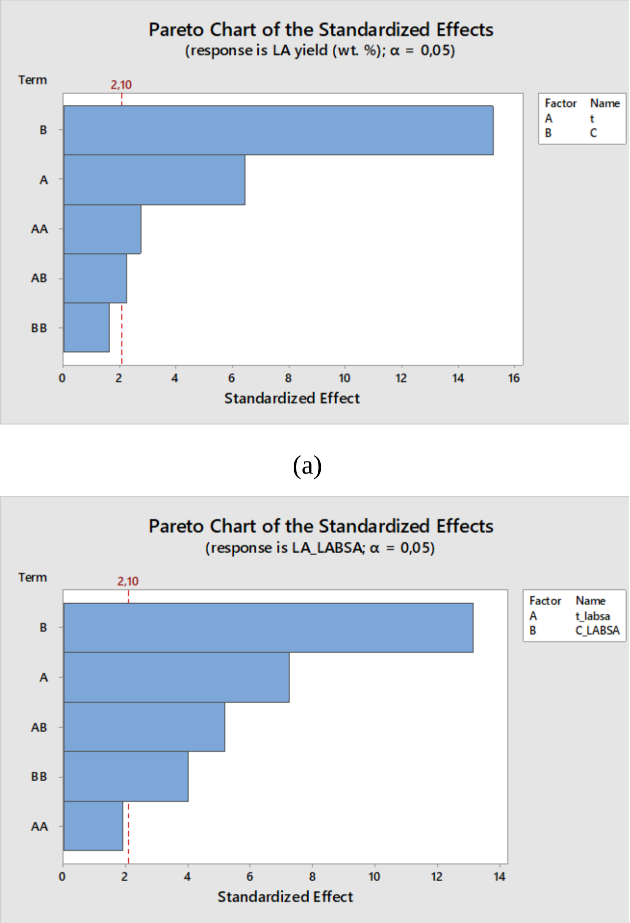
Table 6. ANOVA results for the reactions catalyzed by different concentrations of BSA.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	10558.7	2111.75	47.55	0.000
Linear	2	9838.9	4919.44	110.77	0.000
t	1	2317.4	2317.42	**52.18**	0.000
Conc	1	7653.2	7653.20	**172.33**	0.000
Square	2	860.6	430.28	9.69	0.001
t*t	1	160.3	160.34	3.61	0.074
Conc*Conc	1	700.2	700.21	15.77	0.001
2-Way Interaction	1	1192.8	1192.85	26.86	0.000
t*Conc	1	1192.8	1192.85	26.86	0.000
Error	18	799.4	44.41		
Total	23	11358.1			

The statistical analysis using ANOVA revealed that the P-values for the independent variables were all less than 0.05, indicating that the effects of these variables on the response variable (yield of LA in wt. %) were statistically significant. However, three interactions between the variables showed higher P-values, suggesting that these interactions were not significant for the study.

Table 7. ANOVA results for the reactions catalyzed by different concentrations of LABSA.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	573.992	114.798	56.36	0.000
Linear	2	551.079	275.540	135.27	0.000
t	1	84.133	84.133	41.30	0.000
C	1	473.165	473.165	232.28	0.000
Square	2	20.859	10.429	5.12	0.017
t*t	1	15.293	15.293	7.51	0.013
C*C	1	5.566	5.566	2.73	0.116
2-Way Interaction	1	10.068	10.068	4.94	0.039
t*C	1	10.068	10.068	4.94	0.039
Error	18	36.666	2.037		
Total	23	610.658			

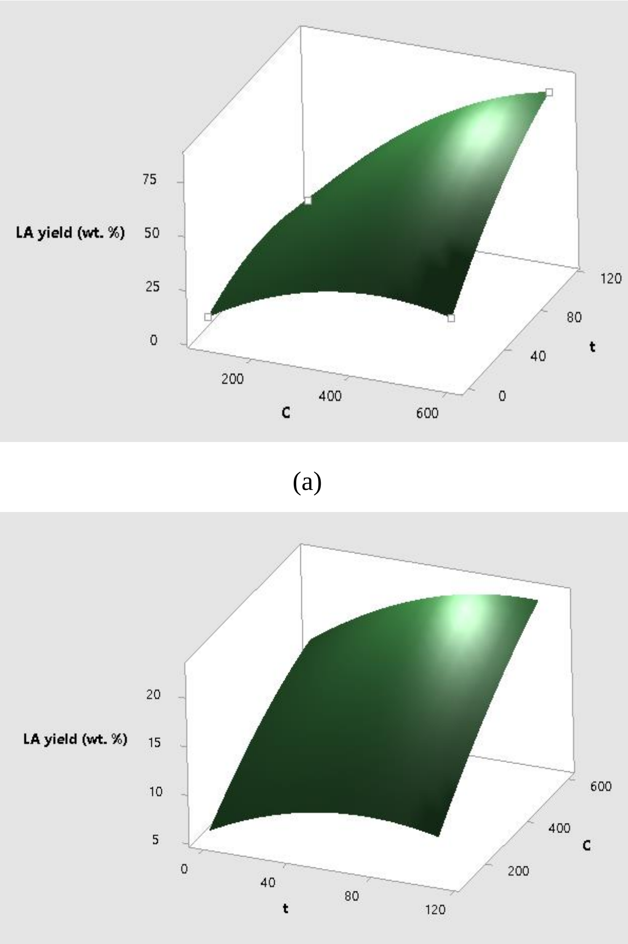


(a)

(b)

Figure 5. Pareto chart for the reactions catalyzed by different concentrations of (a) BSA and (b) LABSA

The Pareto analysis revealed that among the independent variables, catalyst concentration is the most significant parameter on the yield of LA it is followed by reaction time. Also, the effect of catalyst type is very significant, and it can be seen by comparing the optimum yields of LA with BSA (22.65 wt.%) and LABSA (85.9 wt.%). Each variable played a crucial role in determining the outcome of the experiments. To further understand the impact of the independent variables and interactions on the response, a Pareto analysis was conducted. The Pareto chart, depicted in Figure 5, presents the effect (%) of the independent variables and interactions on the response variable. This chart helps visualize the relative importance of each variable and interaction in influencing the yield of LA.



(a)

(b)

Figure 6. Surface plot of LA yield vs catalyst concentration, time for BSA **(**a) Surface plot of LA yield vs catalyst concentration, time for LABSA (b)

To further investigate the interactions between the independent variables and their influence on the yield, surface plots were generated. Figures 6a and 6b depict these surface plots, which provide a visual representation of how the response variable (yield of LA) changes with variations in the catalyst concentration and reaction time for LABSA and BSA, respectively. These plots help in understanding the complex relationships and interactions between the variables and their impact on the overall outcome of the reactions. The optimum yield of LA in runs carried out with the catalyst of BSA is found at 104.4 minutes of reaction time and 600 mM of catalyst concentration as 22.65 wt.% by the Response Optimizer tool. This result indicates that by carefully controlling the catalyst concentration and reaction time, it is possible to enhance the production of LA, thereby maximizing the efficiency of the process. The response optimization results revealed that the maximum yield of LA can be achieved by using 600 mM of LABSA as the catalyst in a reaction time of 110 minutes. Under these optimized conditions, the LA yield was found to be 85.9 wt.%.

Lopes et al. developed a mechanistic model to simulate the kinetics of LA production from sugarcane bagasse, rice husk, and soybean straw [19]. The production process followed a biorefinery concept and consisted of three stages: acid pre-treatment, alkaline pre-treatment, and catalytic depolymerization of cellulose. The study adopted a kinetic model previously developed by Girisuta et al. [10]. Experimental yields under the optimum conditions (190 °C, 7.0% w/v H_2SO_4, 75 min) were 60.5 mol% for sugarcane bagasse, 65.2 mol% for rice husk, and 61.5 mol% for soybean straw.

4. Conclusion and suggestions

In this study, a comprehensive investigation of the biomass hydrolysis process to produce LA was conducted. Hydrothermal conversion of chicory with varying concentrations of BSA (Benzenesulfonic acid) and LABSA (Linear alkyl benzene sulfonic acid) was investigated. The optimization of process conditions was conducted to maximize the LA yield. The optimal combination of processing factors was determined and the highest LA yields that can be achieved with the catalytic systems in this study were predicted. The factors of reaction time, catalyst type, and concentration were found to influence the LA yield. LABSA emerged as the catalyst with the highest overall yields of LA.

The maximum LA yields (wt.%) and concentrations achieved through the experiments of this study were 22.65 wt.% (9.05 g/L) for BSA and 85.9 wt.% (34.37 g/L) for LABSA. These results were obtained for the 600 mM concentrations of these catalysts at 200 °C at 104.4 and 110 min, respectively. Throughout the reactions, the yields of acids in the products mostly increase with time as the sugar yields decrease. The intermediate product 5-HMF is converted into LA rapidly, so the observed concentrations of this compound are very low.

The results of this study were compared with existing literature on LA synthesis, particularly using mineral acid catalysts such as H_2SO_4. The yields obtained with the sulfonic acid catalysts in this study were found to be comparable to those reported in previous research. The findings suggest that BSA and LABSA have the potential to be effective catalysts for the conversion of biomass to LA. The study also highlights the significance of reaction time catalyst concentration as a key factor influencing the hydrothermal conversion of biomass to LA. The findings can aid in the selection and optimization of catalysts and concentrations to maximize the yield of LA in future biomass conversion processes. These results contribute to the ongoing efforts to develop sustainable and efficient processes to produce LA from renewable resources. The use of sulfonic acid catalysts presents a viable alternative to mineral acid catalysts, offering similar or improved yields and reducing the environmental impact associated with mineral acids.

In conclusion, the findings of this study contribute to the growing body of knowledge on LA production and lay the foundation for future advancements in the field of biomass conversion to valuable chemicals.

Acknowledgment

We are appreciative of Ege University's financing of the FGA-2019-20183 research project. We express our gratitude to Prof. Dr. Levent BALLİCE for his tremendous contributions and assistance over the entire project.

Conflict of interest

There is no financial conflict of interest with any institution, organization, or person regarding our article titled "Conversion of chicory into valuable chemical LA and by-products with sulfonic acid catalysts" and there is no conflict of interest between the authors. The authors declare that there is no conflict of interest.

Similarity rate (iThenticate): 15%

References

[1] F.D. James H. Clark, Introduction to Chemicals from Biomass, John Wiley & Sons, 2015.

[2] M. Signoretto, S. Taghavi, E. Ghedini, F. Menegazzo, Catalytic production of levulinic acid (LA) from Actual Biomass, Molecules. 24, 1–20, 2019. https://doi.org/10.3390/molecules24152760.

[3] Z. Fang, R.L. Smith, X. Qi, Production of platform chemicals from sustainable resources, Springer Singapore, 2017.

[4] Q. Qing, Q. Guo, P. Wang, H. Qian, X. Gao, Y. Zhang, Kinetics study of levulinic acid production from corncobs by tin tetrachloride as a catalyst, Bioresour. Technol. 260, 150–156, 2018. https://doi.org/https://doi.org/10.1016/j.biortech.2018.03.073.

[5] S. Kang, J. Fu, G. Zhang, From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis, Renew. Sustain. Energy Rev. 94, 340–362, 2018. https://doi.org/10.1016/j.rser.2018.06.016.

[6] A. Mukherjee, M.-J. Dumont, V. Raghavan, Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities, Biomass and Bioenergy. 72, 143–183, 2015. https://doi.org/https://doi.org/10.1016/j.biombioe.2014.11.007.

[7] C. Liu, X. Lu, Z. Yu, J. Xiong, H. Bai, R. Zhang, Production of levulinic acid from cellulose and cellulosic biomass in different catalytic systems, Catalysts. 10 1–22, 2020.

https://doi.org/10.3390/catal10091006.

[8] W. Wei, S. Wu, Experimental and kinetic study of glucose conversion to levulinic acid in aqueous medium over Cr/HZSM-5 catalyst, Fuel. 225, 311–321, 2018. https://doi.org/https://doi.org/10.1016/j.fuel.2018.03.120.

[9] C. Antonetti, D. Licursi, S. Fulignati, G. Valentini, A.M.R. Galletti, New frontiers in the catalytic synthesis of levulinic acid: From sugars to raw and waste biomass as starting feedstock, Catalysts, 6, 1–29, 2016. https://doi.org/10.3390/catal6120196.

[10] K. Kumar, S. Pathak, S. Upadhyayula, 2nd generation biomass-derived glucose conversion to 5-hydroxymethylfurfural and levulinic acid catalyzed by ionic liquid and transition metal sulfate: Elucidation of kinetics and mechanism, J. Clean. Prod. 256, 120292, 2020,. https://doi.org/10.1016/j.jclepro.2020.120292.

[11] X. Cheng, Q. Feng, D. Ma, F. Xing, X. Zeng, X. Huang, J. Teng, L. Feng, Kinetics for glucose conversion to levulinic acid over solid acid catalyst in γ-valerolactone solution, Biochem. Eng. J. 180, 108360, 2022. https://doi.org/10.1016/j.bej.2022.108360.

[12] J.F. Saeman, Kinetics of Wood Saccharification - Hydrolysis of Cellulose and Decomposition of Sugars in Dilute Acid at High Temperature, Ind. Eng. Chem. 37, 43–52, 1945. https://doi.org/10.1021/ie50421a009.

[13] X. Zheng, Z. Zhi, X. Gu, X. Li, R. Zhang, X. Lu, Kinetic study of levulinic acid production from corn stalk at mild temperature using $FeCl_3$ as catalyst, Fuel, 2017. https://doi.org/10.1016/j.fuel.2016.09.019.

[14] N.A.S. Ramli, N.A.S. Amin, Kinetic study of glucose conversion to levulinic acid over Fe/HY zeolite catalyst, Chem. Eng. J. 283, 150–159, 2017. https://doi.org/10.1016/j.cej.2015.07.044.

[15] W. Weiqi, W. Shubin, Experimental and kinetic study of glucose conversion to levulinic acid catalyzed by synergy of Lewis and Brønsted acids, Chem. Eng. J. 307, 389–398, 2017. https://doi.org/10.1016/J.CEJ.2016.08.099.

[16] W.J.M. Meijer, E.W.J.M. Mathijssen, Crop characteristics and inulin production in chicory, Eur. J. Agron. 1, 99–108, 1992. https://doi.org/https://doi.org/10.1016/S1161-0301(14)80007-5.

[17] X.H. Long, H.B. Shao, L. Liu, L.P. Liu, Z.P. Liu, Jerusalem artichoke: A sustainable biomass feedstock for biorefinery, Renew. Sustain. Energy Rev. 54, 1382–1388, 2016. https://doi.org/10.1016/j.rser.2015.10.063.

[18] P.J.V. Soest, Use of detergents in the analysis of fibrous feeds. II. A Rapid Method for the Determination of Fiber and Lignin, J. Assoc. Off. Agric. Chem. 46, 829–835, 1963.

[19] B. Girisuta, L.P.B.M. Janssen, H.J. Heeres, A kinetic study on the decomposition of 5-hydroxymethyl furfural into levulinic acid, Green Chem. 8, 701–709, 2006. https://doi.org/10.1039/B518176C.

[20] B. Girisuta, K. Dussan, D. Haverty, J.J. Leahy, M.H.B. Hayes, A kinetic study of acid catalysed hydrolysis of sugar cane bagasse to levulinic acid, Chem. Eng. J. 217, 61–70, 2013. https://doi.org/https://doi.org/10.1016/j.cej.2012.11.094.

[21] D.E. Yüksel, L. Ballice, N. Cengiz, M. Sağlam, M. Yüksel, Aromatic sulfonic acid-catalyzed conversion of safflower stalk into levulinic acid, Biomass Convers. Biorefinery, 14, 1105-1116, 2024. https://doi.org/10.1007/s13399-022-02920-4.

[22] S. Kang, G. Zhang, X. Yang, H. Yin, X. Fu, J. Liao, J. Tu, X. Huang, F.G.F. Qin, Y. Xu, Effects of p-Toluenesulfonic Acid in the conversion of glucose for levulinic acid and sulfonated carbon production, Energy and Fuels, 31, 2847–2854, 2017. https://doi.org/10.1021/acs.energyfuels.6b02675.

[23] H. Jeong, S.Y. Park, G.H. Ryu, J.H. Choi, J.H. Kim, W.S. Choi, S.M. Lee, J.W. Choi, I.G. Choi, Catalytic conversion of hemicellulosic sugars derived from biomass to levulinic acid, Catal. Commun. 117, 19–25, 2018. https://doi.org/10.1016/j.catcom.2018.04.016.

[24] C. Chang, X. Ma, P. Cen, Kinetic studies on wheat straw hydrolysis to levulinic acid, Chinese J. Chem. Eng. 17835–839, 2009. https://doi.org/https://doi.org/10.1016/S1004-9541(08)60284-0.

[25] E.S. Lopes, E.C. Rivera, J.C. de Jesus Gariboti, L.H.Z. Feistel, J.V. Dutra, R. Maciel Filho, L.P. Tovar, Kinetic insights into the lignocellulosic biomass-based levulinic acid production by a mechanistic model, Cellulose. 27, 5641–5663, 2020. https://doi.org/10.1007/s10570-020-03183-w.

[26] J. Shen, C.E. Wyman, Center, Hydrochloric Acid-catalyzed levulinic acid formation from cellulose: data and kinetic model to maximize yields, AIChE J. 59, 215–228, 2012. https://doi.org/10.1002/aic.

[27] G.T. Jeong, Catalytic conversion of Helianthus tuberosus L. to sugars, 5-hydroxymethylfurfural and levulinic acid using hydrothermal reaction, Biomass and Bioenergy. 74, 113–121, 2015. https://doi.org/10.1016/j.biombioe.2015.01.014.

[28] C. Chang, P. Cen, X. Ma, Levulinic acid production from wheat straw, Bioresour. Technol. 98, 1448–1453, 2007. https://doi.org/10.1016/j.biortech.2006.03.031.