RESEARCH REPORT

Exploration and Utilization of Indonesian Seaweed as Producer of Levulinic Acid Compound: An Effort to Develop A Marine Natural Resource-Based Industry

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**RESEARCH AND PUBLIC SERVICE INSTITUTE
JENDERAL SOEDIRMAN UNIVERSITY
PURWOKERTO**

2021

RINGKASAN

Indonesia is the biggest archipelago country in the world. It has about 95,186 km of coastal line and 17,504 islands, and also has huge potential of seaweed diversity and biomass. The high diversity and biomass of seaweed in Indonesian waters should be able to be the initial capital for Indonesia's economic growth and support national industry. Unfortunately, this high diversity is not coherent by its use by the community. Until now, only a few species of seaweed have been utilized and cultivated by the people of Indonesia. One of the causes of the lack of utilization of Indonesian seaweed is due to the lack of information on seaweed potential utilization. In this study we try to investigate the potential utilization of seaweed for producing levulinic acid compound. Levulinic acid (LA) is one of the top bio-based platform molecules that can be converted into many valuable chemicals which are needed and applied in industry such as in fuel additives, fragrances, solvents, pharmaceuticals, and plasticizers. It can be produced by acid catalysis from renewable resources, such as sugars, lignocellulosic biomass and waste materials. Research attention is being paid to explore new and potent natural resource for producing levulinic acid compound. Marine provides many potential natural resource candidate for producing levulinic acid compound. Amongst marine organisms, seaweed has been considered as an important source of polysaccharide and therefore has promoted much research on extracting seaweed for producing levulinic acid compound. Seaweed also can be a potential candidates due to their abundance and environmentally benign nature.

Production levulinic acid compound from Indonesian seaweed haven't conducted yet, hence it has huge potential output. There are only few studies on these areas which have been done. The newest study of production of levulinic acid compound from seaweed is now conducted by Laboratory of Bioenergy Engineering, Pukyong National University, South Korea. This laboratory published five research papers about levulinic acid production from seaweed in Q1 Scopus indexed international journal (Jeong et.al, 2015; Lee et al, 2015; Kim et. al, 2016; Park et.al 2018). Hence we would like to collaborate with this laboratory to achieve the targeted finding. Also Our targeted journal are Bioresource Technology, Elsevier (Q1 Scopus) or Bioresource Technology Report, Elsevier (Q1 Scopus) Journal of Applied Phycology (Q1 Scopus) and Sustainability (Q1 Scopus,).

This research is part of a series of studies on the exploration and utilization of Indonesian seaweed to support marine natural resource-based industry. We have been producing 19 international publications in reputable journal indexed SCOPUS (Q1 and Q2) published by Springer and Elsevier, 11 publications in an international seminar and 1 book chapter. The Scopus H index of Chief Researcher is 6, resulted from her publications during the 2010-2018 period. The recognition of the expertise of the chief researcher in the field of seaweed biotechnology was also manifested in various invitations as invited speakers and visiting researchers from various national and international institutions, as well as awards at both national and international levels.

Kata kunci maksimal 5 kata

Seaweed; Indonesian; Levulinic Acid; Industry

A. JUDUL PENELITIAN

Exploration and Utilization of Indonesian Seaweed as Producer of Levulinic Acid Compound: An Effort to Develop A Marine Natural Resource-Based Industry

B. LATAR BELAKANG

Research background

Indonesia has a high diversity and biomass of seaweed because Indonesia is the largest archipelago in the world which has an exclusive economic zone (EEZ) area of 2.7 million square kilometers, has a coastline length of 95,186 kilometers and 17,504 islands. In the Boos expedition (1928) 782 types of seaweed were found consisting of 452 red seaweed, 179 green seaweed and 134 brown seaweed. While on the Snelllius expedition (1984) 1750 species of seaweed were found from several regions in Indonesia. Based on the 2018 report by The State of World Fisheries and Aquaculture, Indonesia is the second largest seaweed producing country in the world with a percentage of 38.7% in 2016 [1].

Top 7 seaweed producer provinces in Indonesia are including Aceh, Lampung, West Java, Central Java, East Java, South East Sulawesi, and South Sulawesi. However, this high diversity and production is not corresponding by its utilization by the community. Despite being the second largest seaweed producer in the world, unfortunately this seaweed production still couldn't give significant contribution to community and national economic growth. Until now, only a few types of seaweed have been used and cultivated by the people of Indonesia. One of the causes of the lack of utilization of Indonesian seaweed is due to the lack of information on diversity and the potential utilization of Indonesian seaweed. This problem induces us to conduct this research. During 2010-2018 we conducted research covering the diversity of seaweed and the use of seaweed in order to support community welfare. Seaweed is a degradable raw material which rich in polysaccharide and can be extracted for levulinic acid compound. Levulinic acid (LA) is considered as one of the twelve "Top Value Added Chemicals from Biomass" reported by DOE/NREL, serving as a platform chemical for the synthesis of various commodities such as plasticizers, polymers, pharmaceutical products, herbicides, and fuel additives [2,3].

Aims of the Research

The aim of this study is to explore and utilize Indonesian seaweed for producing levulinic acid compound. We hope the result of this study can increase the economic value of Indonesian seaweed and support community welfare.

Urgency

Our dependency on fossil fuel based for producing chemical building block become a greatest challenge in industry [4–9]. This compound is classified by the United States Department of Energy as one of the top-12 promising building blocks [10]. Unfortunately, there are many obstacle in levulinic acid's production in commercialization due to the high cost and resource sustainability [11]. To solve this problem, it is very urgent to investigate seaweed as an economically and sustainability viable approach to produce LA. Levulinic acid can be produced from seaweed polysaccharides by thermo-chemical reactions. The utilization of seaweed can be a good solution for the industrial-scale production sustainability. The utilization of Indonesian seaweed for producing this compound may increase its economic value and contribute to increase coastal community welfare.

C. **HASIL PELAKSANAAN PENELITIAN**

This research is part of a series of studies on the exploration and utilization of Indonesian seaweed to support marine natural resource-based industry. In the previous studies we have been focusing on bioethanol production from seaweed and seaweed waste. From our previous studies on seaweed bioethanol, we have published 19 international publications in reputable journal indexed SCOPUS (Q1 and Q2) published by Springer and Elsevier, 11 publications in an international seminar and 1 book chapter

Indonesia is one of the main producers of *Kappahycus* species [1], [2]. Some previous study showed *K. alvarezii* can be hydrolyzed to produce ethanol [3]–[5]Based on our previous study on seaweed bioethanol, we found that we can also produce high value of platform chemical such as HMF, levulinic acid and formic acid. In the bioethanol fermentation from seaweed, we found the main products of sugar degradation are hydroxymethylfurfural (HMF) and levulinic acid. HMF is a by-product from hexose such as glucose and fructose [6], [7]. They, in turn, can be degraded further into levulinic acid and formic acid These three compounds can be used in many industries including the pharmaceutical, food, polymer/plastic, resin, textile, pesticides, fuel/energy, and organic synthesis industries [8], [9]. In this study we focus on the exploration and utilization of seaweed to produce levulinic acid as the high value of platform chemical. Firstly, we explored and collected some carrageenophyte seaweed from different areas in Indonesia. Totally we collected 11 seaweed samples from different areas in Indonesia (Figure 1). We identified the seaweed species morphologically and genetically.

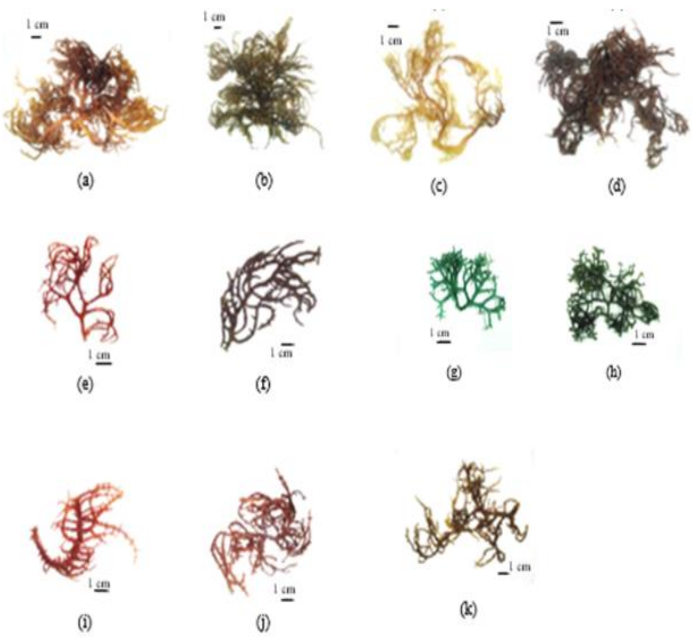

Figure 1. Specimen of *Kappaphycus* and *Eucheuma* samples collected in this study

The seaweed we collected were identified as *Kappaphycus alvarezii* (7 species), *Kappaphycus striatum* (2 species) and *Eucheuma denticulatum* (2 species). We analysed and compared the proximate content (carbohydrate, protein, lipid, and ash) of 11 seaweed species from different areas in Indonesia (Figure 1). A relatively high amount of total carbohydrate was detected in tissues collected in seaweed samples. The biochemical composition of our seaweed samples are comparable to previous study [6], [10], [11].

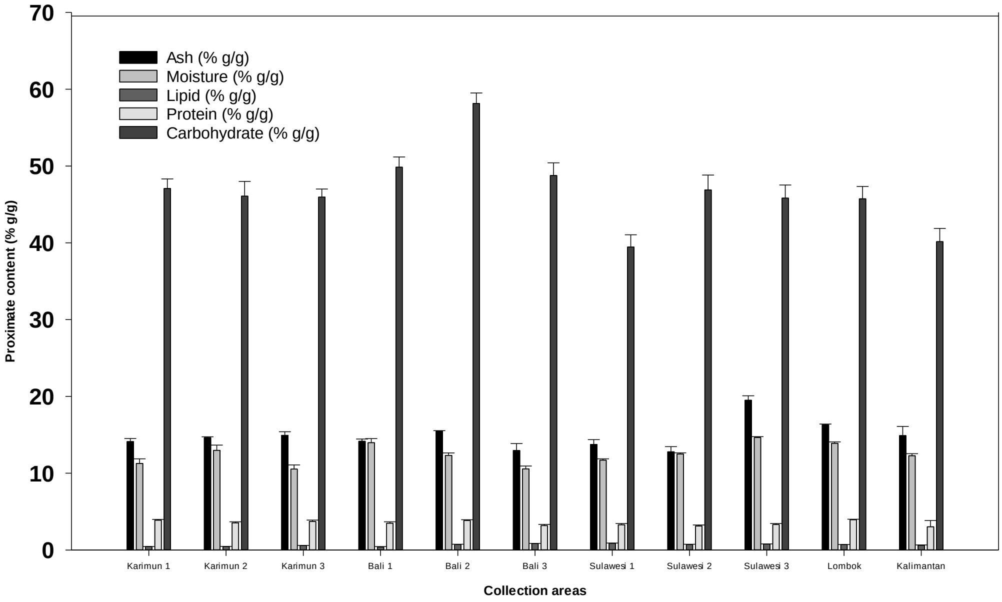

Figure 1. Proximate content of Kappaphycus and Eucheuma species from different areas in Indonesia

Furthermore we hydrolyzed the seaweed samples using 0.2 M sulfuric acid during 15 minutes and anaylsed their reducing sugar, galactose and glucose content (Figure 2). Relatively high amounts of reducing sugars, galactose, and glucose were detected in tissue hydrolysates from seaweed samples that we collected from differentareas in Indonesia.

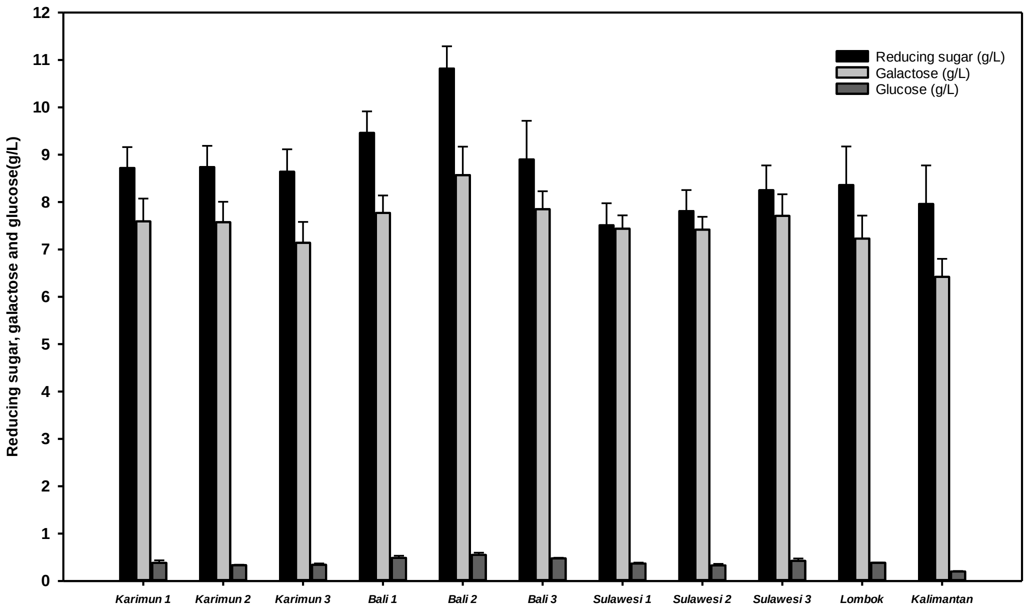

Figure 3. Reducing sugar, galactose and glucose t of *Kappaphycus* and *Eucheuma* species from different areas in Indonesia

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Kappaphycus alvarezii (also known as cottonii) from Bali was selected as the most potential resource for levulinic acid production based on its biochemical content, including its reducing sugar and monosugar. This species is one of the most abundant and easily cultured red seaweeds. The main components of carrageenan are D-galactose-4-sulfate and 3,6-anhydro-D-galactose-2-sulfate, which are potentially fermentable D-typed carbohydrates

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 (Figure 4).

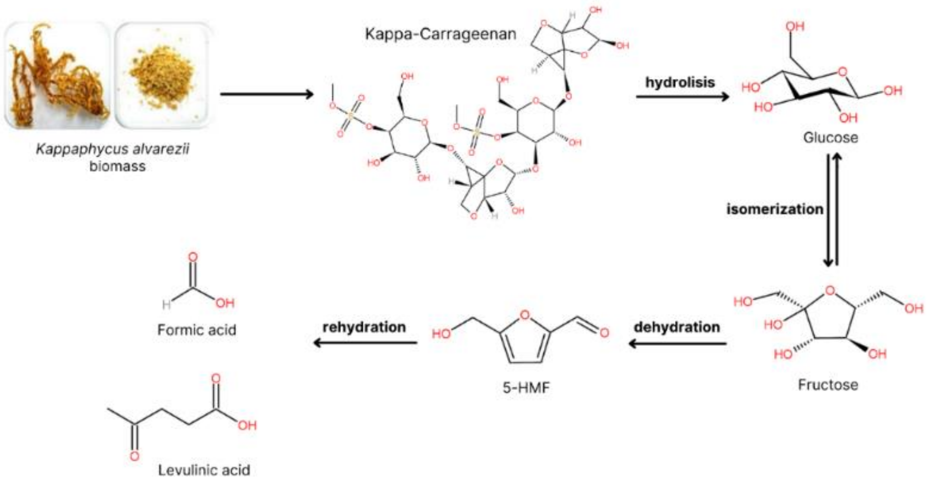

Figure 4. Pathways of levulinic acid production

The pathways of LA production from *K. alvarezii* consisted of four processe as shown in Figure 4. Firstly, the polysaccharide of KA is hydrolysed into glucose. The second process is the isomerization which convert glucose into fructose. The third process is the dehydration process which convert fructose to 5-HMF. The fourth process is the rehydration, which convert the 5-HMF into LA and FA. LA is a 4-oxopentanoic acid with reactive carbonyl and carboxyl groups while FA is a by-product of the rehydration of 5-HMF to LA.

Optimization of Levulinic Acid

The optimization was done by optimizing reaction temperature, catalyst concentration and reaction time in order to get optimum LA production. Hence, in the next step we focused on the optimization of levulinic acid at different rection temperature, catalyst concentration and reaction time and analyzed using response surface methodology (RSM) (Table 1)

Table 1. 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

We also observed the effects of some reaction factor including reaction temperature and time, catalyst concentration, and their interaction on levulinic acid yield as shown in Figure 5.

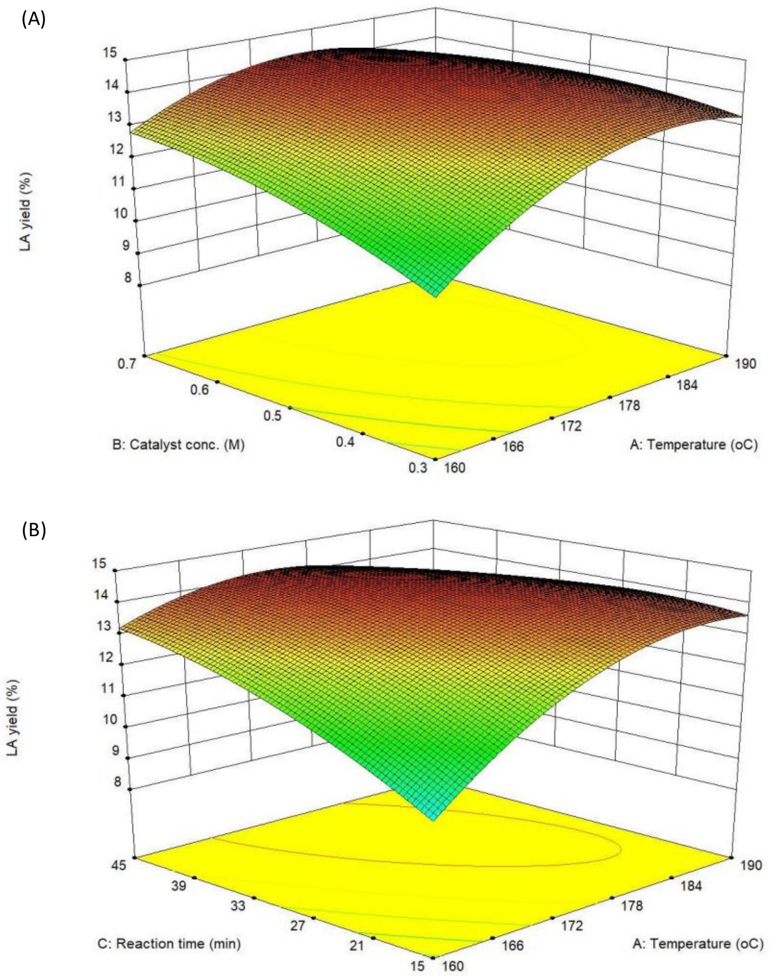

Figure 5. Effects of reaction temperature and time, catalyst concentration on levulinic acid yield

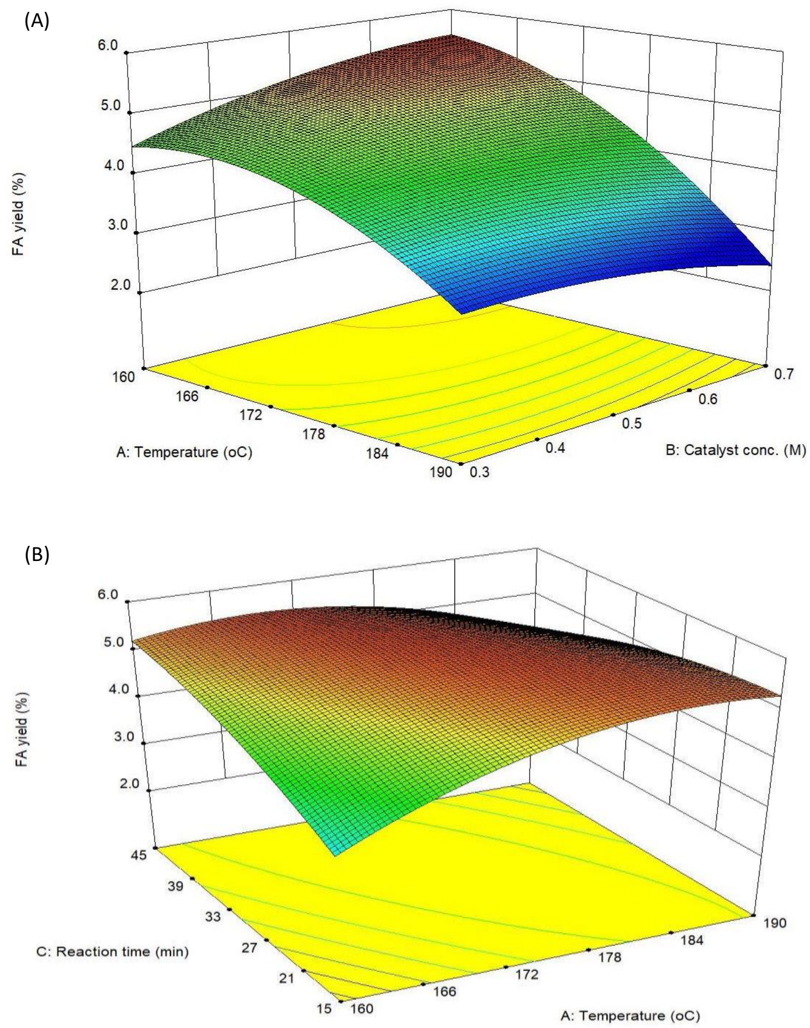

Figure 6. Effects of reaction temperature and time, catalyst concentration on formic acid yield

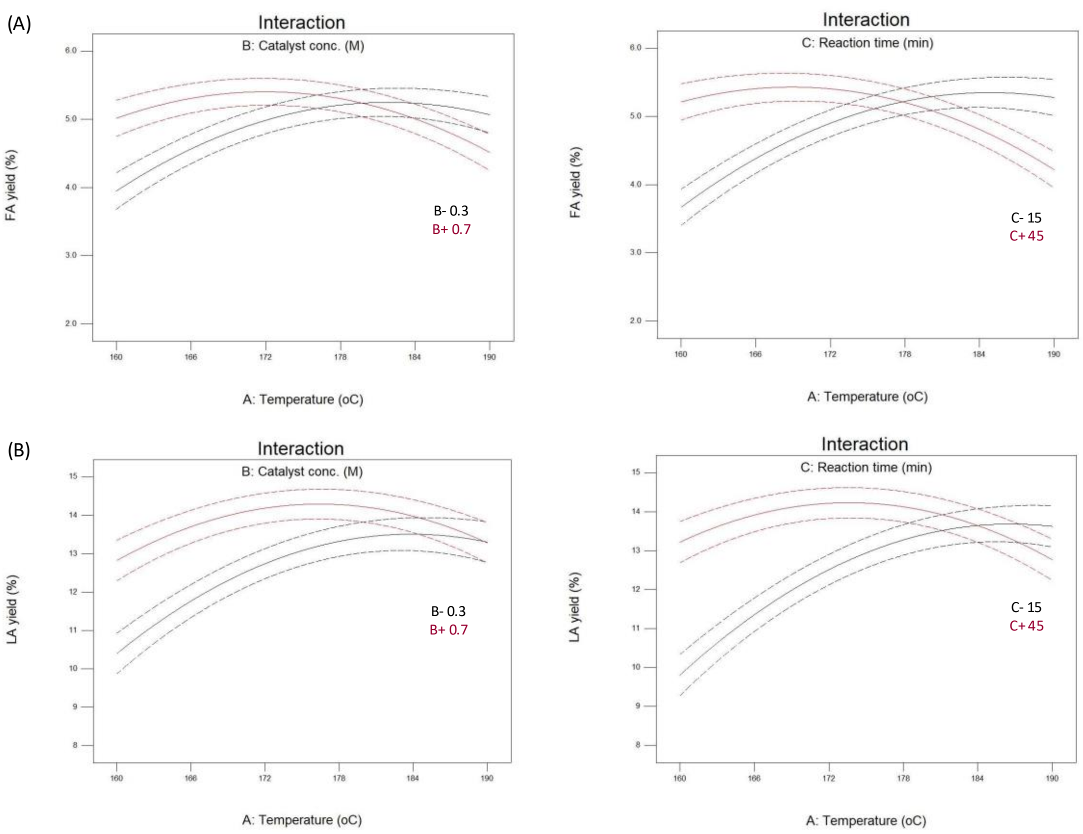

Figure 7. Effects of reaction temperature and time and catalyst concentration on formic (A) and levulinic acid (B) yields.

D. **STATUS LUARAN**: Tuliskan jenis, identitas dan status ketercapaian setiap luaran wajib dan luaran tambahan (jika ada) yang dijanjikan. Jenis luaran dapat berupa publikasi, perolehan kekayaan intelektual, hasil pengujian atau luaran lainnya yang telah dijanjikan pada proposal. Uraian status luaran harus didukung dengan bukti kemajuan ketercapaian luaran sesuai dengan luaran yang dijanjikan. Lengkapi isian jenis luaran yang dijanjikan serta mengunggah bukti dokumen ketercapaian luaran wajib dan luaran tambahan melalui Simlitabmas.

To date, there are 4 outputs have been produced from this research:

1. A publication in the 4th International Conference on Multidisciplinary Approaches for Sustainable Rural Development (ICMA SURE) 2021, entitled," Utilization of Indonesian Seaweed for Bioenergy and Platform Chemical Production. The international conference was held on 7-8 September 2021 (Attachment 1). **The status is published**
2. A copy right entitled, "Production of Levulinic Acid from Macroalgae" **is granted**. (Attachment 2)
3. A manuscript entitled, "The Production of Levulinic Acid from Red Macroalga *Kappaphycus alvarezii* using Methanesulfonic Acid" have been submitted to Bioresource Technology Report Journal (SCOPUS, Q1) and the current **status is**

published (Attachment 3 & 6)

4. A manuscript entitled "Levulinic Acid Production from Macroalgae: Production and Promising Potebtial in Industry have been submitted to Sustainability Journal (SCOPUS, Q1) and the current **status is published** (Attachment 4 & 5)

E. **PERAN MITRA:** Tuliskan realisasi kerjasama dan kontribusi Mitra baik *in-kind* maupun *in-cash* (untuk Penelitian Terapan, Penelitian Pengembangan, PTUPT, PPUPT serta KRUPT). Bukti pendukung realisasi kerjasama dan realisasi kontribusi mitra dilaporkan sesuai dengan kondisi yang sebenarnya. Bukti dokumen realisasi kerjasama dengan Mitra diunggah melalui Simlitabmas.

In this research collaboration we collaborate with the laboratory of Bioenergy Engineering Pukyong National University and Silla University, which contributed in providing laboratory equipment and facilities, conducting joint-publication and conducting joint-research.

F. **KENDALA PELAKSANAAN PENELITIAN**: Tuliskan kesulitan atau hambatan yang dihadapi selama melakukan penelitian dan mencapai luaran yang dijanjikan, termasuk penjelasan jika pelaksanaan penelitian dan luaran penelitian tidak sesuai dengan yang direncanakan atau dijanjikan.

The delay of research fund and the covid-19 pandemic condition effect and hinder the research.

G. **RENCANA TAHAPAN SELANJUTNYA:** Tuliskan dan uraikan rencana penelitian di tahun berikutnya berdasarkan indikator luaran yang telah dicapai, rencana realisasi luaran wajib yang dijanjikan dan tambahan (jika ada) di tahun berikutnya serta *roadmap* penelitian keseluruhan. Pada bagian ini diperbolehkan untuk melengkapi penjelasan dari setiap tahapan dalam metoda yang akan direncanakan termasuk jadwal berkaitan dengan strategi untuk mencapai luaran seperti yang telah dijanjikan dalam proposal. Jika diperlukan, penjelasan dapat juga dilengkapi dengan gambar, tabel, diagram, serta pustaka yang relevan. Jika laporan kemajuan merupakan laporan pelaksanaan tahun terakhir, pada bagian ini dapat dituliskan rencana penyelesaian target yang belum tercapai.

The further step in this study is to optimize the levulinic acid production from the potential candidate that we have screened based on their biochemical content. Hopefully at the end of this research we can finish the optimization.

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H. DAFTAR PUSTAKA: Penyusunan Daftar Pustaka berdasarkan sistem nomor sesuai dengan urutan pengutipan. Hanya pustaka yang disitasi pada laporan kemajuan yang dicantumkan dalam Daftar Pustaka.

[1] H. J. Bixler and H. Porse, "A decade of change in the seaweed hydrocolloids industry," *J. Appl. Phycol.*, vol. 23, no. 3, pp. 321–335, 2011, doi: 10.1007/s10811-010-9529-3.

[2] D. J. McHugh, "Worldwide distribution of commercial resources of seaweeds including

Gelidium,” *Hydrobiologia*, vol. 221, no. 1, pp. 19–29, 1991, doi: 10.1007/BF00028359.

[3] M. D. N. Meinita, J.-Y. Kang, G.-T. Jeong, H. M. Koo, S. M. Park, and Y.-K. Hong, “Bioethanol production from the acid hydrolysate of the carrageenophyte Kappaphycus alvarezii (cottonii),” *J. Appl. Phycol.*, vol. 24, no. 4, 2012, doi: 10.1007/s10811-011-9705-0.

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[6] M. D. N. Meinita, J.-Y. Kang, G.-T. Jeong, H. M. Koo, S. M. Park, and Y.-K. Hong, “Bioethanol production from the acid hydrolysate of the carrageenophyte Kappaphycus alvarezii (cottonii),” *J. Appl. Phycol.*, vol. 24, no. 4, pp. 857–862, Aug. 2011, doi: 10.1007/s10811-011-9705-0.

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[9] T. Werpy and G. Petersen, “Top Value Added Chemicals from Biomass Volume I,” *Us Nrel*, p. Medium: ED; Size: 76 pp. pages, 2004, doi: 10.2172/15008859.

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[11] F. Abd-rahim *et al.*, “Production of high yield sugars from Kappaphycus alvarezii using combined methods of chemical and enzymatic hydrolysis,” *Food Hydrocoll.*, 2014, doi: 10.1016/j.foodhyd.2014.05.017.

Attachment 1: Certificate of Speaker in International Conference (Conducted)

CERTIFICATE

661/UN23.18/PT.01.06/2021

This certificate is awarded to

Dr. Maria Dyah Nur Meinita, M.Sc.

With the title

Utilization of Indonesian Seaweed for Bioenergy and Platform Chemical Production

On International Conference

4 th International Conference on Multidisciplinary Approaches for Sustainable Rural Development 2021

"ICMA-SURE 2021"

"Actualization of Research Culture during The Midst of The Covid-19 Pandemic in Supporting Emancipated Learning"

Purwokerto - Indonesia, 7-8 September, 2021

Prof. Dr. Rifda Naufalin, S.P., M.Si.
Head of LPPM Jenderal Soedirman University

Dr. Norman Arie Prayoga, S.Pi., M. Si.
Chairperson of ICMA-SURE 2021

Attachment 2: Certificate of Copyright (Granted)

REPUBLIK INDONESIA
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SURAT PENCATATAN
CIPTAAN

Dalam rangka pelindungan ciptaan di bidang ilmu pengetahuan, seni dan sastra berdasarkan Undang-Undang Nomor 28 Tahun 2014 tentang Hak Cipta, dengan ini menerangkan:

Nomor dan tanggal permohonan	:	EC00202146964, 15 September 2021
Pencipta		
Nama	:	**Dr. Maria Dyah Nur Meinita, S.Pi., M.Sc., Dr. Amron, S.Pi., M.Si. dkk**
Alamat	:	Jl. Dr Soeparno, Komplek GOR Soesilo Soedarman, Karangwangkal, Kec. Purwokerto Utara, , Kabupaten Banyumas, JAWA TENGAH, 53122
Kewarganegaraan	:	Indonesia
Pemegang Hak Cipta		
Nama	:	**LEMBAGA PENELITIAN DAN PENGABDIAN KEPADA MASYARAKAT (LPPM), UNSOED**
Alamat	:	Jalan Dr. Soeparno, Grendeng,, Purwokerto, JAWA TENGAH, 53122
Kewarganegaraan	:	Indonesia
Jenis Ciptaan	:	**Karya Rekaman Video**
Judul Ciptaan	:	**Production Levulinic Acid From Macroalgae**
Tanggal dan tempat diumumkan untuk pertama kali di wilayah Indonesia atau di luar wilayah Indonesia	:	12 September 2021, di Purwokerto
Jangka waktu pelindungan	:	Berlaku selama 50 (lima puluh) tahun sejak Ciptaan tersebut pertama kali dilakukan Pengumuman.
Nomor pencatatan	:	000274799

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Dr. Freddy Harris, S.H., LL.M., ACCS.
NIP. 196611181994031001

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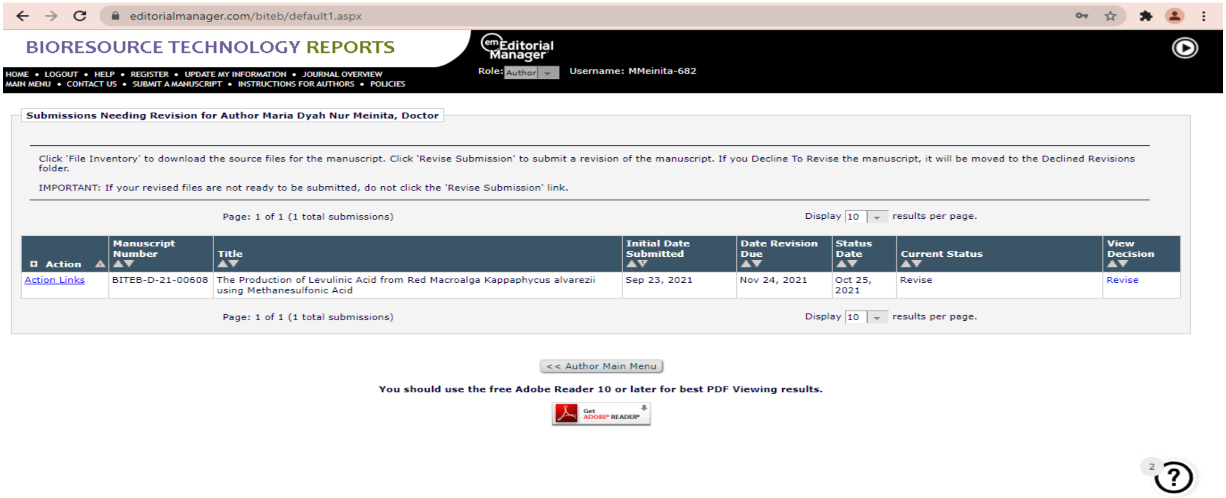
Attachment 3: Progress of manuscript in Bioresource Technology Reports, Scopus Q1 (Revise- Major revision)



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Submissions Needing Revision for Author Maria Dyah Nur Meinita, Doctor

Click 'File Inventory' to download the source files for the manuscript. Click 'Revise Submission' to submit a revision of the manuscript. If you Decline To Revise the manuscript, it will be moved to the Declined Revisions folder.

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Page: 1 of 1 (1 total submissions) Display 10 results per page.

Action	Manuscript Number	Title	Initial Date Submitted	Date Revision Due	Status Date	Current Status	View Decision
Action Links	BITEB-D-21-00608	The Production of Levulinic Acid from Red Macroalga Kappaphycus alvarezii using Methanesulfonic Acid	Sep 23, 2021	Nov 24, 2021	Oct 25, 2021	Revise	Revise

Page: 1 of 1 (1 total submissions) Display 10 results per page.

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Attachment 4: Progress of manuscript in Sustainability, Scopus Q1 (Revise-major revision)

Manuscript Status

Incomplete submissions (5) | **Under processing (5)** | Website Online (30) | Rejected / Withdrawn (60)

Manuscript ID	Journal	Section / Special Issue	Title	Status	Submission Date
sustainability-1446258	Sustainability	S: Resources and Sustainable Utilization	Levulinic Acid Production from Macroalgae: Production and Promising Potential in Industry	Pending major revisions	2021-10-18 05:36:45

Attachment 5: Published paper in Sustainability (Scopus, Q1)

sustainability

MDPI

Review

Levulinic Acid Production from Macroalgae: Production and Promising Potential in Industry

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Abstract: The development of macroalgal biorefinery products as an alternative source of renewable fuels is an opportunity to solve the dependence on fossil fuels. Macroalgae is a potential biomass that can be developed as a raw material for producing platform chemicals such as levulinic acid (LA). In the industrial sector, LA is among the top 12 biomass-derived feedstocks designated by the U.S. Department of Energy as a high-value chemical. Several studies have been conducted on the production of LA from terrestrial-based biomass, however, there is still limited information on its production from macroalgae. The advantages of macroalgae over terrestrial and other biomasses include high carbohydrate and biomass production, less cultivation cost, and low lignin content. Therefore, this study aims to investigate the potential and challenge of producing LA from macroalgae in the industrial sector and determine its advantages and disadvantages compared with terrestrial biomass in LA production. In this study, various literature sources were examined using the preferred reporting items for systematic reviews and meta-analyses (PRISMA) method to identify, screen, and analyze the data of the published paper. Despite its advantages, there are some challenges in making the production of levulinic acid from macroalgae feasible for development at the industrial scale. Some challenges such as sustainability of macroalgae, the efficiency of pretreatment, and hydrolysis technology are often encountered during the production of levulinic acid from macroalgae on an industrial scale.

Keywords: levulinic acid; macroalgae; platform chemical; biomass; polysaccharide

Attachment 5: Published paper in Bioresource Technology Report (Scopus, Q1)

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Case study

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

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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. By 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 pharmacologic, cosmeceutical, 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 macroalga known as one of the most attractive marine bio-based materials which can be developed to produce high value products (Li et al., 2019; Liu et al., 2016). *K. alvarezii* is which have a 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 macroalga 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 macroalga, but also can be produced from its residue waste obtained from carrageenan and agar extraction. During ethanol