

# The production of levulinic acid and formic acid from red macroalga *Kappaphycus alvarezii* using methanesulfonic acid

*by Agus Trianto*

---

**Submission date:** 23-Jun-2022 12:45PM (UTC+0700)

**Submission ID:** 1861677897

**File name:** d\_macroalga\_Kappaphycus\_alvarezii\_using\_methanesulfonic\_acid.pdf (3.72M)

**Word count:** 8233

**Character count:** 42066



## Case study

## The production of levulinic acid and formic acid from red macroalgae *Kappaphycus alvarezii* using methanesulfonic acid

Maria Dyah Nur Meinita<sup>a,b,\*</sup>, Amron Amron<sup>a</sup>, Dicky Harwanto<sup>c</sup>, Agus Trianto<sup>c</sup>, Gwi-Taek Jeong<sup>d</sup>

<sup>a</sup> Faculty of Fisheries and Marine Science, Jenderal Soedirman University, Purwokerto, Indonesia

<sup>b</sup> Center for Maritime Bioscience Studies, Institute of Research and Community Service, Jenderal Soedirman University Purwokerto, Indonesia

<sup>c</sup> Faculty of Fisheries and Marine Science, Diponegoro University, Semarang, Indonesia

<sup>d</sup> Department of Biotechnology, Pukyong National University, Busan, Republic of Korea



## ARTICLE INFO

## Keywords:

Macroalgae  
Levulinic acid  
Biomass  
*K. alvarezii*  
Seaweed

## ABSTRACT

Levulinic acid (LA) and formic acid (FA) are high-value chemicals that can be generated from biomass and are widely used in diverse industries. *Kappaphycus alvarezii* is potential biomass to be developed as raw material for producing LA and FA. Biomass, catalyst, and reaction factor play important roles in LA and FA production. In this research, we investigated the conversion of macroalgae *K. alvarezii* for the production of LA and FA through the thermochemical reaction with methanesulfonic acid (MSA) as an environmental-friendly and strong acidic catalyst under the response surface statistical approach. Optimizing the reaction factors, the highest LA and FA yield of 14.69% and 5.35%, respectively were attained under the conditions of 180 °C reaction temperature, 0.6 M MSA catalyst concentration, 30 min reaction time, and 2.5% biomass load. The application of *K. alvarezii* and green catalyst MSA in LA production can be a new insight into macroalgae biorefinery.

## 1. Introduction

Fossil resource depletion shifts our concept from petroleum-based to biorefinery which produces various fuels and chemicals from bio-based material. The use of these materials is required to overcome the depletion of fossil resources as raw materials in the petroleum refinery (Kamm et al., 2016). Furthermore, macroalgae is a potential and attractive marine bio-based material that can be considered to replace fossil-based resources because its high and easily degradable polysaccharide content can be converted to many useful pharmaceutical, cosmetic, nutraceutical, and fuel compounds (Jeong et al., 2015; Lee et al., 2013; Ruocco et al., 2016; Sadhukhan et al., 2019; Tirtawijaya et al., 2019).

*Kappaphycus alvarezii* is a red macroalgae known as one of the most attractive marine bio-based materials which can be developed to produce high-value products (Li et al., 2018; Liu et al., 2019). *K. alvarezii* is a carrageenophyte macroalgae containing a high amount of carrageenan, which is a polysaccharide consisting of a linear water-soluble sulfated galactans with a repeating backbone of  $\alpha(1-4)$ -3,6-anhydrogalactopyranose and  $\beta(1-3)$ -galactopyranose-4-sulfate (Pereira et al., 2009). *K. alvarezii* is among the largest tropical carrageenophyte

which has great commercial value and are widely used in diverse industries as the main source of carrageenan. The carrageenan industry grows rapidly and produces 57,500 tons, which is the highest sales among other hydrocolloids (Porse and Rudolph, 2017). This species has been cultivated in Asia, Africa, Oceania, America (Fig. 1). Asia produced the highest number of *K. alvarezii* production around 11 million tonnes and Indonesia is the leading manufacturers of this macroalgae worldwide with a total production of around 9 million tonnes or about 85% of the world's total production (FAO, 2020; Pambudi et al., 2010).

Previous research showed *K. alvarezii* can be hydrolyzed chemically and enzymatically to produce ethanol (Hargreaves et al., 2013; Khambhaty et al., 2012; Meinita et al., 2012b). Furthermore, Meinita et al. (2019) and Meinita et al. (2017) revealed that ethanol not only can be produced from macroalgae, but also can be produced from its residue waste obtained from carrageenan agar extraction. During ethanol production, *K. alvarezii* produced levulinic acid (LA), formic acid (FA), and 5-hydroxymethylfurfural (5-HMF) as by-products (Meinita et al., 2012a). LA is one of the most potential high-value chemicals derived from KA biomass which can be converted into a diverse high-value product in the food, pharmaceutical, nutraceutical industries

\* Corresponding author at: Faculty of Fisheries and Marine Science, Jenderal Soedirman University, Purwokerto, Indonesia.  
E-mail address: [maria.meinita@unsoed.ac.id](mailto:maria.meinita@unsoed.ac.id) (M.D.N. Meinita).

<https://doi.org/10.1016/j.biteb.2022.100954>

Received 23 September 2021; Received in revised form 9 January 2022; Accepted 9 January 2022

Available online 12 January 2022

2589-014X/© 2022 Elsevier Ltd. All rights reserved.

(Mukherjee and Raghavan, 2014). The DOE/NREL selected the LA as one of the twelve "Top Value Added Chemicals from Biomass" among over 300 possible building block candidates (Werpy and Petersen, 2004). LA can be converted into various high-value products such as chemicals, fuel and food additives, pharmaceuticals, medicines, agricultural products, solvents, and polymers (Leal Silva et al., 2018). Another important chemical intermediate which widely used in various industries is FA. Among potential chemical compounds, FA is also known as a versatile chemical intermediate with unique properties, including strong, non-toxicity, favorable energy density, simplicity, and biodegradability (Liu et al., 2015). Up to now, mostly LA and FA are produced commercially from petroleum pathways. Hence, the utilization of macroalgae biomass is expected to overcome our dependence on petroleum.

Another challenge in LA and FA production from biomass is to overcome corrosion and equipment blockage (Rackemann et al., 2016). This challenge should be considered if we develop LA production on an industrial scale. To overcome this challenge we try to use MSA which is a derivative of sulfuric acid and eco-friendly green catalyst because it is relatively low corrosive (Rackemann et al., 2016). Furthermore, compared to inorganic acids, MSA has some advantages, including less oxidation, low toxicity and corrosivity, non-foaming, strong acidity (pKa = 1.9), and high biodegradability (Gernon et al., 1999; Rackemann et al., 2016; Wickleder and Logemann, 2013). MSA is a compound that plays an important role in the global biogeochemical sulfur cycle so it can be degraded and recycled easily by microorganisms (Baker et al., 1991; Henriques and De Marco, 2015). Due to its advantages, MSA has been considered as a green catalyst that is safe for chemical synthesis. This study aimed to investigate the use *K. alvarezii* for the production of levulinic acid (LA) from using methanesulfonic acid (MSA) as a green catalyst. This study also observed the optimal reaction condition of LA production. A central composite design in the response surface statistical methodology and combined severity factor was applied to observe the optimum conversion conditions and reaction interaction in the process of *K. alvarezii* transition to levulinic acid by acidic hydrolysis. The application of *K. alvarezii* and green catalyst MSA in LA production can be developed as a sustainable macroalgae biorefinery, where we can produce biofuel, high added-value molecules, and other valuable compounds.

### 1.1. Materials

*Kappaphycus alvarezii* was freshly obtained from Indonesia, and then

cleaned and rinsed using distilled water to remove salt and debris. Subsequently, the macroalgae sample was dried under the shade then ground into powder. The reagent grade of MSA (Samchun Pure Chemical Co., Ltd., Korea) and the analytical grade of LA and FA (Sigma-Aldrich, USA) were used in this study.

### 1.2. Proximate composition analysis

The proximate compositions of *K. alvarezii* were analyzed using the phenol sulfuric acid method for carbohydrate (Meinita et al., 2018; Kochert, 1978), quantified gravimetrically method for lipid (Radin, 1981), Lowry method for protein (Lowry et al., 1951). The ash content was weighed after heating the sample at 575 °C for 5 h (Meinita et al., 2018).

### 1.3. Yield calculation

The LA or FA yield based on the weight of the *K. alvarezii* was calculated using the following equation:

$$\text{LA or FA yield (\%)} = \frac{\text{mass of the produced LA or FA in product}}{\text{mass of } K. alvarezii \text{ substrate}}$$

### 1.4. Batch experimental procedure

The hydrothermal experimental reactor consisted of a reactor equipped with proportional integral derivative (PID) temperature controller (TC200P, Misung Scientific Co., Ltd., Korea) to monitor and maintain the temperature. This equipment was filled with oil and pre-heated for 5–10 min to reach desired and stable hydrothermal reaction. The KA samples were placed in a 50 mL stainless steel reactor equipped with a magnetic stirrer and dissolved in MSA, where different catalyst amounts, reaction temperature, and time were applied. Subsequently, the device was soaked using tap water to reduce the heat after the reaction was completed. Furthermore, the hydrolysate supernatants were recovered by a 15 min centrifugation at 17,000 rpm, and the pH was adjusted with sodium hydroxide to 6.5. The supernatants were then taken and filtered using a 0.2 μm syringe filter for further HPLC analysis (Jeong et al., 2015; Jeong and Park, 2010).

### 1.5. Experimental design and statistical analysis

A 5 level, 3-factor central composite trial of the response surface methodology was composed using Design-Expert 9 statistical software

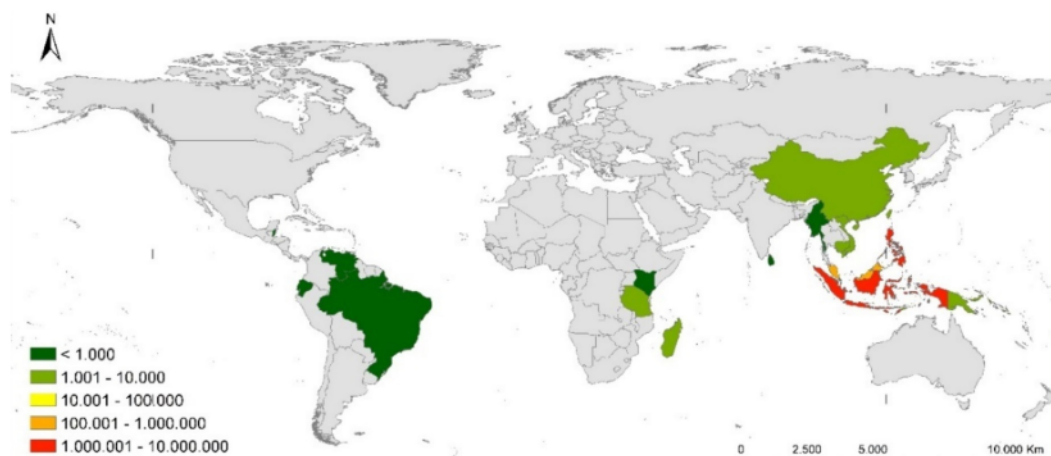


Fig. 1. Global production of *K. alvarezii* (ton ww) in 2019 based on Fishstat 2021.

(Stat-Ease, Inc., USA). Furthermore, a total of 20 experiments consisting of 8, 6, and 5 factorial, axial, and central composite rotatable points, respectively were conducted to observe reciprocal interaction (Jeong et al., 2009; Jeong and Park, 2009). The three reaction factors included catalyst concentration (0.164–0.7 M), reaction temperature (149.8–200.2 °C), and reaction time (4.77–55.23 min). Also, the model was determined by multiple regressions while the coefficient of determination ( $R^2$ ) and analysis of variance (ANOVA) were used to evaluate the model quality (Jeong et al., 2015; Jeong and Park, 2010).

## 1.6. Analysis

LA and FA concentrations were separated and quantified using HPLC (Agilent 1100, USA). The separation of LA and FA were done using a Bio-Rad1 Aminex-87H column under the conditions of 6 °C oven temperature, at 0.6 mL/min flow rate of mobile phase, and using 5 mM sulfuric acid as mobile phase. A refractive index detector was used as the detector in this study (Jeong et al., 2015; Jeong and Park, 2010).

## 2. Results and discussion

KA contains about 32.95–61.7% of carrageenan and is widely used in food, nutraceutical, and pharmaceutical industries (Góes and Reis, 2012; Meinita et al., 2019). KA also contains high-value molecules and compounds including carbohydrate, protein, lipid, ash, and monosaccharide which can be developed into high-value products derived from the sugar content. This high-value product can be simultaneously produced together with the production of carrageenan. The proximate and monosaccharide content of *K. alvarezii* is shown in Table 1.

The conversion of macroalgae polysaccharides to platform chemicals such as MF, LA, and FA has been attracted research interest in recent years. In this study, we observed the production of LA from *K. alvarezii* which is containing high and easily-degraded polysaccharide content. This polysaccharide can be depolymerised via hydrolysis into glucose, galactose, and fructose and then converted to 5-HMF, LA, and FA (Fig. 2). The pathways of LA production from *K. alvarezii* consisted of four processes. Firstly, the polysaccharide of KA is hydrolysed into

**Table 1**  
Proximate and monosaccharide content of *K. alvarezii*.

Component	Content	Reference
Proximate (% dw)	67.74 ± 0.55	(Gereniu et al., 2017)
Carbohydrate	59.58 ± 0.88	(Abd-Rahim et al., 2014)
	67.8 ± 10.40	(Meinita et al., 2012b)
	58.15 ± 1.36	This study
	14.51–15.48	(Gereniu et al., 2017)
Ash	19.70 ± 0.09	(Abd-Rahim et al., 2014)
	18.4 ± 0.5	(Meinita et al., 2012b)
	15.51 ± 0.03	This study
	12.61 ± 0.46	(Gereniu et al., 2017)
Moisture	14.23 ± 0.32	(Abd-Rahim et al., 2014)
	16.7 ± 0.7	(Meinita et al., 2012b)
	12.32 ± 0.32	This study
	4.24 ± 0.27	(Gereniu et al., 2017)
Protein	5.74 ± 0.89	(Abd-Rahim et al., 2014)
	3.6 ± 0.9	(Meinita et al., 2012b)
	3.83 ± 0.11	This study
	0.50 ± 0.25	(Gereniu et al., 2017)
Lipid	0.75 ± 0.22	(Abd-Rahim et al., 2014)
	0.60 ± 0.01	(Meinita et al., 2012b)
	0.72 ± 0.02	This study
	0.75 ± 0.22	(Abd-Rahim et al., 2014)
Monosaccharide (mol %)		
Galactose	30.0–33.2	(Lechat et al., 1997)
3,6-anhydrogalactose	22.8–27.2	(Lechat et al., 1997)
6-O-methyl galactose	0.9–1.4	(Lechat et al., 1997)
Glucose	1.8–2.6	(Lechat et al., 1997)
Xylose	0.8–0.9	(Lechat et al., 1997)
Sulphate	35.8–42	(Lechat et al., 1997)

glucose. The second process is isomerization which converts glucose into fructose. The third process is the dehydration process which converts fructose to 5-HMF. The fourth process is rehydration, which converts the 5-HMF into LA and FA (Rackemann and Doherty, 2011). LA is a 4-oxo-pentanoic acid with reactive carbonyl and carboxyl groups while FA is a by-product of the rehydration of 5-HMF to LA.

In our previous study of ethanol production from *K. alvarezii*, we found after acid hydrolysis using 0.2 M sulfuric acid for 15 min resulted 4.67 ± 0.96 g/L of 5-HMF and 1.07 ± 0.02 g/L of levulinic acid (Meinita et al., 2012b). Further study on the optimization of reaction temperature, catalyst concentration, and reaction time is needed to get the optimum LA production. Hence, in this study, we focused on the optimization of levulinic acid at the different reaction temperatures, catalyst concentration, and reaction time and analyzed using response surface methodology (RSM).

### 2.1. Predicted model

A 5-level, 3-factor central composite design was used to obtain an optimum reaction condition and assessed the reciprocal interactions of the reaction factors through the MSA catalyzed hydrothermal reaction of LA. Table 2 shows the production values for both acids vary according to the treatment combination of all factors such as catalyst, reaction temperature, and time, where the LA product values were entirely greater than FA.

The lowest product values for both FA and LA were obtained by a combination of 160 °C temperature treatment, 0.3 M catalyst, and 15 min reaction time with a product concentration of 1.46 and 4.00 g/L, respectively, equivalent to a product yield of 2.92 and 8.00%. Meanwhile, the highest product value was produced by a combination of 160 °C temperature treatment, 0.7 M catalyst, and 45 min reaction time with a product concentration of 2.84 and 7.26 g/L, equivalent to 5.69 and 14.51%.

The best prediction model of treatment on product value from FA and LA was generated from the second-order polynomial fitting model using Design Expert 9 statistical software (Table 3). This quadratic model was very suitable for use as a predictive model for both FA and LA with a determination coefficient of 0.95 and 0.94, respectively. These high determination coefficient values showed the predicted values compared to the actual values were reliable. Therefore, this quadratic equation model was used to predict the relationship between the treatment and the measured parameters.

The ANOVA results showed the quadratic model between treatments and product values for both FA and LA were very significant with an F-test probability of  $P < 0.01$ . Furthermore, all linear ( $X_1$ ,  $X_2$ , and  $X_3$ ), interaction ( $X_1X_2$ ,  $X_1X_3$ ), and quadratic coefficients ( $X_1^2$ ,  $X_2^2$ ,  $X_3^2$ ) for both the FA and LA models showed significant results with F-values 45.42 and 36.34, respectively.

In the LA model, all linear coefficients were positive. Hence, the entire treatment had a positive effect on the value of the resulting product. The temperature treatment had the highest effect with a coefficient of 0.84, while the catalyst and reaction time only had a value of 0.61 and 0.64, respectively. Meanwhile, the interaction and quadratic coefficients had a negative value; hence all the treatments had a negative effect on the value of the product produced. The combination of temperature treatment with time gave a greater contribution than with catalyst in terms of the interaction of each treatment, where the decrease in the value of the resulting product had a coefficient of  $-1.23$  and  $-1.07$ , respectively. Meanwhile, the reaction temperature had a higher quadratic effect on the decrease in product value with a coefficient of  $-1.23$  compared to catalyst and reaction time with values of  $-0.44$  and  $-0.54$ , respectively.

Similar to the LA model, all linear coefficients were positive in FA, hence all the treatments had a positive effect on the value of the resulting product. The largest linear contribution was also produced by temperature with a coefficient of 0.15 although this value was

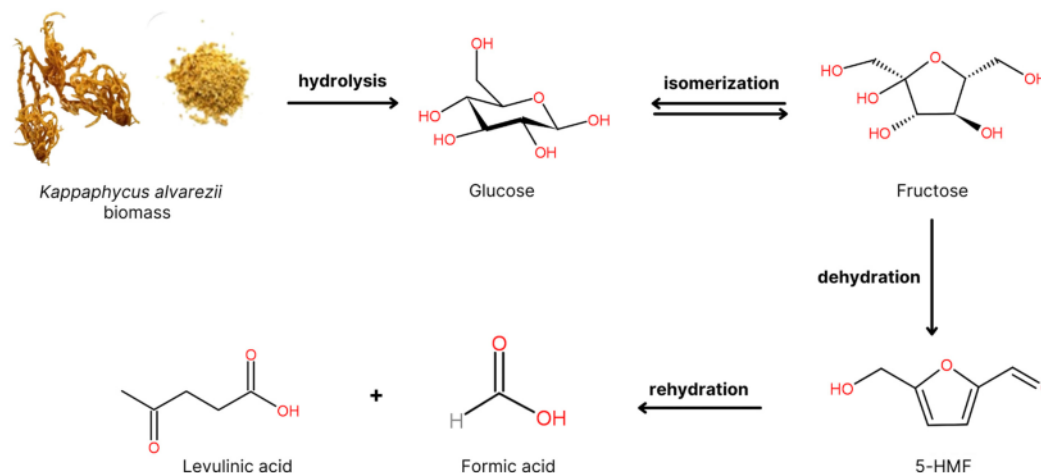


Fig. 2. Pathways of levulinic acid and formic acid production from *K. alvarezii*.

Table 2  
Experimental design and results for the 5-level, 3-factor central composite design of response surface methodology.

X1, Temp. (°C)	X2, Cat. (M)	X3, Time (min)	Product concentration (g/L)		Product yield (%)	
			FA	LA	FA	LA
175.00	0.50	4.77	2.27 ± 0.10	5.95 ± 0.17	4.55 ± 0.20	11.90 ± 0.33
175.00	0.50	30.00	2.80 ± 0.25	7.13 ± 0.28	5.61 ± 0.51	14.26 ± 0.55
175.00	0.50	30.00	2.78 ± 0.17	7.06 ± 0.10	5.56 ± 0.34	14.12 ± 0.19
190.00	0.30	15.00	2.52 ± 0.02	6.45 ± 0.06	5.04 ± 0.05	12.90 ± 0.12
190.00	0.30	45.00	2.23 ± 0.05	5.99 ± 0.12	4.46 ± 0.09	11.99 ± 0.23
160.00	0.30	45.00	2.24 ± 0.13	5.77 ± 0.18	4.48 ± 0.25	11.54 ± 0.35
175.00	0.84	30.00	2.45 ± 0.30	6.73 ± 0.30	4.90 ± 0.06	13.47 ± 0.60
175.00	0.16	30.00	2.38 ± 0.09	6.16 ± 0.02	4.75 ± 0.18	12.32 ± 0.04
190.00	0.70	15.00	2.52 ± 0.02	6.45 ± 0.06	5.04 ± 0.05	12.90 ± 0.12
175.00	0.50	30.00	2.77 ± 0.09	7.11 ± 0.00	5.55 ± 0.18	14.21 ± 0.00
160.00	0.70	15.00	2.04 ± 0.43	5.31 ± 0.76	4.07 ± 0.85	10.62 ± 1.53
160.00	0.30	15.00	1.46 ± 0.03	4.00 ± 0.06	2.92 ± 0.06	8.00 ± 0.12
200.23	0.50	30.00	2.01 ± 0.17	6.18 ± 0.03	4.02 ± 0.33	12.36 ± 0.05
175.00	0.50	55.23	2.43 ± 0.28	6.67 ± 0.38	4.86 ± 0.57	13.33 ± 0.75
190.00	0.70	45.00	1.80 ± 0.01	6.34 ± 0.02	3.59 ± 0.01	12.68 ± 0.04
160.00	0.70	45.00	2.84 ± 0.04	7.26 ± 0.01	5.69 ± 0.08	14.51 ± 0.03
175.00	0.50	30.00	2.74 ± 0.28	7.19 ± 0.18	5.47 ± 0.56	14.38 ± 0.36
149.77	0.50	30.00	1.68 ± 0.02	4.49 ± 0.05	3.35 ± 0.04	8.98 ± 0.11
175.00	0.50	30.00	2.74 ± 0.19	7.00 ± 0.06	5.47 ± 0.38	14.00 ± 0.13
175.00	0.50	30.00	2.57 ± 0.10	6.88 ± 0.14	5.14 ± 0.19	13.77 ± 0.27

Table 3  
19<sup>th</sup> model equation for FA and LA responses resulting from experimental design.

Response (%)	Final equation in terms of actual factors	Model	R <sup>2</sup>
LA	$= 14.12 + 0.84 \times x_1 + 0.61 \times x_2 + 0.64 \times x_3 - 0.61 \times x_1 x_2 - 1.07 \times x_1 x_3 - 1.23 \times x_1^2 - 0.44 \times x_2^2 - 0.54 \times x_3^2$	Quadratic	0.95
FA	$= 5.46 + 0.15 \times x_1 + 0.13 \times x_2 + 0.12 \times x_3 - 0.40 \times x_1 x_2 - 0.65 \times x_1 x_3 - 0.16 \times x_1^2 - 0.21 \times x_2^2 - 0.25 \times x_3^2$	Quadratic	0.94

insignificant compared to catalyst and time with values of 0.13 and 0.12, respectively. Furthermore, the difference was shown by the interaction and quadratic effect, where all treatments had a negative coefficient value; hence each treatment had a negative contribution to the value of the product produced. The interaction of the catalyst treatment with the reaction time had a greater influence than with temperature. Meanwhile, the quadratic temperature treatment had a more significant effect on decreasing the value of the product compared to the catalyst and reaction time.

The results of the model validation showed there was a linear correlation between the prediction model and the results of the research (Fig. 3). This indicates the quadratic model was appropriate for predicting the effect of treatment on the value of both FA and LA products. Meanwhile, the predictive model was accurate in forecasting the impact of the combined level of reaction temperature, catalyst concentration, and reaction time on FA (Fig. 3A) and LA (Fig. 3B) to the optimum value of 5.69% and 14.51%, respectively. This optimum value was ideal for both acids which can be produced by the effect of a combination of treatment levels. Furthermore, although the actual value of each product from the experimental results were only 2.92% and 8.00% for FA and LA, respectively, this predicted model can forecast a lower product value.

## 2.2. Effects and reciprocal interactions of reaction factors

The effects and reciprocal interactions of reaction factors on FA and LA production were shown using the 3D surface plots of each factor under constant zero level reaction conditions. Fig. 4 shows the 3D surface plot of effects of reaction temperature, catalyst concentration, reaction time, and their interactions on the FA product values under constant reaction conditions. Reaction temperature, catalyst concentration, and reaction time are three main reaction factors on FA and LA

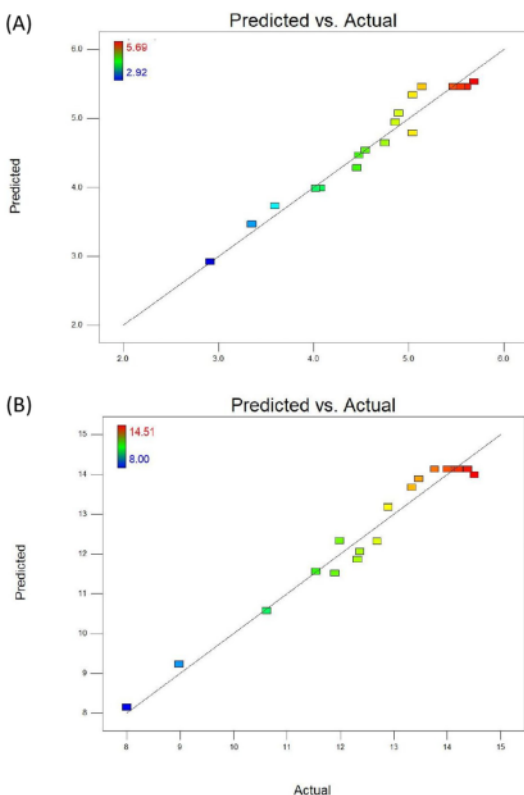


Fig. 28 Actual vs predicted formic acid (A) and levulinic acid (B) yields based on the reciprocal interaction of reaction factors.

product. The effect of reciprocal interaction between reaction temperature and catalyst concentration under a constant reaction time of 60 min on the FA yield is shown in Fig. 4A. The FA yield decreased quadratically in line with the increase in the temperature for all catalyst concentration levels (0.3–0.7 M) and varied based on the temperature level along with the increase in catalyst concentration. The FA yield increased quadratically at temperature levels below 172 °C and tended to be stable between 172 and 182 °C as a result of an increase in the catalyst concentration level. Furthermore, the increase in catalyst concentration level had an impact on the quadratic decrease in the FA yield at a temperature range over 182 °C. The highest FA yield was attained from the interaction between the lowest temperature level (160 °C) with the highest catalyst concentration (0.7 M). Fig. 4B shows the effect of reciprocal interaction between reaction temperature and time in a constant catalyst concentration (0.5 M) on the FA yield. Generally, LA yield changed quadratically (increasing and then decreasing) along with the increasing temperature, however, the pattern of change varied according to the level of reaction time. At lower reaction time levels, the FA yield tends to increase quadratically with the increase of temperature and it decreased when the temperature reached 190 °C. The quadratic pattern of FA yield changes as the level of reaction time increases with each temperature level. This increasing reaction time at low-temperature levels caused a tendency to quadratically decrease the FA yield, while at a longer reaction time at high temperature a reverse effect occurs. The highest FA yield was attained from the reciprocal interaction of a decrease in reaction time level accompanied by an increase of temperature or vice versa.

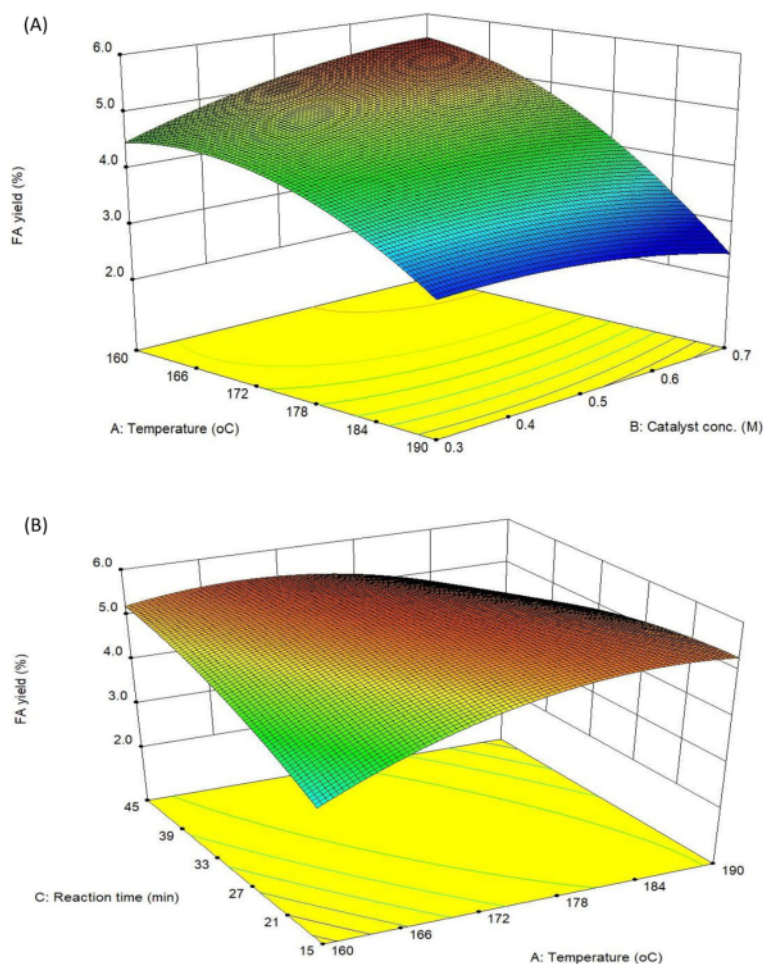
Fig. 5 shows the effects of temperature, catalyst, time, and their interactions on the LA yield. Fig. 5A shows the effect of the reciprocal

interaction between reaction temperature and catalyst concentration under a constant reaction time of 30 min on the LA yield. Generally, the product value changes quadratically (increased and then decreased) based on the increase in temperature, and the changing pattern varied based on the catalyst concentration level. At lower catalyst concentration levels, the LA yield tends to increase with the increase of temperature and decreased when the temperature reached 190 °C. The quadratic pattern of the LA yield changes based on the increase of catalyst concentration, where it tends to decrease with increasing catalyst concentration. On the other hand, the opposite condition occurs, LA yield decreased quadratically at low-temperature levels due to an increase in catalyst concentration for each level. Meanwhile, an increase in catalyst concentration at a high-temperature level caused a quadratic increase in LA yield. The highest LA yield was obtained from reciprocal interaction between a decrease in temperature level accompanied by an increase of catalyst concentration or vice versa. Fig. 5B shows the effect of the reciprocal interaction between reaction temperature and time on the LA yield at a constant 0.5 M catalyst concentration. Similarly, LA yield resulting from the reciprocal interaction between these factors had a similar quadratic pattern. This pattern also occurs in the FA yield discussed earlier, where the FA yield varied according to the reaction time along with the increase in temperature, and vice versa. At lower reaction time levels, the LA yield also tended to increase quadratically with increasing temperature, and vice versa. The increase in reaction time at low-temperature levels also caused a tendency for a quadratic decrease in the product value and vice versa. Furthermore, the highest LA value was obtained from the reciprocal interaction between a decrease of reaction time accompanied by an increasing temperature or vice versa.

The high value of LA product at high temperature treatment for all treatment combinations indicates that biomass conversion into LA is very efficient at high temperature (Jeong et al., 2015; Jeong and Park, 2010; Omari et al., 2012). In addition to high temperature treatment, catalyst concentration and longer reaction time cause the conversion of biomass by the catalyst to be more efficient (Jeong, 2014; Jeong et al., 2015). Conversion of glucose to FA is also efficient at high temperature conditions (Jeong, 2014; Jeong et al., 2015; Jeong and Park, 2010). Similarly, high FA values also occur as a result of the catalyst and reaction time which causes the efficiency of converting glucose to FA (Jeong, 2014; Jeong and Park, 2010). However, there are limitations of temperature level, concentration, and reaction time because excessive conditions cause unwanted side reactions. Byproduct formation such as humin and other decomposition products were generated from excessive condition (Liu et al., 2015).

Fig. 6 shows the effects of reaction temperature and time, catalyst concentration, and their reciprocal interaction on formic acid and levulinic acid yield. The value of the FA yield (actual and 95% CI) in Fig. 6A (left) changed quadratically as a result of an increase in temperature under a constant time reaction of 30 min at both the catalyst concentration level of 0.3 and 0.7 M. Furthermore, at the lower and higher catalyst concentration levels of 0.3 M and 0.7 M, respectively, the FA yield increased at lower temperatures until it reached a peak at 178 °C and 184 °C, then decreased. Although both catalyst concentrations had the same quadratic pattern along with an increase in temperature, the optimum temperature of both catalyst concentrations was different, which implied a diverse trend of change. Also, a similar FA yield was generated from the two levels of catalyst concentration (0.3 and 0.7 M), where the interaction between these levels occurred at 180 °C; hence the reciprocal interaction between these temperatures with different catalyst concentration levels produces a similar FA yield.

Fig. 6A (right) shows the quadratic change in the FA yield (actual and 95% CI) due to an increase in temperature under a constant catalyst concentration of 0.5 M at both the reaction times of 15 and 45 min. Furthermore, at the lower and higher reaction time levels of <15 min and >45 min, respectively, the FA yield increased quadratically until it approached its optimum temperature of 190 °C and 170 °C, respectively,



10  
Fig. 4. Effects of reaction temperature and time, catalyst concentration, and their reciprocal interaction 8 formic acid yield under constant reaction conditions. (A) represents 8 reciprocal interaction between reaction temperature and catalyst concentration under a constant reaction time of 60 min, and (B) represents 10 reciprocal interaction between reaction temperature and reaction time under a constant catalyst concentration of 0.5 M.

then decreased. The difference between these two levels was the disparity in the optimum temperature, where the reciprocal interaction results in the highest LA yield. Also, the reciprocal interaction of the two levels produced the same FA yield at 178 °C, hence all levels of reaction time will have a constant value at that temperature.

Fig. 6B shows the effects of reaction temperature and time, as well as catalyst concentration on formic acid under constant reaction conditions. The reaction pattern of LA yield is similar to FA yield. The yield of LA (actual and 95% CI) also changed quadratically with increasing temperature under constant time reaction of 30 min at both the catalyst concentration levels of 0.3 and 0.7 M (Fig. 4B, left) and under constant catalyst concentration at both the reaction time levels of 15 and 45 min (Fig. 6B, right).

The LA yield increased quadratically until it approached its optimum temperature of 178 and 190 °C, respectively, and then decreased at both the concentration levels of 0.3 and 0.7 M. Similar LA yield was generated when the two levels interacted at a temperature of 190 °C. Furthermore, as a form of reciprocal interaction between temperature and reaction time, the product value also increased quadratically until it approached its optimum level of 174 and 190 °C, respectively, and then decreased at both the reaction time levels of 15 and 45 min. The interaction of these

two-time reaction levels at a temperature of 184 °C produces a similar yield.

The reciprocal interaction pattern of reaction temperature and time, as well as catalyst concentration on FA yield, was similar to LA product yield, i.e. the quadratic pattern. However, the different coefficient values caused discrepancies in the optimum temperature. The higher quadratic and interaction coefficient on LA, resulting in a sharper quadratic pattern compare to FA both for the interaction of reaction temperature with catalyst concentration and time. Furthermore, the optimum temperature in LA production was higher compared to FA production in both interactions due to different coefficient values.

The level of treatment, both temperature, catalyst concentration, and reaction time are important because the mechanism for converting carbohydrates (fructose, glucose, and cellulose) into LA and FA products is a long and complex process (Morone et al., 2015; Rackemann et al., 2014, 2016; Rackemann and Doherty, 2011). As shown in Fig. 2, the conversion of glucose into FA and LA products is through isomerization, dehydration, and rehydration processes (Rackemann and Doherty, 2011). In extreme reaction conditions (high temperature, high catalyst concentration, and long reaction time), products such as 5-HMF will be easily transformed into LA and FA by rehydration so that the value of the

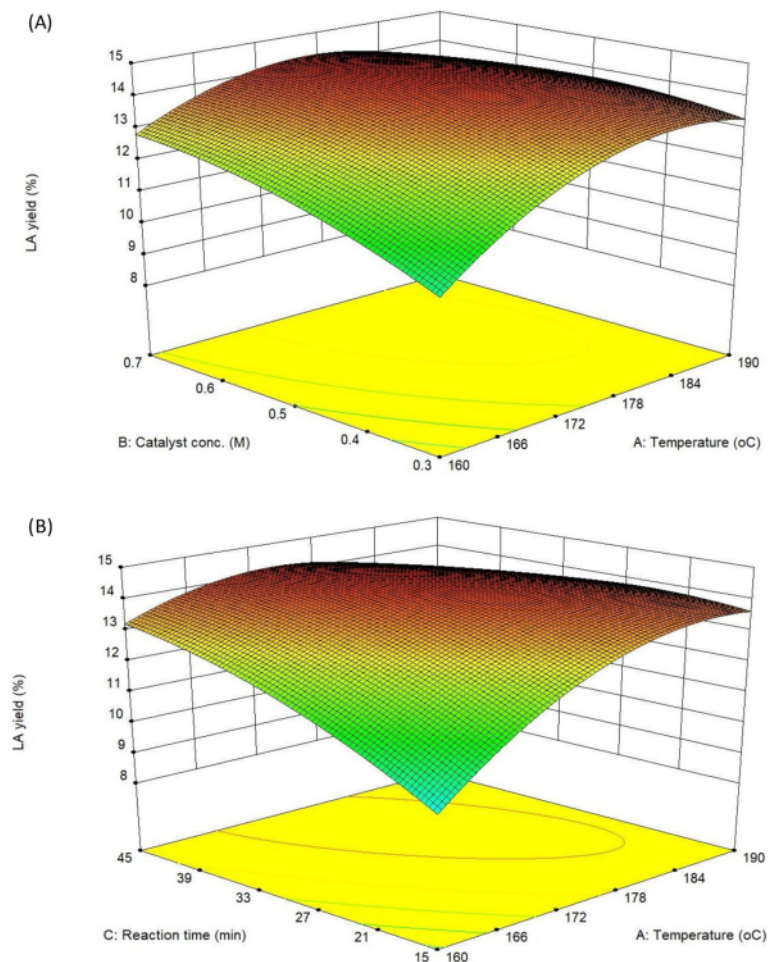


Fig. 5. Effects of reaction temperature and time, catalyst concentration, and their reciprocal interaction on levulinic acid yield under constant reaction conditions. (A) represents the reciprocal interaction between reaction temperature and catalyst concentration under a constant reaction time of 30 min, and (B) represents reciprocal interaction between reaction temperature and reaction time under a constant catalyst concentration of 0.5 M.

LA and FA products becomes optimal (Jeong, 2014; Jeong et al., 2015). However, due to side reactions from the decomposition of LA and FA, there is a limit to the optimal value of the treatment level, both temperature, catalyst concentration and reaction time.

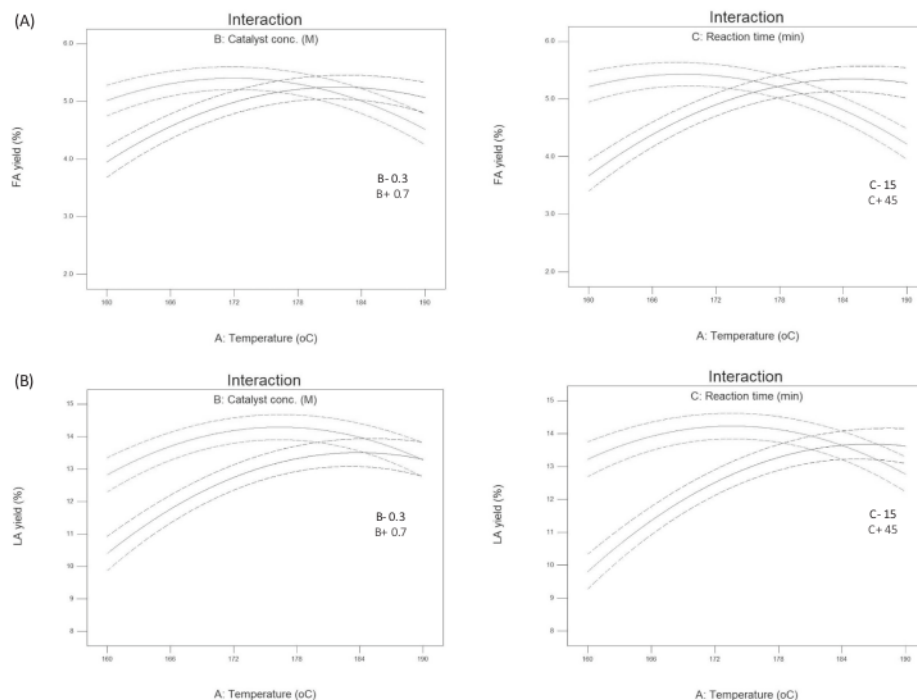
### 2.3. Optimization of levulinic acid and formic acid production

Optimization of the reaction factor was obtained using the response surface statistical approach with a reaction temperature range of 149.77–200.23 °C, catalyst concentration 0.16–0.84 M, and reaction time of 4.77–55.23 min. The optimal predictive values for LA (7.24 g/L, 14.4%) and FA (2.69 g/L, 5.39%) were generated by the treatment level of 180 °C reaction temperature, 0.60 M catalyst concentration, and 30 min reaction time. Furthermore, yields of  $13.90 \pm 0.02\%$  LA and  $5.22 \pm 0.01\%$  FA on a biomass basis were used in the verification of the predicted model under the optimized reaction condition. These verified results sufficiently fit the predicted yields of these acids. However, these results need to be considered more carefully in comparing yields due to the difference in biomass properties.

This treatment combination was used as a constant reaction condition to optimize the effect of the biomass percentage factor on the FA

and LA product values. Table 4 shows the effect of the biomass factor under constant reaction conditions on the product concentration and yield. The product concentration of both acids has significant differences based on the discrepancies in biomass levels, where the maximum product concentration value was produced by the highest biomass level and vice versa. However, product yield had a reverse outcome. This was particularly for the LA product yield, where some levels of biomass such as 2.50% and 5.00%, 7.50% and 10.00% as well as 12.50% and 15.00% do not significantly affect the value of the product although there are significant differences. The production values of both acids decreased logarithmically based on the increase in biomass, where a sharp decrease was seen below 2% and a gentle decline occurred thereafter. Furthermore, the LA value was generally higher than the FA products with a greater decline and if the biomass has a continued increase, the product value will be constant at about 4.8% and 12.0% for FA and LA, respectively. The product values of both FA and LA decreased logarithmically as biomass increased. Both sharp declines were seen when biomass was below 2% and a gentle decline occurred thereafter. Values in LA were generally higher than values for FA products and the decline was also greater. If the biomass continues to be increased, the product value will be constant with a value of around 4.8% for FA and 12.0% for





**Fig. 6.** Effects of reaction temperature and time, as well as catalyst concentration on formic acid (A) and levulinic acid (B) yields. The solid and dot lines represent the actual and 95% CI while the left and right signify the interaction of reaction temperature with catalyst concentration under constant reaction time of 30 min and reaction time under constant catalyst concentration of 0.5 M, respectively.

**Table 4**  
Product concentration and product yield of FA and LA based on the biomass factor. <sup>a–f</sup> represents the significant differences in CI 95% ( $P < 0.05$ ).

Biomass (%)	Product concentration (g/L)		Product Yield (%)	
	FA	LA	FA	LA
2.50	1.33 ± 0.02 <sup>a</sup>	3.64 ± 0.04 <sup>a</sup>	5.35 ± 0.06 <sup>e</sup>	14.69 ± 0.17 <sup>f</sup>
5.00	2.60 ± 0.01 <sup>b</sup>	6.96 ± 0.01 <sup>b</sup>	5.22 ± 0.01 <sup>c</sup>	13.93 ± 0.02 <sup>e</sup>
7.50	3.81 ± 0.04 <sup>c</sup>	9.93 ± 0.16 <sup>c</sup>	5.05 ± 0.05 <sup>b</sup>	13.09 ± 0.21 <sup>d</sup>
10.00	5.08 ± 0.05 <sup>d</sup>	12.92 ± 0.07 <sup>d</sup>	5.12 ± 0.05 <sup>b</sup>	12.97 ± 0.07 <sup>c</sup>
12.50	6.10 ± 0.01 <sup>e</sup>	15.59 ± 0.10 <sup>e</sup>	4.87 ± 0.01 <sup>a</sup>	12.53 ± 0.08 <sup>b</sup>
15.00	7.23 ± 0.03 <sup>f</sup>	18.12 ± 0.14 <sup>f</sup>	4.80 ± 0.02 <sup>a</sup>	12.02 ± 0.10 <sup>a</sup>

LA.

#### 2.4. Comparison of levulinic acid production from macroalgae

Several studies on LA production from macroalgae have been conducted (Cao et al., 2019; Galletti et al., 2019). Comparison between recent study with the previous studies of the LA production from macroalgae using various catalysts is shown in Table 5. Galletti et al. (2019) reported green macroalgae *Chaetomorpha linum* and *Valonia aegagropila* produced 19% and 16% of LA, respectively. These optimum yields were obtained at 190 and 200 °C respectively, during 45 min, using 4.7% H<sub>2</sub>SO<sub>4</sub> and 5% of each macroalgae biomass. Cao et al. (2019) also reported 16% of LA yield was produced from red macroalgae *Gracilaria lemaneiformis* at 180 °C, during 20 min, using 5% of macroalgae biomass and 0.2 M H<sub>2</sub>SO<sub>4</sub>. The previous studies on LA production from macroalgae were using H<sub>2</sub>SO<sub>4</sub> as catalyst while in this study we used MSA. To date, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) is the most popular catalyst in LA production. However, the use of sulfuric acid causes some problems to the environment, due to its high corrosive and difficulty to recycle. This study

**Table 5**  
Levulinic acid production from macroalgae.

Material	Catalyst	Optimum condition	Yield (%)	References
<i>Chaetomorpha linum</i>	H <sub>2</sub> SO <sub>4</sub>	5% biomass, 4.7% H <sub>2</sub> SO <sub>4</sub> , 190 °C, 45 min	19	(Galletti et al., 2019)
<i>Valonia aegagropila</i>	H <sub>2</sub> SO <sub>4</sub>	5% biomass, 4.7% H <sub>2</sub> SO <sub>4</sub> , 200 °C, 45 min	16	(Galletti et al., 2019)
<i>Gracilaria lemaneiformis</i>	H <sub>2</sub> SO <sub>4</sub>	5% biomass, 0.2 M H <sub>2</sub> SO <sub>4</sub> , 180 °C, 20 min	16.3	(Cao et al., 2019)
<i>Kappaphycus alvarezii</i>	MSA	2.5% biomass, 180 °C, 0.6 M MSA, 30 min	14.7	This study

showed the LA yield achieved from macroalgae using MSA is comparable with the LA yield produced from macroalgae using sulfuric acid.

### 3. Conclusion

This study showed that the conversion of red-macroalgae *K. alvarezii* to LA and FA can be conducted by thermochemical reaction using MSA as an environmental-friendly and strong acidic catalyst. Furthermore, by optimization of reaction factors, the maximum yields of LA (14.69%) and FA (5.35%) were obtained under 180 °C, 0.6 M MSA, 30 min, and 2.5% biomass loading conditions. In conclusion, the utilization of macroalgae and MSA as an eco-friendly green catalyst and strong acidic catalysts had a valuable potential in the production of levulinic acid and formic acid which can contribute to overcome our dependency on petroleum-based chemical production.

**CRedit authorship contribution statement**

**Maria Dyah Nur Meinita:** Investigation, Data curation, Analysis, Validation, Visualization, Writing - original draft;

**Amron, Dicky Harwanto, Agus Trianto:** Investigation, Data curation, Writing - review & editing;

**Gwi-Taek Jeong:** Conceptualization, Supervision, Data curation, Methodology, 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.

**Acknowledgment**

This research was supported by the World Class Research (WCR) Grant, Ministry of Research, Technology and Higher Education of the Republic of Indonesia, Grant number: T/1409/UN23.18/PT.01.01/2021.

**References**

- Abd-Rahim, F., Wasoh, H., Zakaria, M.R., Ariff, A., Kapri, R., Ramli, N., Siew-Ling, L., 2014. Production of high yield sugars from *Kappaphycus alvarezii* using combined methods of chemical and enzymatic hydrolysis. *Food Hydrocoll.* 42, 309–315. <https://doi.org/10.1016/j.foodhyd.2014.05.017>.
- Baker, S.C., Kelly, D.P., Murrell, J.C., 1991. Microbial degradation of methanesulphonic acids missing link in the biogeochemical sulphur cycle. *Nature* 354, 737–740.
- Cao, L., Yu, I.K.M., Cho, D.W., Wang, D., Tsang, D.C.W., Zhang, S., Ding, S., Wang, L., Ok, Y.S., 2019. Microwave-assisted low-temperature hydrothermal treatment of red seaweed (*Gracilaria lemaneiformis*) for production of levulinic acid and algae hydrochar. *Bioresour. Technol.* 273, 251–258. <https://doi.org/10.1016/j.biortech.2018.11.013>.
- FAO, 2020. *The State of World Fisheries and Aquaculture 2020*. Food and Agriculture Organization of United Nations, Rome.
- Galletti, A.M.R., Antonetti, C., Licursi, D., Mussi, L., Balestri, E., Lardicci, C., 2019. Levulinic acid production from the green macroalgae *Chaetomorpha linum* and *Valonia aegagropila* harvested in the orbetello lagoon. *Chem. Eng. Trans.* 74, 103–108. <https://doi.org/10.3303/CET1974018>.
- Gereniu, C.R.N., Saravana, P.S., Getachew, A.T., Chun, B.-S., 2017. Characteristics of functional materials recovered from Solomon Islands red seaweed (*Kappaphycus alvarezii*) using pressurized hot water extraction. *J. Appl. Phycol.* 29, 1609–1621. <https://doi.org/10.1007/s10811-017-1052-3>.
- Gemon, M.D., Wu, M., Buszta, T., Jamney, P., 1999. Environmental benefits of methanesulfonic acid: Comparative properties and advantages. *Green Chem.* 1, 127–140. <https://doi.org/10.1039/a900157c>.
- Góes, H.G.De, Reis, R.P., 2012. In: Temporal Variation of the Growth Carrageenan Yield and Quality of *Kappaphycus alvarezii* (Rhodophyta, Gigartinales) Cultivated at Sepetiba Bay, Southeastern Brazilian Coast, pp. 173–180. <https://doi.org/10.1007/s10811-011-9665-4>.
- Hargreaves, P.I., Barcelos, C.A., da Costa, A.C.A., Pereira, N., 2013. Production of ethanol 3G from *Kappaphycus alvarezii*: evaluation of different process strategies. *Bioresour. Technol.* 134, 257–263. <https://doi.org/10.1016/j.biortech.2013.02.002>.
- Henriques, A.C., De Marco, P., 2015. Methanesulfonate (MSA) catabolic genes from marine and estuarine bacteria. *PLoS One* 10, 1–16. <https://doi.org/10.1371/journal.pone.0125735>.
- Jeong, G.T., 2014. Production of levulinic acid from glucosamine by dilute-acid catalyzed hydrothermal process. *Ind. Crop. Prod.* <https://doi.org/10.1016/j.indcrop.2014.08.006>.
- Jeong, G.T., Park, D.H., 2009. Optimization of biodiesel production from castor oil using response surface methodology. *Appl. Biochem. Biotechnol.* 156, 1–11. <https://doi.org/10.1007/s12010-008-8468-9>.
- Jeong, G.T., Park, D.H., 2010. Production of sugars and levulinic acid from marine biomass *Gelidium amansii*. *Appl. Biochem. Biotechnol.* 161, 41–52. <https://doi.org/10.1007/s12010-009-8795-5>.
- Jeong, G.T., Yang, H.S., Park, D.H., 2009. Optimization of transesterification of animal fat ester using response surface methodology. *Bioresour. Technol.* 100, 25–30. <https://doi.org/10.1016/j.biortech.2008.05.011>.
- Jeong, G.T., Ra, C.H., Hong, Y.K., Kim, J.K., Kong, I.S., Kim, S.K., Park, D.H., 2015. Conversion of red-algae *Gracilaria verrucosa* to sugars, levulinic acid and 5-hydroxymethylfurfural. *Bioprocess Biosyst. Eng.* 38, 207–217. <https://doi.org/10.1007/s00449-014-1259-5>.
- Kamm, B., Gruber, P.R., Kamm, M., 2016. Biorefineries-industrial processes and products. *Ullmann's Encycl. Ind. Chem.* 1–38. [https://doi.org/10.1002/14356007.104\\_101.pub2](https://doi.org/10.1002/14356007.104_101.pub2).
- Khambhaty, Y., Mody, K., Gandhi, M.R., Thampy, S., Maiti, P., Brahmabhatt, H., Eswaran, K., Ghosh, P.K., 2012. *Kappaphycus alvarezii* as a source of bioethanol. *Bioresour. Technol.* 103, 180–185. <https://doi.org/10.1016/j.biortech.2011.10.015>.
- Kochert, G., 1978. Carbohydrate determination by the phenol-sulfuric acid method. In: Hellebust, J.A., Craigie, J.S. (Eds.), *Handbook of Physiological Methods, Physiological and Biochemical Methods, II*. Cambridge University Press, Cambridge, pp. 95–97.
- Leal Silva, J.F., Grekin, R., Mariano, A.P., Maciel Filho, R., 2018. Making levulinic acid and ethyl levulinate economically viable: a worldwide technoeconomic and environmental assessment of possible routes. *Energy Technol.* 6, 613–639. <https://doi.org/10.1002/ente.201700594>.
- Lechat, H., Amat, M., Mazoyer, J., Gallant, D.J., Buléon, A., Lahaye, M., 1997. Cell wall composition of the carrageenophyte *Kappaphycus alvarezii* (Gigartinales, Rhodophyta) partitioned by wet sieving. *J. Appl. Phycol.* 9, 565–572. <https://doi.org/10.1023/A:1007960413070>.
- Lee, Ji Ye, Li, P., Lee, Jieun, Ryu, H.J., Oh, K.K., 2013. Ethanol production from *Saccharina japonica* using an optimized extremely low acid pretreatment followed by simultaneous saccharification and fermentation. *Bioresour. Technol.* 127, 119–125. <https://doi.org/10.1016/j.biortech.2012.09.122>.
- Li, Y., Liu, N., Wang, X., Tang, X., Zhang, L., Meinita, M.D.N., Wang, G., Yin, H., Jin, Y., Wang, H., Liu, C., Chi, S., Liu, T., Zhang, J., 2018. Comparative genomics and systematics of *Betaphycus*, *Eucluea*, and *Kappaphycus* (Solieriaceae: Rhodophyta) based on mitochondrial genome. *J. Appl. Phycol.* <https://doi.org/10.1007/s10811-018-1450-1>.
- Liu, N., Zhang, L., Tang, X., Wang, X., Meinita, M.D.N., Wang, G., Chen, W., Liu, T., 2019. Complete plastid genome of *Kappaphycus alvarezii*: insights of large-scale rearrangements among Florideophyceae plastid genomes. *J. Appl. Phycol.* 31. <https://doi.org/10.1007/s10811-019-01815-8>.
- Liu, X., Li, S., Liu, Y., Cao, Y., 2015. Formic acid: a versatile renewable reagent for green and sustainable chemical synthesis. *Chin. J. Catal.* 36, 1461–1475. [https://doi.org/10.1016/S1872-2067\(15\)60861-0](https://doi.org/10.1016/S1872-2067(15)60861-0).
- Lowry, O.H., Rosebrough, N.J., Farr, A.L., Randall, R.J., 1951. Protein measurement with the Folin phenol reagent. *J. Biol. Chem.* 193, 265–275.
- Meinita, M.D.N., Hong, Y.-K., Jeong, G.-T., 2012a. Detoxification of acidic catalyzed hydrolysate of *Kappaphycus alvarezii* (cottonii). *Bioprocess Biosyst. Eng.* 35. <https://doi.org/10.1007/s00449-011-0608-x>.
- Meinita, M.D.N., Kang, J.-Y., Jeong, G.-T., Koo, H.M., Park, S.M., Hong, Y.-K., 2012b. Bioethanol production from the acid hydrolysate of the carrageenophyte *Kappaphycus alvarezii* (cottonii). *J. Appl. Phycol.* 24. <https://doi.org/10.1007/s10811-011-9705-0>.
- Meinita, M.D.N., Marhaeni, B., Hong, Y.-K., Jeong, G.-T., 2017. Enzymatic saccharification of agar waste from *Gracilaria verrucosa* and *Gelidium latifolium* for bioethanol production. *J. Appl. Phycol.* 29. <https://doi.org/10.1007/s10811-017-1205-4>.
- Meinita, M.D.N., Marhaeni, B., Oktaviani, D.F., Jeong, G.T., Hong, Y.K., 2018. Comparison of bioethanol production from cultivated versus wild *Gracilaria verrucosa* and *Gracilaria gigas*. *J. Appl. Phycol.* 30, 143–147. <https://doi.org/10.1007/s10811-017-1297-x>.
- Meinita, M.D.N., Marhaeni, B., Jeong, G.-T., Hong, Y.-K., 2019. Sequential acid and enzymatic hydrolysis of carrageenan solid waste for bioethanol production: a biorefinery approach. *J. Appl. Phycol.* 31. <https://doi.org/10.1007/s10811-019-1755-8>.
- Morone, A., Apte, M., Pandey, R.A., 2015. Levulinic acid production from renewable waste resources: Bottlenecks, potential remedies, advancements and applications. *Renew. Sust. Energ. Rev.* 51, 548–565. <https://doi.org/10.1016/j.rser.2015.06.032>.
- Mukherjee, A., Raghavan, V., 2014. Review Sustainable Production of Hydroxymethylfurfural and Levulinic Acid : Challenges and Opportunities. <https://doi.org/10.1016/j.biombioe.2014.11.007>.
- Omari, K.W., Besaw, J.E., Kerton, F.M., 2012. Hydrolysis of chitosan to yield levulinic acid and 5-hydroxymethylfurfural in water under microwave irradiation. *Green Chem.* 14, 1480–1487. <https://doi.org/10.1039/c2gc35048c>.
- Pambudi, L.T., Meinita, M.D.N., Ariyati, R.W., 2010. In: *Seaweed Cultivation in Indonesia Recent Status*, 4, pp. 6–10.
- Pereira, L., Amado, A.M., Critchley, A.T., Velde, F.Van, De, Ribeiro-claro, P.J.A., 2009. Food Hydrocolloids Identification of selected seaweed polysaccharides (phyco-colloids) by vibrational spectroscopy (FTIR-ATR and FT-Raman). *Food Hydrocoll.* 1–7. <https://doi.org/10.1016/j.foodhyd.2008.11.014>.
- Porse, H., Rudolph, B., 2017. The seaweed hydrocolloid industry: 2016 updates, requirements, and outlook. *J. Appl. Phycol.* <https://doi.org/10.1007/s10811-017-1144-0>.
- Rackemann, D.W., Doherty, W.O., 2011. The conversion of lignocellulosics to levulinic acid. *Biofuels* 5, 198–214. <https://doi.org/10.1002/bbb>.
- Rackemann, D.W., Bartley, J.P., Doherty, W.O.S., 2014. Methanesulfonic acid-catalyzed conversion of glucose and xylose mixtures to levulinic acid and furfural. *Ind. Crop. Prod.* 52, 46–57. <https://doi.org/10.1016/j.indcrop.2013.10.026>.
- Rackemann, D.W., Bartley, J.P., Harrison, M.D., Doherty, W.O.S., 2016. The effect of pretreatment on methanesulfonic acid-catalyzed hydrolysis of bagasse to levulinic acid, formic acid, and furfural. *RSC Adv.* 6, 74525–74535. <https://doi.org/10.1039/c6ra14772k>.
- Radin, N.S., 1981. Extraction of lipids with hexane-isopropanol. *Method. Enzymol.* 72, 5–7.
- Ruocco, N., Costantini, S., Guariniello, S., Costantini, M., 2016. Polysaccharides from the marine environment with pharmacological, cosmeceutical and nutraceutical potential. *Molecules* 21, 1–16. <https://doi.org/10.3390/molecules21050551>.
- Sadhukhan, J., Gadkari, S., Martinez-Hernandez, E., Ng, K.S., Shemfe, M., Torres-García, E., Lynch, J., 2019. Novel macroalgae (seaweed) biorefinery systems for

- integrated chemical, protein, salt, nutrient and mineral extractions and environmental protection by green synthesis and life cycle sustainability assessments. *Green Chem.* 21, 2635–2655. <https://doi.org/10.1039/c9gc00607a>.
- Tirtawijaya, G., Nazmul Haque, M., Choi, J.S., Moon, I.S., Meinita, M.D.N., Choi, J.-S., Hong, Y.-K., 2019. Spinogenesis and synaptogenesis effects of the red seaweed *Kappaphycus alvarezii* and its isolated cholesterol on hippocampal neuron cultures. *Prev. Nutr. Food Sci.* 24 <https://doi.org/10.3746/pnf.2019.24.4.418>.
- Werpy, T., Petersen, G., 2004. Top Value Added Chemicals from Biomass, I. US NREL, 76 pp.
- Wicklleder, M.S., Logemann, C., 2013. New chemistry of noble metals, comprehensive inorganic chemistry II. In: From Elements to Applications, Second edition. Elsevier Ltd. <https://doi.org/10.1016/B978-0-08-097774-4.00222-9>

# The production of levulinic acid and formic acid from red macroalga *Kappaphycus alvarezii* using methanesulfonic acid

---

## ORIGINALITY REPORT

---

10%

SIMILARITY INDEX

%

INTERNET SOURCES

10%

PUBLICATIONS

%

STUDENT PAPERS

---

## PRIMARY SOURCES

---

- 1 Hao Chen, Hui Wang, Zhaoyang Chen, Huicong Zhao, Limin Geng, Nan Gao, Chengshan Yi, Hongming Xu. "Research progress on the spray, combustion and emission of polyoxymethylene dimethyl ethers as a diesel blend fuel: A review", *Fuel*, 2022  
Publication 1%

---
- 2 Gwi-Taek Jeong. "Production of Sugars and Levulinic Acid from Marine Biomass *Gelidium amansii*", *Applied Biochemistry and Biotechnology*, 10/16/2009  
Publication 1%

---
- 3 Hairui Ji, Cuihua Dong, Guihua Yang, Zhiqiang Pang. "Production of levulinic acid from lignocellulosic biomass with a recyclable aromatic acid and its kinetic study", *BioResources*, 2018  
Publication 1%

---

4

Berna Nis, Burcak Kaya Ozsel. "Efficient direct conversion of lignocellulosic biomass into biobased platform chemicals in ionic liquid-water medium", *Renewable Energy*, 2021

Publication

1 %

5

Deepthi Hebbale, T.V. Ramachandra. "Third-generation bioethanol: status, scope, and challenges", *Elsevier BV*, 2022

Publication

<1 %

6

Olivia Paniz Fleig, Emília Savioli Lopes, Elmer Ccopa Rivera, Rubens Maciel Filho, Laura Plazas Tovar. "Concept of rice husk biorefining for levulinic acid production integrating three steps: Multi-response optimization, new perceptions and limitations", *Process Biochemistry*, 2018

Publication

<1 %

7

Adenilson Renato Rudke, Cristiano José de Andrade, Sandra Regina Salvador Ferreira. "Kappaphycus alvarezii macroalgae: An unexplored and valuable biomass for green biorefinery conversion", *Trends in Food Science & Technology*, 2020

Publication

<1 %

8

Jian Zhang, Xuanjun Wang, Zhiyong Huang, Qilong Han, Shuyan Li, Hui Liu. " Preparation and reaction dynamics on biodiesel made

<1 %

from seed oil and methanol ", Journal of Renewable and Sustainable Energy, 2013

Publication

---

9

Kyeong Eop Kang, Gwi-Taek Jeong, Don-Hee Park. "Rapeseed-straw enzymatic digestibility enhancement by sodium hydroxide treatment under ultrasound irradiation", Bioprocess and Biosystems Engineering, 2012

Publication

---

<1 %

10

Sang-Hyoun Kim, Ackmez Mudhoo, Arivalagan Pugazhendhi, Rijuta Ganesh Saratale et al. "A perspective on galactose-based fermentative hydrogen production from macroalgal biomass: Trends and opportunities", Bioresource Technology, 2019

Publication

---

<1 %

11

Bryan R. Moser. "Biodiesel production, properties, and feedstocks", In Vitro Cellular & Developmental Biology - Plant, 03/25/2009

Publication

---

<1 %

12

N. Sh. El-Gendy, S. F. Deriase, D. I. Osman. "The Optimization of Bio-diesel Production from Waste Frying Oil Using Response Surface Methodology and the Investigation of Correlations for Changes in Basic Properties of Bio-petro-diesel Blends", Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2014

Publication

<1 %

---

13 Wenbing Chen, Hanwen Hu, Qinjie Cai, Suping Zhang. "Synergistic Effects of Furfural and Sulfuric Acid on the Decomposition of Levulinic Acid", *Energy & Fuels*, 2020

Publication

<1 %

---

14 Collin Rudolf Nobbs Gereniu, Periaswamy Sivagnanam Saravana, Adane Tilahun Getachew, Byung-Soo Chun. "Characteristics of functional materials recovered from Solomon Islands red seaweed (*Kappaphycus alvarezii*) using pressurized hot water extraction", *Journal of Applied Phycology*, 2017

Publication

<1 %

---

15 Maricelly Martínez Aguilar, Xavier Duret, Thierry Ghislain, Doan P. Minh, Ange Nzihou, Jean-Michel Lavoie. "A simple process for the production of fuel additives using residual lignocellulosic biomass", *Fuel*, 2020

Publication

<1 %

---

16 Subhabrata Paul, Rita Kundu. "Antiproliferative activity of methanolic extracts from two green algae, *Enteromorpha intestinalis* and *Rizoclonium riparium* on HeLa cells", *DARU Journal of Pharmaceutical Sciences*, 2013

Publication

<1 %

---

17

Luciane C Mendes, Hilary C de Menezes, M Aparecida, A.P da Silva. "Optimization of the roasting of robusta coffee (*C. canephora* conillon) using acceptability tests and RSM", *Food Quality and Preference*, 2001

Publication

&lt;1 %

18

Pablo G. del Río, Joana S. Gomes-Dias, Cristina M.R. Rocha, Aloia Romaní, Gil Garrote, Lucília Domingues. "Recent trends on seaweed fractionation for liquid biofuels production", *Bioresource Technology*, 2020

Publication

&lt;1 %

19

Sandra Helena da Cruz, Bruce S. Dien, Nancy N. Nichols, Badal C. Saha, Michael A. Cotta. "Hydrothermal pretreatment of sugarcane bagasse using response surface methodology improves digestibility and ethanol production by SSF", *Journal of Industrial Microbiology & Biotechnology*, 2011

Publication

&lt;1 %

20

X. Zhang, W. Huang. "Optimization of the Transesterification Reaction Using Response Surface Methodology from Rapeseed Oil", *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 2011

Publication

&lt;1 %

21

Liu, Xiang, Shushuang Li, Yongmei Liu, and Yong Cao. "Formic acid: A versatile renewable

&lt;1 %



reagent for green and sustainable chemical synthesis", Chinese Journal of Catalysis, 2015.

Publication

---

22

Rajiv Chandra Rajak, Samuel Jacob, Beom Soo Kim. "A holistic zero waste biorefinery approach for macroalgal biomass utilization: A review", Science of The Total Environment, 2020

Publication

---

23

Dibyendu Mondal, Kamalesh Prasad. " : A Potential Sustainable Resource for Fertilizers and Fuels ", Wiley, 2017

Publication

---

24

Jeong Ah Kim, Sun Bok Lee. "Production of 3,6-anhydro-D-galactose from  $\kappa$ -carrageenan using acid catalysts", Biotechnology and Bioprocess Engineering, 2016

Publication

---

25

Niyam Dave, Raja Selvaraj, Thivaharan Varadavenkatesan, Ramesh Vinayagam. "A critical review on production of bioethanol from macroalgal biomass", Algal Research, 2019

Publication

---

26

Yuan Yuan, Duncan J. Macquarrie. " Microwave Assisted Acid Hydrolysis of Brown Seaweed for Bioethanol Production and

<1 %

<1 %

<1 %

<1 %

<1 %

Characterization of Alga Residue ", ACS  
Sustainable Chemistry & Engineering, 2015

Publication

---

27

Bassam Alkotaini, Hyunseok Koo, Beom Soo Kim. "Production of polyhydroxyalkanoates by batch and fed-batch cultivations of *Bacillus megaterium* from acid-treated red algae", Korean Journal of Chemical Engineering, 2016

Publication

---

28

Hongxin Fu, Jialei Hu, Xiaolong Guo, Jun Feng, Yanan Zhang, Jufang Wang. " High-Selectivity Butyric Acid Production from Hydrolysate by ", Industrial & Engineering Chemistry Research, 2020

Publication

---

29

Inn Shi Tan, Keat Teong Lee. "Comparison of different process strategies for bioethanol production from *Eucheuma cottonii* : An economic study", Bioresource Technology, 2016

Publication

---

30

J. Jayaprabakar, S.S. Dawn, A. Ranjan, P. Priyadharsini, R.J. George, S. Sadaf, C. Rajeswara Rajha. "Process optimization for biodiesel production from sheep skin and its performance, emission and combustion characterization in CI engine", Energy, 2019

Publication

---

<1 %

<1 %

<1 %

<1 %

31

Kaemwich Jantama. "Eliminating side products and increasing succinate yields in engineered strains of *Escherichia coli* C", *Biotechnology and Bioengineering*, 12/01/2008

Publication

---

<1 %

32

Kelloway, Adam, and Prodromos Daoutidis. "Process Synthesis of Biorefineries: Optimization of Biomass Conversion to Fuels and Chemicals", *Industrial & Engineering Chemistry Research*, 2013.

Publication

---

<1 %

33

Laura G. Covinich, Nicolás M. Clauser, Fernando E. Felissia, María E. Vallejos, María C. Area. "The challenge of converting biomass polysaccharides into levulinic acid through heterogeneous catalytic processes", *Biofuels, Bioproducts and Biorefining*, 2019

Publication

---

<1 %

34

Leichang Cao, Iris K.M. Yu, Dong-Wan Cho, Di Wang, Daniel C.W. Tsang, Shicheng Zhang, Shiming Ding, Linling Wang, Yong Sik Ok. "Microwave-assisted low-temperature hydrothermal treatment of red seaweed (*Gracilaria lemaneiformis*) for production of levulinic acid and algae hydrochar", *Bioresource Technology*, 2019

Publication

---

<1 %

35

Matheus O. de Souza, Rafael Garrett, Marcelo M. Pereira, Leandro S. M. Miranda. " Use of Biomass for the Production of Carbohydrate Isopropylidene-Ketal-Based Biocrude ", Energy & Fuels, 2017

Publication

&lt;1 %

36

Michael Y. Roleda, Zae-Zae A. Aguinaldo, Bea A. Crisostomo, Lourie Ann R. Hinaloc et al. "Discovery of novel haplotypes from wild populations of Kappaphycus (Gigartinales, Rhodophyta) in the Philippines", ALGAE, 2021

Publication

&lt;1 %

37

Ou, Chunyan, Song Chen, Yonghai Liu, Jiangjuan Shao, Sidong Li, Tingming Fu, Wenling Fan, Hui Zheng, Qin Lu, and Xiaolin Bi. "Study on the thermal degradation kinetics and pyrolysis characteristics of chitosan-Zn complex", Journal of Analytical and Applied Pyrolysis, 2016.

Publication

&lt;1 %

38

Retno Ringgani, Muhammad Mufti Azis, Rochmadi, Arief Budiman. "Kinetic Study of Levulinic Acid from Spirulina platensis Residue", Applied Biochemistry and Biotechnology, 2022

Publication

&lt;1 %

39

Sunil S. Joshi, Amit D. Zodge, Kiran V. Pandare, Bhaskar D. Kulkarni. "Efficient Conversion of

&lt;1 %

Cellulose to Levulinic Acid by Hydrothermal Treatment Using Zirconium Dioxide as a Recyclable Solid Acid Catalyst", Industrial & Engineering Chemistry Research, 2014

Publication

---

40

Vivek Kumar, Anjali Singh, Madhu Bala Tyagi, Ashok Kumar. "Chapter 32 Microbial Community Composition and Functions Through Metagenomics", Springer Science and Business Media LLC, 2017

Publication

---

<1 %

41

Deepthi Hebbale, T. V. Ramachandra. "Optimal sugar release from macroalgal feedstock with dilute acid pretreatment and enzymatic hydrolysis", Biomass Conversion and Biorefinery, 2021

Publication

---

<1 %

42

Frederic Delbecq, Yantao Wang, Anitha Muralidhara, Karim El Ouardi, Guy Marlair, Christophe Len. "Hydrolysis of Hemicellulose and Derivatives—A Review of Recent Advances in the Production of Furfural", Frontiers in Chemistry, 2018

Publication

---

<1 %

43

George Meredite Cunha de Castro, Norma Maria Barros Benevides, Maulori Curié Cabral, Rafael De Souza Miranda et al. "**Optimized acid hydrolysis of the polysaccharides**

<1 %

from the seaweed *Solieria filiformis*  
(Kützing) P.W. Gabrielson for bioethanol  
production", *Acta Scientiarum. Biological  
Sciences*, 2017

Publication

---

44

Javier Remón, Tianzong Li, Christopher J.  
Chuck, Avtar S. Matharu, James H. Clark.  
"Toward Renewable-Based, Food-  
Applicable Prebiotics from Biomass: A  
One-Step, Additive-Free, Microwave-  
Assisted Hydrothermal Process for the  
Production of High Purity Xylo-  
oligosaccharides from Beech Wood  
Hemicellulose", *ACS Sustainable  
Chemistry & Engineering*, 2019

Publication

---

<1%

45

Nicola Di Fidio, Claudia Antonetti, Anna  
Maria Raspolli Galletti. "Microwave-  
assisted cascade exploitation of giant reed  
(*Arundo donax* L.) to xylose and levulinic  
acid catalysed by ferric chloride",  
*Bioresource Technology*, 2019

Publication

---

<1%

Exclude quotes On

Exclude matches Off

Exclude bibliography On