

Bukti Korespondensi Publikasi Artikel
Catalytic Pyrolysis of Spirulina platensis Residue (SPR): Thermochemical
Behavior and Kinetics

Secara keseluruhan proses submit sampai publish ditampilkan dalam table berikut:

Tanggal	Korespondensi		Lampiran
	Author	Editor Jurnal	
19 April 2019	Submit pertama	Paper tidak mendapat respon	1
8 Desember 2019	Paper submit ulang	Balasan email dari editor	2
21 Maret 2020	Author memilih regular	Penawaran untuk Submit di regular atau special issue (email)	3
3 Pebruari 2020	Under review	Pemberitahuan dr editor untuk revisi. Masukan dr Reviewer 1, 2 dan 3	4
06 April 2020	Hasil review		5
23 April 2021	Revisi ke dua		6
4mei 2020	Revisi ke tiga	Notifikasi dari editor tentang accepted	7
11 Mei 2020	accepted	Email keputusan editor tentang penyampaian saran/rekomendasi dari reviewer beserta lampiran artikel hasil review.	8
12 Mei 2020	Pembayaran	Email dari editor memberikan notifikasi tentang deadline revisi	9
11 Juni 2020	Result of Line editing of the paper	Email konfirmasi pengiriman perbaikan artikel dan respon comment dari penulis	10
15 Juni 2020	Receipt of line editing Revise Manuscript	Email keputusan dari editor bahwa artikel sudah diterima	11
7 Juli 2020	Final Proof reading & copyright form	Email editor tentang penyampaian ucapan "Congratulation"	12
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21 Juli 2020.	Artikel Terpublikasi Online Pada Jurnal International Journal Of Technology, Vol 11 Edisi 3 Pada Tanggal 21 Juli 2020. https://ijtech.eng.ui.ac.id/article/view/2967	(Lampiran 14, Bukti Email Artikel Terpublikasi Online)	15

April 15, 2019

Editor

Dr. Mohammed Ali Berawi

International Journal of Technology

With the approval and on behalf of all authors, I submit our paper entitled “**Catalytic Pyrolysis of *Spirulina Platensis* Residue (SPR): Thermochemical Behaviour and Kinetics**”, which we would like to publish in *International Journal of Technology*. The authors declare that the research contained in this paper is original and is not currently under revision anywhere else.

If you feel that the manuscript is appropriate for your journal, we suggest the following reviewers:

1. Prof. Hadiyanto; **hadiyanto@live.undip.ac.id**
2. Dr. Nelson Saksono; **nelson@che.ui.ac.id**
3. Dr. Arif Hidayat: **ariffhid@gmail.com**

Please address all correspondence concerning this manuscript to me at **abudiman.ugm@gmail.com**.

The authors of this paper really hope you find it suitable for publication in *International Journal of Technology*.

Thank you for your consideration of this manuscript.

Yours sincerely,



Arief Budiman

Professor,

Chemical Engineering Department,

Gadjah Mada University, Jl. Grafika 2, Yogyakarta 55284, Indonesia

Phone No: 62816-4262-111, Fax No: 62274-555320

Email: **abudiman@ugm.ac.id**

LAMPIRAN 1

SUBMIT, 19 APRIL 2019

The screenshot shows a Gmail interface with a search bar containing "IJTech". The email being viewed is titled "Fwd: [IJTech] Revision reminder for manuscript #CE-2967". The sender is Arief Budiman (abudiman@ugm.ac.id). The email content includes a forwarded message from IJTech with the following details:

- From: IJTech <info@ijtech.eng.ui.ac.id>
- Date: Jun, 12 Apr 2019 00:10
- Subject: [IJTech] Revision reminder for manuscript #CE-2007
- To: <abudiman@ugm.ac.id>

The main body of the email contains the following text:

International Journal of Technology

Revision Reminder

Ms ID #CE-2967
Title: CATALYTIC PYROLYSIS OF SPIRULINA PLATENSISRESIDUE (SPR): THERMOCHEMICAL BEHAVIOUR, KINETICS, YIELDS AND COMPOSITIONS
Author(s): Arief Budiman, Siti Jamilatun, Budhijanto budhijanto, Rochmadi rochmadi, Avido Yulestyan, Muhammad Aziz, Jun-ichiro Hayashi

Dear Prof. Arief Budiman:

This is a polite reminder that we recently requested a revision of your manuscript, which is now due on **19 Apr 2019**. If we do not receive your revision within that time, we will assume that you are not sending a revision and this constitutes your manuscript being inactivated.

If you need additional time to complete your revision, please informing us of the date you expect to submit it via email to ijtech@eng.ui.ac.id.

Please ignore this message if you have uploaded your revised manuscript on the website.

Yours sincerely,
Dr. Ngaman Susanto
ngaman@eng.ui.ac.id
Managing Editor
International Journal of Technology (IJTech)
p-ISSN: 2250-9914
e-ISSN: 2250-9910
<http://www.ijtech.eng.ui.ac.id>

IJTech is currently indexed in SCOPUS and Emerging Sources Citation Index (ESCI) Thomson Reuters

At the bottom of the email, there are buttons for "Balas" (Reply) and "Teruskan" (Forward).

LAMPIRAN 2

8 Desember 2019

The screenshot shows a Gmail interface on a Windows desktop. The browser address bar shows a search for 'IJTech' on a Gmail account. The email in focus is from 'Siti Jamilatun <sitijamilatun@che.uad.ac.id>' to the 'Managing Editor of IJTech'. The email body contains the following text:

PAPER SUBMIT Kotak Masuk x

To
Managing Editor of **IJTech**

Please update the progress paper entitled "CATALYTIC PYROLYSIS OF SPIRULINA PLATENSIS RESIDUE (SPR): THERMOCHEMICAL BEHAVIOUR AND KINETICS" which I have submitted since March 10, 2019.

Here I attach the proof of submitting the paper

Thank you

Regards
Siti Jamilatun
Chemical Engineering
Ahmad Dahlan University
Yogyakarta

An attached PDF file is visible with the title 'CATALYTIC PYROL...'. The Windows taskbar at the bottom shows the time as 11:31 on 28/06/2022 and the weather as 30°C Hujan ringan.

LAMPIRAN 3

21 Maret 2020

Penawaran untuk Submit di regular atau special issue

The screenshot shows a Gmail interface with the following elements:

- Browser Address Bar:** mail.google.com/mail/u/0/#search/IJTech/FMfcgxwHMPnFZnJNfcqbKnVxDXSRCWpm
- Gmail Header:** Search for "IJTech", "Aktif" status, and user profile "UNIVERSITAS AHMAD DAHLAN".
- Left Sidebar:** Navigation menu including "Email" (9,537), "Kotak Masuk", "Berbintang", "Ditunda", "Penting", "Terkirim", "Draf" (198), "Kategori", "Unwanted" (1), "Ciutkan", "Chat" (+), "Ruang" (+), and "Rapat".
- Selected Email:**
 - Sender:** International Journal of Technology (www.ijtech.eng.ui.ac.id)
 - Subject:** Article Processing Charge (APC) Confirmation for Manuscript #CE-2967
 - Body:**

Dear Prof. Arief Budiman,

Greetings from Jakarta!

This email is regarding a new policy about Article Processing Charge (APC) in International Journal of Technology (IJTech).

As you may find in [our website](#), all articles accepted for publication since January 1st, 2020 are subjected to Article Processing Charge (APC) of US\$ 550 (for regular publication) and US\$ 650 (for Special Edition publication). [Click here](#) for more detailed information.

Since some authors may not be aware about this new policy, please indicate whether you are **agree to this policy**, or **disagree and withdraw** your submitted manuscript entitled "CATALYTIC PYROLYSIS OF SPIRULINA PLATENSIS RESIDUE (SPR): THERMOCHEMICAL BEHAVIOUR AND KINETICS". Note that the APC is charged only after the manuscript is accepted for publication.

Please indicate your choice by clicking one of the following buttons:

Agree and continue the process:
[Continue](#)

If the above link does not work, copy-paste this link in your browser to continue:
<http://ijtech.eng.ui.ac.id/dashboard/isAgreeAPC/a8a4fea756b59f0530964956479f3d67/1>

Disagree and withdraw:
[Withdraw](#)

If the above link does not work, copy-paste this link in your browser to withdraw:
<http://ijtech.eng.ui.ac.id/dashboard/isAgreeAPC/a8a4fea756b59f0530964956479f3d67/2>

We are sorry for the inconvenience that may appear due to this new policy and appreciate whatever decision you will take in response to this matter. We look forward to receiving your confirmation at your earliest convenience.

With kind regards,

LAMPIRAN 4

3 Pebruari 2020: Under review

The screenshot shows a Gmail interface on a Windows desktop. The browser address bar shows a search for 'IJTech'. The Gmail search bar also contains 'IJTech'. The left sidebar shows the 'Email' section with categories: Kotak Masuk (9,537), Berbintang, Ditunda, Pending, Terkirim, Draf (198), Kategori, Unwanted (1), and Ciutkan. The 'Chat' section lists several contacts. The 'Ruang' section shows a meeting titled 'Meeting Prodi Teknik KI...'. The main email content is as follows:

Re: PAPER SUBMIT_SITI JAMILATUN (CE-2967) Eksterna Kotak Masuk x

IJTech <ijtech@eng.ui.ac.id> kepada saya ▾
Sen, 3 Feb 2020 08.51

Dear Ms. Siti Jamilatun,

Thank you for your email to International Journal of Technology, On behalf of our Editor, allow me to reply to your queries as the following.

We are really sorry for the inconvenience that may arise.
Your paper is still under a review process and we always keep reminding the reviewer to review your paper.
We have also invited new reviewers to review your paper. For your information, although many invitations were delivered, unfortunately, we have no positive feedback yet.

You will be notified soon after the comments received.

Thanks for your understanding, if there's any other way that we can help, please let us know.

...
Kind regards,
Secretariat **IJTech**
International Journal of Technology (**IJTech**)
ISSN : 2086-9614
<http://www.ijtech.eng.ui.ac.id>

Siti Jamilatun <sitijamilatun@che.uad.ac.id> kepada IJTech ▾
Sen, 3 Feb 2020 18.51

Thank you for informing me.

...

Siti Jamilatun <sitijamilatun@che.uad.ac.id> kepada Arief ▾
Sab, 21 Mar 2020 16.19

At the bottom, there is a 'Rapat' section with 'Balas' and 'Teruskan' buttons. A document preview for 'R1-CE-2918-201...docx' is visible. The Windows taskbar at the bottom shows the search bar, taskbar icons, and system tray with weather information (30°C Hujan ringan) and time (11:39 28/06/2022).

List of Changes

Manuscript:

Catalytic Pyrolysis of Spirulina platensis Residue (SPR): Thermochemical Behaviour and Kinetics

Response and Revision made by Author(s)

Reviewer #1:

No	Comments	Revision/Changes
1	There is no strong argument why the authors chose silica/alumina catalyst in their work. The particular feature offered by the authors in the manuscript is catalysis aspect in the pyrolysis, but it seems that the consideration in catalyst selection is at little extent. Therefore, purpose of the research is not clearly defined	One suitable catalyst for upgrading the bio-oil is silica-alumina, which is widely used to support the production of petrochemicals, chemicals, and energy. High acidity (low Si/Al) is useful in the petroleum cracking in order to increase the oxidation of CO (Wang et al., 2019).
2	There should be variation of catalyst characteristics to allow correlation between the characteristics and the pyrolysis results. Analogous to this work, in catalytic plastic pyrolysis, some workers have succeeded to obtain effect of acidity and pore size of catalysts on the drop of activation energy in comparison with thermal pyrolysis. Catalyst of Al ₂ O ₃ .SiO ₂ is mostly used for hydrodeoxygenation and it is not relevant to the work proposed.	Tan (2018) reported that the catalytic fast pyrolysis on durian skin using silica-alumina catalyst (surface area of 877.07 m ² /g, average pore diameter of 24.03 Å, pore size of 1.7–170 nm, total pore volume of 0.53 cm ³ /g, and SiO ₂ /Al ₂ O ₃ of 5) can reduce O/C from 0.21 (without catalyst) to 0.03. Further investigation on the catalytic thermal decomposition of SPR is crucially demanded to accelerate the development of bio-oil production
4	References contain all authors referred in the manuscript	Oke

Reviewer #2:

No	Comments	Revision/Changes												
1	The paper deals with the effect of alumina catalyst on thermal decomposition behavior and its kinetic studies during pyrolysis reaction. The introduction is well organized and fits the scope.	oke												
2	The paper deals with the effect of alumina catalyst on thermal decomposition behavior and its kinetic studies during pyrolysis reaction. The introduction is well organized and fits the scope.	oke												
3	It is recommended to add stage division time in Table 1 to support the statement in text "It can be explained that the use of the catalyst can decrease the activation energy so that it can accelerate the reaction resulting in pyrolysis to be achieved shorter in the lower temperature range" It is suggested to use references to support statement of ... The peaks in the pyrolysis	<p>Table 1 Stages division upon catalytic and non-catalytic pyrolysis of SPR</p> <table border="1"> <thead> <tr> <th>Catalyst/SPR</th> <th>1:1</th> <th>1:2</th> <th>Without catalyst</th> </tr> </thead> <tbody> <tr> <td>Stage I, °C (drying)</td> <td>30-230</td> <td>30-230</td> <td>30-230</td> </tr> <tr> <td>Stage II, °C (pyrolysis)</td> <td>230-555</td> <td>230-565</td> <td>230-570</td> </tr> </tbody> </table>	Catalyst/SPR	1:1	1:2	Without catalyst	Stage I, °C (drying)	30-230	30-230	30-230	Stage II, °C (pyrolysis)	230-555	230-565	230-570
Catalyst/SPR	1:1	1:2	Without catalyst											
Stage I, °C (drying)	30-230	30-230	30-230											
Stage II, °C (pyrolysis)	230-555	230-565	230-570											

	<p>zone indicate the release of volatile matter, i.e., decomposition of proteins and carbohydrates occurring through the termination of O–O, N–O, C–N, N–H, N=N, C=N, C–C, C=C, O=H, C–O, O–H, C=O, and C–H bonds. Please explain or give examples of proposed new reaction pathways that support your statement on Ea decreases due to the catalyst during pyrolysis.</p>	<table border="1"> <tr> <td data-bbox="817 215 1008 277">Stage III, °C (gasification)</td> <td data-bbox="1008 215 1136 277">555–1000</td> <td data-bbox="1136 215 1264 277">565–1000</td> <td data-bbox="1264 215 1409 277">570–1000</td> </tr> <tr> <td data-bbox="817 277 1008 340">Pyrolysis time (Stage II), min</td> <td data-bbox="1008 277 1136 340">14.68</td> <td data-bbox="1136 277 1264 340">15.07</td> <td data-bbox="1264 277 1409 340">15.10</td> </tr> </table> <p>This phenomenon is the same with the study by De Wild et al. (2011), when the peak peaks in Zones 1 and 2, there is a breaking of the bonds of O–O, N–O, C–N, N–H, N=N, and C=N at the decomposition of proteins, then termination of C bonds C, C=C, and O=H bonds in cellulose decomposition, completion of C–C, C–O, O–H, C=O and C–H bonds in hemicellulose decomposition, and termination of C bonds C, C=O and C–O in lignin decomposition.</p>	Stage III, °C (gasification)	555–1000	565–1000	570–1000	Pyrolysis time (Stage II), min	14.68	15.07	15.10
Stage III, °C (gasification)	555–1000	565–1000	570–1000							
Pyrolysis time (Stage II), min	14.68	15.07	15.10							
4	The references mostly updated.	Oke								
5	This manuscript need minor revision before accepted for publication.	Oke. Have revised								

LAMPIRAN 5

06 APRIL 2020: HASIL REVIEW

The image displays three sequential screenshots of an email thread from IJTech Editor Decision. The first screenshot shows the initial decision: "Dear Prof. Arief Budiman, We have finished the review and made decision on your manuscript entitled [CATALYTIC PYROLYSIS OF SPIRULINA PLATENSIS RESIDUE (SPR): THERMOCHEMICAL BEHAVIOUR AND KINETICS] which was submitted to International Journal of Technology. We have decided that your manuscript **Need to be Revised**." The second screenshot shows the reviewer's comments and a table of scores:

Originality	2 (fair)
Technical	3 (average)
Methodology	2 (fair)
Readability	4 (above average)
Practicability	2 (fair)
Organization	3 (average)
Importance	3 (average)

 The third screenshot shows the editor's response: "The manuscript need minor revision before accepted for publication. Please login into application <http://ijtech.eng.ui.ac.id/login> for more detail. You must respond to this revise and resubmit request before 13 Apr 2020, after which point we will presume that you have withdrawn your submission from International Journal of Technology (IJTech) Online System."

List of Changes

Manuscript:

Catalytic Pyrolysis of *Spirulina platensis* Residue (SPR): Thermochemical Behaviour and Kinetics

Response and Revision made by Author(s)

Reviewer #1:

No	Comments	Revision/Changes
1	The statement "High acidity (low Si/Al) is useful in the petroleum cracking in order to increase the oxidation of CO (Wang et al., 2019)" is not clear to explain the relevance of oxidation of CO with the present work which investigated kinetics, not oxidation of CO.	One suitable catalyst for upgrading the bio-oil is silica-alumina, which is widely used to support the production of petrochemicals, chemicals, and energy. The Al ₂ O ₃ can promote the formation of aromatic compounds, such as polycyclic aromatic hydrocarbons. SiO ₂ with low acidity can also help remove oxygenated and inhibit the formation of coke on the catalyst because of its porosity medium (Aho et al., 2013; Busca, 2019; Jamilatun et al., 2019c; Wang et al., 2019).
2	The statement "Tan (2018) reported that the fast catalytic pyrolysis on durian skin using silica-alumina catalyst (surface area of 877.07 m ² /g, the average pore diameter of 24.03 Å, the pore size of 1.7–170 nm, total pore volume of 0.53 cm ³ /g, and SiO ₂ /Al ₂ O ₃ of 5) could reduce O/C from 0.21 (without catalyst) to 0.03" does not reflect the present work which investigated kinetics, not O/C ratio.	Jamilatun (2019c) reported that the catalytic pyrolysis on SPR using silica-alumina catalyst (surface area of 240.553 m ² /g, the pore size of 3.3 nm, the average pore volume of 0.199 cm ³ /g, and SiO ₂ /Al ₂ O ₃ of 1.71) could reduce oxygenated compounds 37.47 (without catalyst) to 12.82 % (a decrease by 65.80 %). Further investigation on the catalytic thermal decomposition of SPR is crucially demanded to accelerate the development of bio-oil production (Jamilatun et al., 2019b; Jamilatun et al., 2019c; Sunarno et al., 2018; Wang et al., 2019). Its kinetic analysis and thermal decomposition mechanisms to obtain activation energy data (A) and reaction kinetics constant (k) from catalytic pyrolysis are the critical tools for designing reactor developments for industrial-scale bio-oil production (Li et al., 2013).
3	Referring to the statement, "At the same time, Balasundram (2017) has conducted catalytic pyrolysis of coconut and rice husk with a nickel-cerium/alumina catalyst", it seems not closely related to the present work.	Have revised. On the other hand, research on catalytic pyrolysis using TGA method of microalgae raw materials is very few. It is difficult to find papers that discuss thermochemically

		and the kinetics of reactions with TGA using alumina-silica catalysts.
4	Therefore, authors should clearly state the objective of the research, such that what is written in the Introduction relevant to the present work and clearly show the novelty of the present work.	<p>Novelty.</p> <p>Jamilatun (2019c) reported that the catalytic pyrolysis on SPR using silica-alumina catalyst (surface area of 240.553 m²/g, the pore size of 3.3 nm, the average pore volume of 0.199 cm³/g, and SiO₂/Al₂O₃ of 1.71) could reduce oxygenated compounds 37.47 (without catalyst) to 12.82 % (a decrease by 65.80 %). Further investigation on the catalytic thermal decomposition of SPR is crucially demanded to accelerate the development of bio-oil production (Jamilatun et al., 2019b; Jamilatun et al., 2019c; Sunarno et al., 2018). Its kinetic analysis and thermal decomposition mechanisms to obtain activation energy data (A) and reaction kinetics constant (k) from catalytic pyrolysis are the critical tools for designing reactor developments for industrial-scale bio-oil production (Li et al., 2013). On the other hand, research on catalytic pyrolysis using TGA method of microalgae raw materials is very few. Jamilatun (2017b) reported that analysis of thermal decomposition and pyrolysis reaction kinetics of SPR with TGA indicates that the activation energy (E_a) for the heating rate of 20oC / min for zones 1 and 2 is 41,102 KJ / mol and 0,0001240 KJ / mol. It is difficult to find papers that discuss thermochemically and the kinetics of reactions with TGA using alumina-silica catalysts. For this reason, research on the "Catalytic Pyrolysis of Spirulina platensis Residue (SPR): Thermochemical Behavior and Kinetics" needs to be developed.</p>
5	Statements "This paper discusses the characteristics of thermal decomposition using a silica-alumina (SiO ₂ /Al ₂ O ₃) catalyst, including the extent of the catalyst's effect on SPR weight reduction, as well as the heat release and heat requirement during the process" should	<p>Have revised</p> <p>This paper discusses the characteristics of thermal decomposition using a silica-alumina (SiO₂/Al₂O₃) catalyst, including the</p>

	revise because heat release and heat requirement were not evaluated	extent of the catalyst's effect on SPR weight reduction. This work uses TG and DTG curves to obtain the temperature range for Stage I (drying), Stage II (pyrolysis), and Stage III (gasification). The kinetic reaction was calculated through a one-step global non-isothermal model and solved with a least-squares fitting using MATLAB simulation.
6	The statement "Tan (2018) reported that the fast catalytic pyrolysis on durian skin using silica-alumina catalyst (surface area of 877.07 m ² /g, the average pore diameter of 24.03 Å, the pore size of 1.7–170 nm, total pore volume of 0.53 cm ³ /g, and SiO ₂ /Al ₂ O ₃ of 5) could reduce O/C from 0.21 (without catalyst) to 0.03" does not reflect the present work which investigated kinetics, not O/C ratio reduction.	Have revised. Jamilatun (2019c) reported that the catalytic pyrolysis on SPR using silica-alumina catalyst (surface area of 240.553 m ² /g, the pore size of 3.3 nm, the average pore volume of 0.199 cm ³ /g, and SiO ₂ /Al ₂ O ₃ of 1.71) could reduce oxygenated compounds 37.47 (without catalyst) to 12.82 % (a decrease by 65.80 %). Novelty research is in point 4 and 5
7	In abstract, the aims of the present work and conclusion for the ratio 1:2 should be added	Have revised The presence of catalyst was able to reduce Ea to the lowest value from 41.10 KJ/mol (without catalyst) to 40.77 KJ/mol (weight ratio 1:2) and 39.46 KJ/mol (weight ratio of 1:1) in Zone 1. However, the increase of catalyst amount was not in line with the increase of reaction rate velocity (k) and resulted in a reasonably low Arrhenius constant of 593.30, 406.31, and 266.37, respectively.

Reviewer #2:

No	Comments	Revision/Changes
1	Reviewer 2 accepts all explanations	No revisions

LAMPIRAN 6

23 APRIL 2021: REVISI KE 2

The image displays three sequential screenshots of an email from the IJTech Editor Decision, detailing the revision process for a manuscript. The email is addressed to Prof. Arif Budiman and concerns the manuscript titled "CATALYTIC PYROLYSIS OF SPIRULINA FLATENSIS RESIDUE (SPR): THERMOCHEMICAL BEHAVIOUR AND KINETICS".

First Screenshot (Top): Shows the initial decision and review details. The editor notes that the manuscript needs to be revised based on reviewer feedback. The reviewer's comments are summarized as follows:

- Reviewer (1) Introduction:** The statement "High acidity (low SiAl) is useful in the petroleum cracking in order to increase the oxidation of CO (Wang et al., 2018)" is not clear to explain the relevance of oxidation of CO with the present work which investigated kinetics, not oxidation of CO. 2. The statement "Tan (2018) reported that the catalytic fast pyrolysis on durian skin using silica-alumina catalyst (surface area of 877.07 m²/g, average pore diameter of 24.03 Å, pore size of 1.7–170 nm, total pore volume of 0.53 cm³/g, and SiO₂/Al₂O₃ of 5) can reduce C₁₀ from 0.21 (without catalyst) to 0.03" does not reflect the present work which investigated kinetics, not C₁₀ ratio. 3. Referring to the statement at the same time, Sibaenondra (2017) has conducted a catalytic pyrolysis of coconut and rice husk with a nickel-cobalt/alumina catalyst, it seems not closely related to the present work. 4. Therefore, authors should clearly state the objective of the research such that what are written in introduction relevant to the present work and clearly show the novelty of the present work. 5. Statements "This paper discusses the characteristics of thermal decomposition using a silica-alumina (SiO₂/Al₂O₃) catalyst, including the extent of the catalyst's effect on SPR weight reduction, as well as the heat release and heat requirement during the process" should be revised because heat release and heat requirement were not evaluated.

Second Screenshot (Middle): Shows the reviewer's evaluation of the manuscript. The scores are as follows:

Originality	3 (average)
Technical	4 (above average)
Methodology	4 (above average)
Readability	3 (average)
Practicability	3 (average)
Organization	3 (average)
Importance	2 (poor)

Additional Comment: In abstract, the aims of the present work and conclusion for the ratio 1:2 should be added.

Attachment File: -

Third Screenshot (Bottom): Shows the final decision and instructions for the next steps. The reviewer's final comments are:

- Reviewer (2) Introduction:** Acceptable
- Methodology:** Acceptable
- Results and Discussion:** Acceptable
- References:** Acceptable
- Other:** Acceptable

The editor provides the following instructions:

- Please login into application <http://ijtech.ums.ac.id/login> for more detail.
- You must respond to this revise and resubmit request before **30 Apr 2020**, after which point we will presume that you have withdrawn your submission from International Journal of Technology (IJTech) Online System.

The email concludes with a signature from Dr. Nyoman Suardana, Managing Editor of International Journal of Technology (IJTech), with contact information: nyoman@ums.ac.id and p-ISSN: 2086-9614.

LAMPIRAN 7

4 MEI 2020: REVISI KE 3

The image shows two screenshots of an email from the IJTech Editor Decision. The top screenshot shows the beginning of the email, and the bottom screenshot shows the end of the email, including a table of reviewer scores and a signature.

[IJTech] Editor Decision (Escorted) Kotak Masuk

IJTech -nonyan@ijtech.eng.ui.ac.id
kepada abudimari, saya, budhianto, rochmadi, arido_y, maziz, juchiro_hayashi

Sen, 4 Mei 2020 12:58

Decision Result - Revise

Dear **Prof. Arief Budiman**

We have finished the review and made decision on your manuscript entitled [**CATALYTIC PYROLYSIS OF SPIRULINA PLATENSIS RESIDUE (SPR): THERMOCHEMICAL BEHAVIOUR AND KINETICS**] which was submitted to International Journal of Technology.

We have decided that your manuscript **Need to be Revised**

We also send you the review result from the reviewers. Here is the detail review result:

Notes from Editor:
Please revise according to the reviewer's comment

Reviewer (1)

Introduction:
1. Statement " It is difficult to find papers that discuss thermochemically and the kinetics of reactions with TGA using alumina-silica catalysts" should be revised to "It has been nearly none of research work on thermochemistry and kinetics of catalytic pyrolysis reactions using TGA." 2. Statement "For this reason, research on the Catalytic Pyrolysis of Spirulina platensis Residue (SPR), Thermochemical Behavior and Kinetics" needs to be developed" should be revised to "For this reason, research on catalytic pyrolysis of Spirulina platensis residue (SPR) particularly related to pyrolysis thermochemical behavior and kinetics need to be

particularly related to pyrolysis thermochemical behavior and kinetics need to be developed".

Methodology:
no revision

Results and Discussion:
no revision

References:
no revision

Other:
The title should be revised to "Thermochemical Behaviour and Kinetics of Catalytic Pyrolysis of Spirulina platensis Residue (SPR)"

Originality	4 (above average)
Technical	3 (average)
Methodology	4 (above average)
Readability	4 (above average)
Practicability	3 (average)
Organization	4 (above average)
Importance	2 (fair)

Additional Comment:
none

Attachment File:
-

Please login into application <http://ijtech.eng.ui.ac.id/login> for more detail.

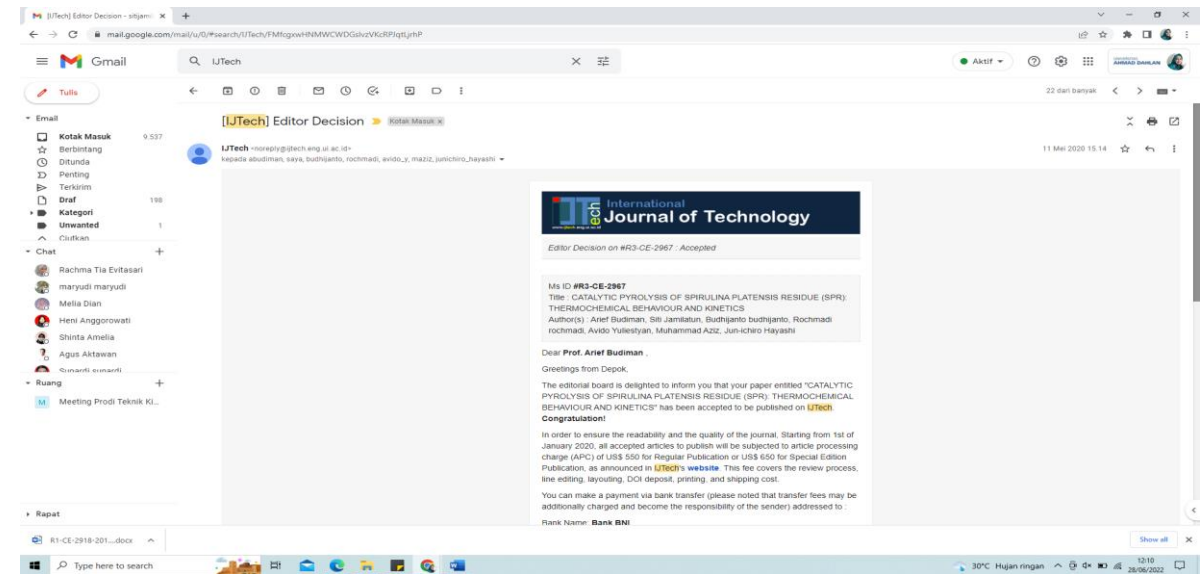
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Yours sincerely,
Dr. Nyoman Suwartha
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LAMPIRAN 8

11 MEI 2020: ACCEPTED



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Editor Decision on #R3-CE-2967 - Accepted

Ms ID #R3-CE-2967
Title: CATALYTIC PYROLYSIS OF SPIRULINA PLATENSIS RESIDUE (SPR): THERMO-CHEMICAL BEHAVIOUR AND KINETICS
Author(s): Arief Budiman, Siti Jamiatun, Budjanto, Rochmadi, Rochmadi, Awiyo Yulianyan, Muhammad Aziz, Jun-ichiro Hayashi

Dear **Prof. Arief Budiman**,

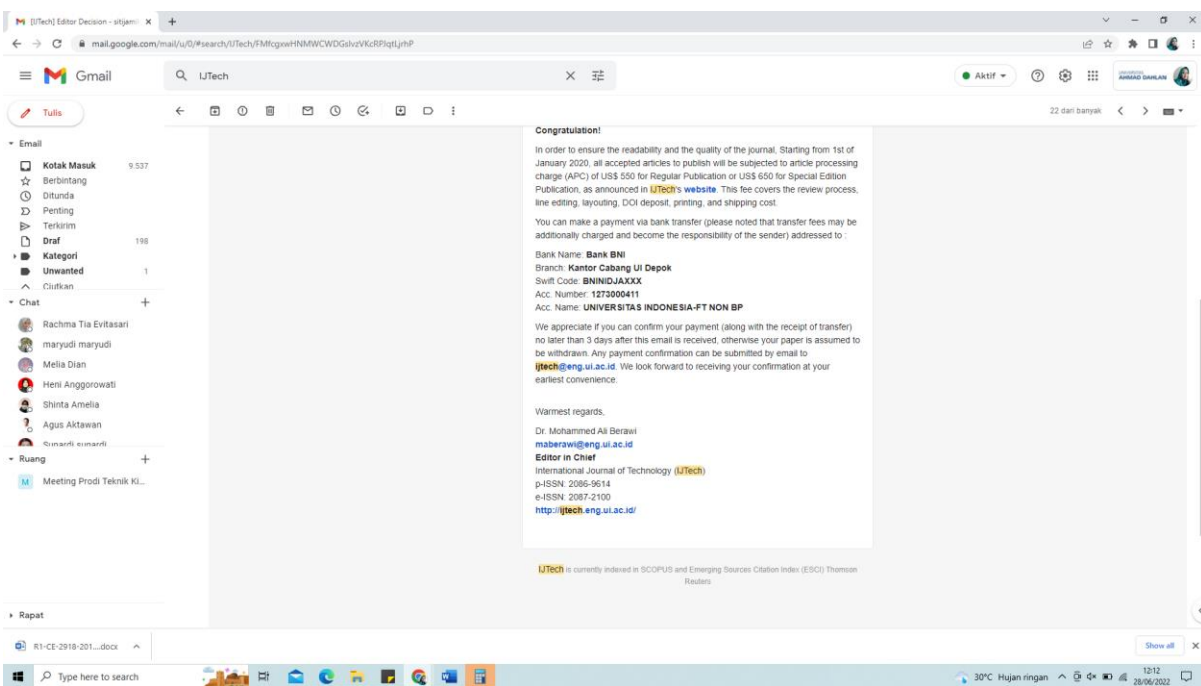
Greetings from Depok.

The editorial board is delighted to inform you that your paper entitled "CATALYTIC PYROLYSIS OF SPIRULINA PLATENSIS RESIDUE (SPR): THERMO-CHEMICAL BEHAVIOUR AND KINETICS" has been accepted to be published on **IJTech**.
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LAMPIRAN 9

12 MEI 2020: PEMBAYARAN

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LAMPIRAN 11.

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 - From:** IJTech <ijtech@eng.ui.ac.id> kepada abudiman, saya, budhijanto, rochmadi, avido_y, maziz, junichiro_hayashi
 - Date:** Kam, 11 Jun 2020 12.59
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LAMPIRAN 12

15 JUNI 2020: Receipt of line editing Revise Manuscript

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LAMPIRAN 13

7 JULI 2020: Final Proof reading & copyright form

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- Text of Email:**

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The editorial boards delighted to inform you that your paper has been accepted to be published in **IJTech** next Volume 11 Issue 3, July 2020. Congratulations!

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Enclosed please find the copyright form and the paper for a final check and please confirm that the article ready for printing. Any confirmation of the final check should be submitted no later than **July 09, 2020**. Copyright form can be printed, signed, scanned and send by email to ijtech@eng.ui.ac.id.

On behalf of editorial boards, we want to express you and your collaborators our deep appreciation for your contribution to **IJTech**.

We look forward to receiving the copyright form and proofs at your earliest convenience.

Yours sincerely,

Dr. Mohammed Ali Berawi
maberawi@eng.ui.ac.id
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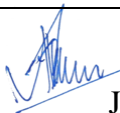
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LAMPIRAN 16

10 JULI 2020: Final proof reading & copyright form

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Dear Prof. Arief Budiman,

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Thank you.

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The Windows taskbar at the bottom shows several open applications: 'CE-2967 - 46-55....docx', 'LAMPIRAN 14- Co...pdf', 'Copyright Form-IJ...pdf', 'Bukti Bayar APC_C...pdf', 'Bukti Bayar APC_C...pdf', and 'R1-CE-2918-201...docx'. The system tray on the right shows the date and time as '28/06/2022 12:31' and the weather as '30°C Hujan ringan'.



Catalytic Pyrolysis of *Spirulina platensis* Residue (SPR): Thermochemical Behavior and Kinetics

Siti Jamilatun¹, Budhijanto², Rochmadi², Avido Yuliestyan³, Muhammad Aziz^{4,6}, Jun-ichiro Hayashi⁵, Arief Budiman^{2*}

¹Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Ahmad Dahlan, Jalan Kapas 9, Yogyakarta 55166, Indonesia

²Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jalan Grafika 2, Yogyakarta 55284, Indonesia

³Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Pembangunan Nasional "Veteran" Yogyakarta, Jalan SWK 104, Yogyakarta 55283, Indonesia

⁴Institute of Innovative Research, Tokyo Institute of Technology, i6-25, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550 Japan

⁵Institute for Material Chemistry and Engineering, Kyushu University, Kasuga 816-8580 Japan

⁶Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

Abstract. The pyrolysis characteristics of *Spirulina platensis* residue (SPR) with silica–alumina catalysts were investigated using thermogravimetric analysis (TGA). The effects of differing amounts of catalysts on thermochemical behavior and kinetics parameters (pre-exponential factor in Arrhenius equation [A] and activation energy [Ea]) were studied. The experiment was carried out from 30 to 1000°C at a heating rate of 20°C/min for the case of non-catalytic and catalytic pyrolysis (silica–alumina). For the catalytic pyrolysis, also of interest were the catalyst-to-SPR weight ratios of 1:1 and 1:2. The TGA curve and differential thermogravimetric peak analysis results suggest that the use of catalysts in pyrolysis (particularly at a catalyst-to-SPR weight ratio of 1:1) reduces both pyrolysis time and temperature range to 14.68 min and 230–555°C, respectively. The kinetic parameters were then calculated in a one-step global non-isothermal model and solved using a least squares method in MATLAB. The presence of catalyst was able to reduce Ea to the lowest value from 41.10 kJ/mol (without catalyst) to 40.77 kJ/mol (weight ratio of 1:2) and 39.46 kJ/mol (weight ratio of 1:1) in Zone 1. However, the increase of catalyst quantity was not in line with the increase of reaction rate constant (k) and resulted in reasonably low A of, respectively, 593.30, 406.31, and 266.37.

Keywords: Activation energy, Catalytic pyrolysis; Pre-exponential factor; *Spirulina platensis* residue

1. Introduction

By 2040, the world's energy demand is estimated to have increased by 56%, with fossil fuels still contributing about 80% of the required supply (Anggorowati et al., 2018). This expectation has motivated an acceleration of the utilization of renewable sources, including algae. Microalgae such as *Spirulina platensis* have tremendous potential to be converted as a renewable fuel (Pradana et al., 2018). After the removal of lipid content by extraction, biomass in the form of *Spirulina platensis* residue (SPR), used as a biofuel material, has the

*Corresponding author's email: abudiman@ugm.ac.id, Tel/Fax.: +62-274-902170
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potential to be converted through a process of pyrolysis (Jamilatun et al., 2017a; Kusrini et al., 2018; Jamilatun et al., 2019a).

Generally, a biofuel derived from the pyrolysis of SPR exhibits several deficiencies, including the presence of high levels of oxygenous and nitrogenous compounds. However, these disadvantages can be overcome through the use of a catalyst to reduce the levels of oxygenous and nitrogenous compounds (Bui et al., 2016). One suitable catalyst for upgrading the bio-oil is silica–alumina, which is widely used to support the production of petrochemicals, chemicals, and energy. The Al_2O_3 can promote the formation of aromatic compounds, such as polycyclic aromatic hydrocarbons. And with its low acidity, SiO_2 can also help remove oxygenated compounds and inhibit the formation of coke on the catalyst thanks to the porous medium (Aho et al., 2013; Busca, 2019; Jamilatun et al., 2019c). Jamilatun (2019c) reported that the catalytic pyrolysis on SPR using a silica–alumina catalyst (surface area of $240.553 \text{ m}^2/\text{g}$, pore size of 3.3 nm , average pore volume of $0.199 \text{ cm}^3/\text{g}$, and $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 1.71) could reduce oxygenated compounds 37.47% (without catalyst) to 12.82% (a decrease of 65.80%). Further investigation on the catalytic thermal decomposition of SPR is crucially demanded to accelerate the development of bio-oil production (Sunarno et al., 2018; Jamilatun et al., 2019b; Jamilatun et al., 2019c). Its kinetic analysis and the thermal decomposition mechanisms necessary to obtain pre-exponential factor (A) and the reaction kinetics constant (k) from catalytic pyrolysis are the critical tools for designing reactor developments for industrial-scale bio-oil production (Li et al., 2013).

One effective method of analyzing both thermal decomposition and reaction kinetics is thermogravimetry (TG). Thermogravimetric analysis (TGA) has become a proven technique for investigating the non-catalytic pyrolysis of algae, including *Chlorella* sp., *Tetraselmis suecica* (Kassim et al., 2014), *Spirulina* extraction wastes (Li et al., 2013; Jamilatun et al., 2017b), and *Sargassum* sp. (Kim et al., 2013). On the other hand, there is minimal research on catalytic pyrolysis using the TGA method with microalgae raw materials, but Jamilatun et al. (2017b) reported that analysis of thermal decomposition and pyrolysis reaction kinetics of SPR with TGA indicated that the activation energy (E_a) for the heating rate of $20^\circ\text{C}/\text{min}$ for Zones 1 and 2 was $41.102 \text{ kJ}/\text{mol}$ and $0.0001240 \text{ kJ}/\text{mol}$. However, there has been almost no research work conducted on thermochemistry and kinetics of catalytic pyrolysis reactions using TGA. For this reason, research on catalytic pyrolysis of SPR needs to be developed, particularly with regard to pyrolysis thermochemical behavior and kinetics.

Based on TGA data, reaction kinetics can be approximated using a one-step reaction model derived from the Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose methods (Kassim et al., 2014; Quan et al., 2016). In this method, a one-stage global single-reaction model can be determined via various approaches, such as the distributed activation energy model (DAEM), the iso-conventional method from Vyazovkin (Marriott et al., 2016), and nonlinear least squares regression (Kim et al., 2013). To the best knowledge of the authors, there is no previous study on biomass kinetic reactions incorporating natural and straightforward processes. Hence, as an alternative to establishing a one-stage global single-reaction model, a reaction model using a least squares method and MATLAB simulation tools was developed in this study. The data of catalytic thermal decomposition characteristics of SPR in TGA are required to determine the reaction kinetics, and the kinetics data are necessary to design the pyrolysis equipment for bio-oil production (Kim et al., 2013; Kassim et al., 2014; Quan et al., 2016).

This paper discusses the characteristics of thermal decomposition using a silica–alumina ($\text{SiO}_2/\text{Al}_2\text{O}_3$) catalyst, including the extent of the catalyst's effect on SPR weight

reduction. This work uses TG and differential thermogravimetric (DTG) curves to obtain the temperature ranges for Stage I (drying), Stage II (pyrolysis), and Stage III (gasification). The kinetic reaction was calculated through a one-step global non-isothermal model and solved with a least squares fitting using MATLAB simulation.

2. Methods

2.1. Materials

Blue-green microalgae, *Spirulina platensis*, were extracted to produce algal oil and a solid residue. The built residue (SPR) was used as the raw material for this research. The wet SPR was initially dried at 70°C in an oven to a constant weight and then homogenized until its size reached about 0.105–0.177 mm. Analyses of the protein, lipid, and carbohydrate contents of the SPR sample, together with calorific value analysis, were performed at the Research and Development Center for Mineral and Coal Technology (TEKMIRA), Bandung, Indonesia (Jamilatun et al., 2017a).

The catalyst used in this research was SiO₂/Al₂O₃, obtained from PT PERTAMINA Balongan Indonesia. The specifications of the SiO₂/Al₂O₃ were: (i) the ratio of SiO₂/Al₂O₃ was 1.67, and (ii) based on the BET method, the pore had a surface area of 240.553 m²/g, with a pore diameter of 3.3 nm and mean pore volume of 0.199 cm³/g to the total pore volume, and the contents of Na₂O, K₂O, CaO, and Fe₂O₃ were 0.48%, 0.017%, 0.035%, and 0.282%, respectively. SEM-EDX analysis revealed that the SiO₂/Al₂O₃ catalyst comprised C, O, Al, and Si of 12.33, 55.73, 15.42, and 16.51 wt.%, respectively (Jamilatun et al., 2017b; Jamilatun et al., 2019c).

2.2. Methods and Analysis

2.2.1. Pyrolysis test with TGA and thermochemical behavior

Thermal decomposition was examined using a TG–DTA (Perkin Elmer Pyris Diamond) at Leather Technology Academy, Yogyakarta (Politeknik ATK Yogyakarta). The mass of SPR, including the catalyst mixture (1:1 and 1:2 ratios) for each experiment, was 4–8 mg. Heating was carried out at a temperature range of 30 to 1000°C, and a rate of 20°C/min in the presence of 20 mL/min nitrogen gas. The selected heating rate had been previously tested by Jamilatun et al. (2017a).

2.2.2. Kinetics analysis

The one-stage global single-reaction model was used to obtain the reaction rate constant (*k*), including *A* and *E_a*. Although the pyrolysis of SPR biomass includes various very complex reactions, they can be considered as a single overall reaction (Kassim et al., 2014), with the equation for the reaction given as (Agrawal and Chakraborty, 2013)



As shown in Equation 1, the pyrolysis with TG is non-isothermal, which can be observed as the change in SPR mass over time until the end of pyrolysis. The formed volatile matter mass could not be observed. The conversion change at any time (*dX/dt*) is affected by *k*, as the function of temperature (*T*), and conversion (*f(X)*) (Agrawal and Chakraborty, 2013).

$$\frac{dX}{dt} = k(T) \cdot f(X) \quad (2)$$

for,

$$f(X) = (1-X)^n \quad (3)$$

where n is the order of the reaction (this is assumed to be one). Moreover, the SPR conversion (X) is calculated using the following equation (Quan et al., 2016):

$$X = \frac{m_o - m_t}{m_o} \quad (4)$$

where X represents the conversion as a function of weight (m) from time 0 to time t . By initially providing the values of A , E_a , and universal gas constant (R) data, k can be calculated using

$$k = A \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

Combining Equations 2–5 results in

$$\frac{dX}{dt} = A \cdot \exp\left(\frac{-E_a}{RT}\right) (1-X)^n \quad (6)$$

$$T = T_0 + \beta(t) \quad (7)$$

$$\beta = \frac{dT}{dt} \quad (8)$$

where β is the heating rate ($^{\circ}\text{C}/\text{s}$), T_0 and T are the initial temperature and the temperature at a given t (K), respectively.

The A and E_a were then validated using the least squares method. The sum of squared errors (SSE) was calculated using the method in Jamilatun et al. (2017b):

$$\text{SSE} = \sum\{(X)_{\text{model}} - (X)_{\text{data}}\}^2 \quad (9)$$

3. Results and Discussion

3.1. Thermal Decomposition and Thermochemical Characteristics

The catalytic thermal decomposition characteristics of SPR were evaluated at a heating rate of $20^{\circ}\text{C}/\text{min}$ in the presence of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst. The results of the thermal decomposition for the catalyst-to-SPR weight ratios of 1:1, 1:2, and without catalyst can be seen in Figure 1, and the division of stages information is listed in Table 1.

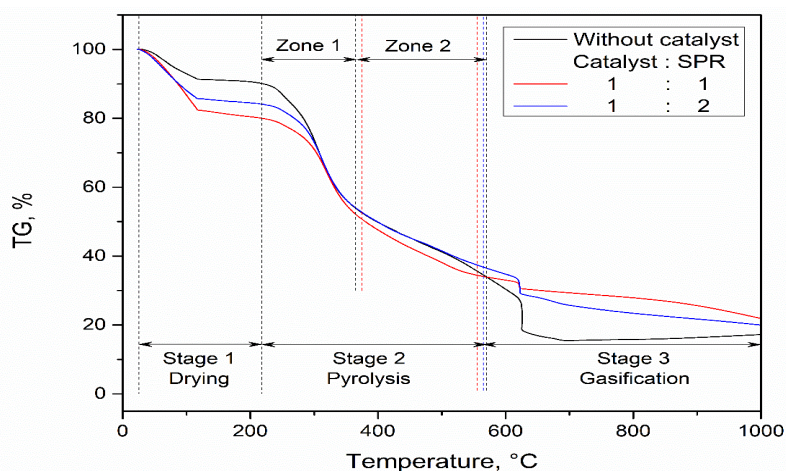


Figure 1 Thermal decomposition of SPR for the cases of the catalytic process with catalyst-to-SPR weight ratios of 1:1 and 1:2 and non-catalytic method at a heating rate of $20^{\circ}\text{C}/\text{min}$

The weight reduction of the SPR (obtained from the slope of the curve) can be seen in Figure 1. Catalytic and non-catalytic thermal decompositions exhibited a similar temperature range ($30\text{--}230^{\circ}\text{C}$) in Stage I. Catalytic pyrolysis exhibited slight differences in

the temperature range for the ratios of 1:1 and 1:2, as shown in Table 1. The temperature ranges were 230–555°C and 230–565°C in Stage II, and 555–1000°C and 565–1000°C in Stage III, respectively. This temperature range contrasts with the non-catalytic pyrolysis, which exhibited a temperature range of 230–570°C in Stage II and 570–1000°C in Stage III. These phenomena may indicate that the catalyst reduces E_a ; hence, the reaction proceeds more rapidly, resulting in faster pyrolysis (14.68 min) than without a catalyst (15.10 min).

Table 1 Division of stages upon catalytic and non-catalytic pyrolysis of SPR

Catalyst/SPR	1:1	1:2	Without catalyst
Stage I, °C (drying)	30–230	30–230	30–230
Stage II, °C (pyrolysis)	230–555	230–565	230–570
Stage III, °C (gasification)	555–1000	565–1000	570–1000
Pyrolysis time (Stage II), min	14.68	15.07	15.10

Furthermore, Stage II can be subdivided into two pyrolysis zones: Zone 1 (230–375°C for the 1:1 ratio and 230–365°C for the 1:2 ratio), with a rapid rate of weight reduction, and Zone 2 (375–555°C for the 1:1 ratio and 365–565°C for the 1:2 ratio), with a slower reduction rate. Meanwhile, for non-catalytic pyrolysis, Zones 1 and 2 ended at 350 and 570°C, respectively. Based on that, the use of a catalyst seems to affect the final temperature of the pyrolysis. In Zone 1, the final pyrolysis temperature with the catalyst (375°C) was higher than that without the catalyst (350°C), while in Zone 2, the temperature with the catalyst was lower (555°C) than that without the catalyst (570°C). Overall, without considering the presence of the pyrolysis zone, pyrolysis was achieved faster with the use of a catalyst, with a temperature range of 230–555 °C, as compared to without a catalyst at 230–570°C. This can be explained by the use of the catalyst possibly decreasing the activation energy so that it can accelerate the reaction, resulting in pyrolysis being achieved more quickly and in the lower temperature range.

DTG curves might be used to shed some light, based on the catalytic thermal decomposition of proteins and lipids, following the peaks summarized in Table 2 as a representation of the curves shown in Figure 2. The magnitude of the peak can describe the effect of temperature increase on the release of volatile matter (wt.%) for each time (min).

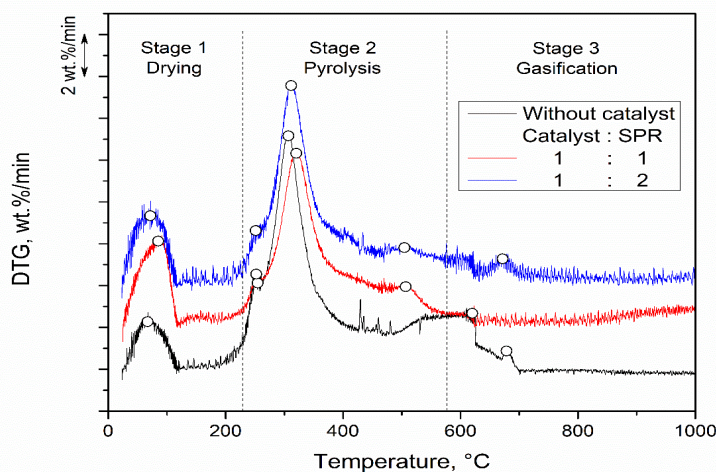


Figure 2 TG-DTG curve for catalytic thermal decomposition of SPR at a heating rate of 20°C/min: (a) the catalyst-to-SPR weight ratio of 1:1; (b) catalyst-to-SPR weight ratio of 1:2

From Figure 2, it can be observed that at a 20°C/min heating rate and 1:1 weight ratio, one peak was present in Stage I, three peaks were present in Stage II, and only one peak was present in Stage III. The evaporation of water (via O–H bond termination) occurred at 82.05°C at a rate of 4.35 wt.%/min. In the first zone of Stage II, two peaks were present at 262.30 and 318.05°C, with weight loss rates equal to 2.18 and 8.40 wt.%/min, respectively. Conversely, only one peak was observed in Zone 2, at 516.76°C, with a weight loss rate of 1.78 wt.%/min. The peaks in the pyrolysis zone indicate the release of volatile matter, meaning the decomposition of proteins and carbohydrates occurring through the termination of O–O, N–O, C–N, N–H, N=N, C=N, C–C, C=C, O=H, C–O, O–H, C=O, and C–H bonds. This phenomenon is the same as in a study by [de Wild et al. \(2011\)](#), showing that at the peaks in Zones 1 and 2, there is a breaking of the O–O, N–O, C–N, N–H, N=N, and C=N bonds with the decomposition of proteins, then a termination of C bonds C, C=C, and O=H bonds in cellulose decomposition, completion of C–C, C–O, O–H, C=O, and C–H bonds in hemicellulose decomposition, and termination of C bonds C, C=O and C–O in lignin decomposition.

Using a similar method applied to deduct the information in the 1:1 weight ratio case, peaks for non-catalytic thermal decomposition and catalytic decomposition at a 1:2 weight ratio were determined, and the results are shown in Table 2 and Figure 2b. For the non-catalytic process, a peak was observed at a similar position in Stage II, meaning in the temperature range where pyrolysis occurred. The volatile matter was released at a rate of 11.28 wt.%/min during non-catalytic decomposition at 305.62°C. Meanwhile, for catalytic decomposition, in summary, three peaks initially appeared at lower temperatures (253.95, 312.67, and 506.56°C) for the 1:2 ratio than for the 1:1 ratio (at 262.3, 318.05 and 516.77°C). However, the rates of volatile matter release with catalyst-to-SPR weight ratios of 1:1 and 1:2 were relatively similar, at 2.18–2.89, 8.40–9.78, and 1.78–1.83 wt.%/min.

Table 2 Peaks observed on DTG curves for catalytic and non-catalytic thermal decomposition of SPR at a heating rate of 20°C/min

Catalyst/SPR		Without catalyst	1:1	1:2
Stage I (Drying)				
Peak 1	Temperature, °C	65.38	82.05	68.26
	DTG, wt.%/min	2.31	4.35	3.41
Stage II (Pyrolysis)				
Peak 1	Temperature, °C	254.60	262.30	253.95
	DTG, wt.%/min	4.40	2.18	2.89
Peak 2	Temperature, °C	305.62	318.05	312.67
	DTG, wt.%/min	11.28	8.40	9.78
Peak 3	Temperature, °C	610.44	516.77	506.56
	DTG, wt.%/min	2.91	1.78	1.83
Stage III (Gasification)				
Peak 1	Temperature, °C	681.08	618.83	675.65
	DTG, wt.%/min	0.97	0.51	1.45

3.2. Reaction Kinetics

The reaction kinetics of catalytic pyrolysis for the one-stage global single-reaction model can be derived from Equation 1, while the values of A and Ea can be calculated using Equations 2–5. By employing a least squares approach, the SSE calculation in MATLAB can be performed using Equation 9. The temperature (T) in Equation 8 is the pyrolysis temperature as influenced by time (t) and heating rate (β). Therefore, the relationship

between temperature (T_{data} and T_{model}) and pyrolysis time (t) in Zones 1 and 2 must be evaluated for the relative error. Evidence that the relative error is small can be observed in the selected experimental data for the catalyst-to-SPR ratio of 1:1; the results are presented in Figure 3a.

From Figure 3a, it can be observed that the line of temperature (T_{model}) versus time (t) in Zones 1 and 2 coincide with the scatter data (T_{data} vs. t). This relationship can be interpreted as evidence that the relationships between experimental data and models have the same relative values. Furthermore, the calculated conversion (X_{model}) and the conversion observed in the experiment (X_{data}) were employed to calculate the SSE using Equation 9. The relationship between both of these conversions with time (t) at a catalyst-to-SPR weight ratio of 1:1 can be seen in Figure 3b.

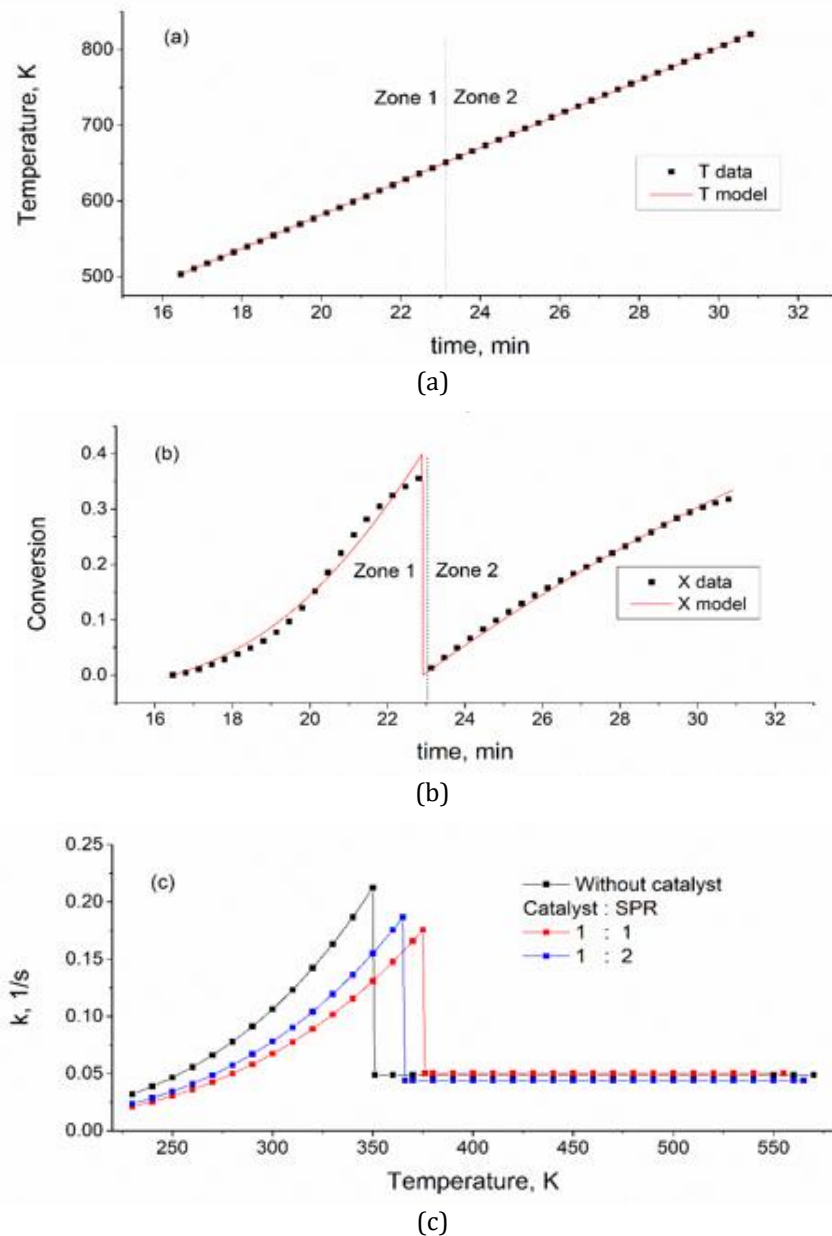


Figure 3 Kinetic parameters calculated for SPR pyrolysis at a heating rate of 20°C/min in Zones 1 and 2 for a catalyst-to-SPR weight ratio of 1:1: (a) relationship between time (t) and pyrolysis temperature (T); (b) relationship between time (t) and conversion (X); (c) relationship between the rate of reaction constant (k) and reaction temperature (T) with and without the catalyst

From the results of the simulation, with the values of A and E_a without and with a catalyst provided in Table 3, it can be observed that without the catalyst, A and E_a were 593.30 and 41.10 kJ/mol, respectively. In contrast, at a catalyst-to-SPR ratio of 1:1, these values became 266.37 and 39.46 kJ/mol, respectively, and at a catalyst-to-SPR ratio of 1:2, the values were 406.31 and 40.771 kJ/mol, respectively. The use of the catalyst decreased E_a due to the addition of new reaction pathways. Because catalytic pyrolysis is a very complex mechanism, the obtained E_a is affected by many reactions, including cracking, decarboxylation, decarbonylation, hydrocracking, hydrogenation, and hydrodeoxygenation (Purwanto et al., 2015; Supramono et al., 2015).

The decline of E_a can be interpreted as evidence that the catalytic pyrolysis reaction occurs more readily. In the calculation of k in Table 3 for Zone 1, it can be observed that with an increase of pyrolysis temperature, k rose accordingly. However, it appears that at a heating rate of 20°C/min and without the catalyst, the value of k is only slightly higher than with the catalyst. This is due to the shift in the final pyrolysis temperature range, meaning it shifts to higher temperatures; therefore, in the case without the catalyst, k is even higher than that with the catalyst (Kim et al., 2013; Marriott et al., 2016; Quan et al., 2016).

In addition, Table 3 also shows the calculated data for A , E_a , and k for Zone 2. It can also be observed that irrespective of the presence of a catalyst, the value of A is relatively similar. In contrast, the E_a value with the catalyst (0.0552–0.0853 J/mol) is much lower than without the catalyst (0.1421 J/mol). The values of k with and without the catalyst are almost the same (in the range of 0.0488–0.0505 s⁻¹), indicating that the temperature rise does not affect the amount of k , yielding relatively stable k values. The value of E_a in Zone 2 is a composite E_a of many reactions during pyrolysis (Li et al., 2013).

Table 3 Reaction kinetic parameters of the SPR with and without the catalyst at a heating rate of 20°C/min for Zones 1 and 2

Catalyst/ SPR	A	E_a (kJ/mol)	SSE	Temperature range, (°C)		k (s ⁻¹) low temp.	k (s ⁻¹) high temp.
Zone 1							
Without	593.30	41.10	0.0506	230	350	0.0320	0.2124
1:2	406.31	40.77	0.1005	230	365	0.0237	0.1865
1:1	266.37	39.46	0.0924	230	375	0.0213	0.1755
Zone 2							
Without	0.0488	1.42x10 ⁻⁴	0.0421	351	570	0.0488	0.0488
1:2	0.0440	5.52x10 ⁻⁵	0.0298	365	565	0.0440	0.0440
1:1	0.0505	8.53x10 ⁻⁵	0.0151	375	555	0.0505	0.0505

Table 3 lists the kinetic parameters, and the results are presented in Figure 3c, showing the relationship between the SPR pyrolysis temperature and k for the catalyst-to-SPR ratios of 1:1 and 1:2 in Zones 1 and 2. Both with and without the catalyst, at a heating rate of 20°C/min in Zone 1, k during the pyrolysis is relatively low (0.021248–0.212346 sec⁻¹), about one-third of that at a heating rate of 40°C/min (0.0759–0.6797 sec⁻¹) (Jamilatun et al., 2017a). The value of k with the catalyst is slightly lower (0.021248–0.175527 sec⁻¹) than that without the catalyst (0.031980–0.212346 sec⁻¹). As for Zone 2, the curves coincide with each other to show the same k value (0.044000–0.050449 sec⁻¹), which is not affected by temperature rise. Due to the influence of A , this value seems to be low (0.0440–0.0505 sec⁻¹). The small amount of k in Zone 2 indicates that mass transfer had begun to take effect. As observed, the presence of catalysts causes a reduction in E_a .

However, its reaction rate decreases due to the lower value of k , contributed by the decline of A . Such phenomena may indicate a reduction of the molecular collision because it is hindered by the presence of the catalyst.

4. Conclusions

This study evaluated TG-DTG analyses as a feasible method for determining SPR pyrolysis characteristics. The release of volatile matter, seen in the DTG curve as a sharp peak, was observed in non-catalytic pyrolysis. In contrast, volatile matter release was relatively similar in the presence of the catalyst. Based on TG-DTG data, the presence of catalyst was able to reduce the pyrolysis time and temperature range, with observed data of 230–570°C (15.10 min); 230–565°C (15.07 min), and 230–555°C (14.68 min) for the cases of no catalyst, catalyst-to-SPR weight ratio of 1:2, and catalyst-to-SPR weight ratio of 1:1, respectively. In the same case sequence, the kinetic study reported the reduction of activation energy in Zone 1 as 41.10, 40.77, and 39.46 kJ/mol. However, the pre-exponential factor supports also appeared lower, at 593.30, 406.31, and 266.37. The reduction of activation energy due to the use of the catalyst is not in line with the increase of k due to the quite low pre-exponential factor. However, the rate in Zone 2 was not significantly affected because the values of the kinetic parameters were rather small and relatively similar to one another, in the range of 8.53×10^{-5} – 1.42×10^{-4} kJ/mol and 0.0505–0.0488 for each activation energy and pre-exponential factor, respectively.

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