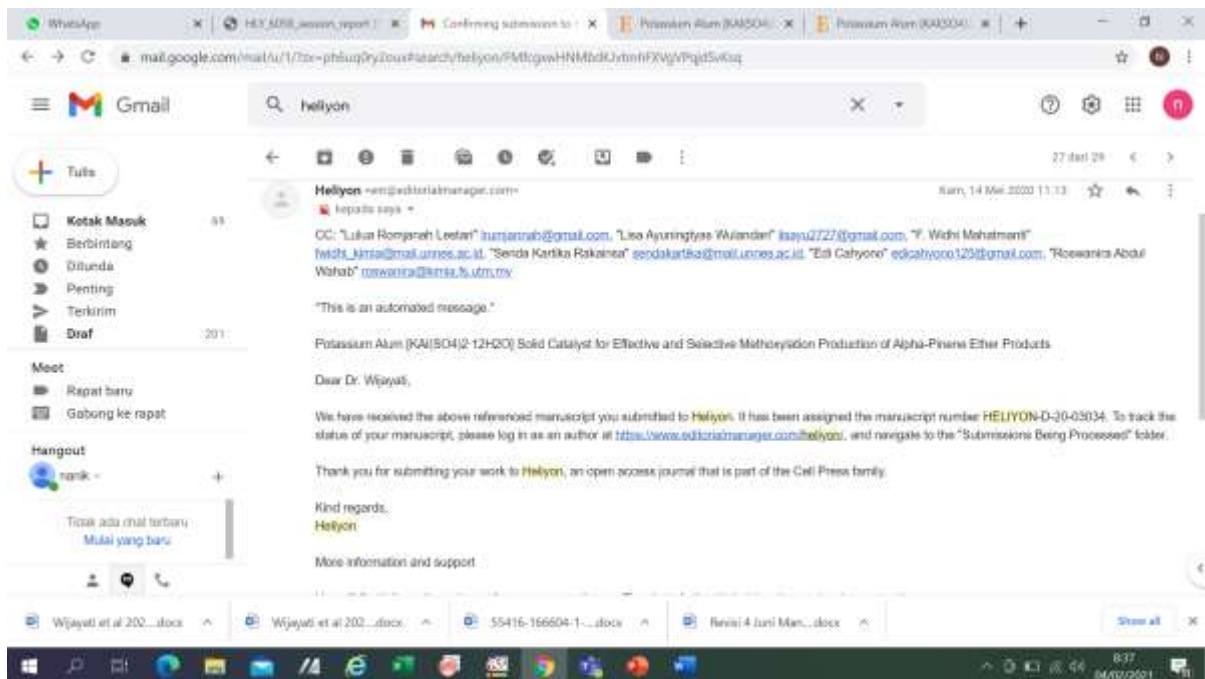


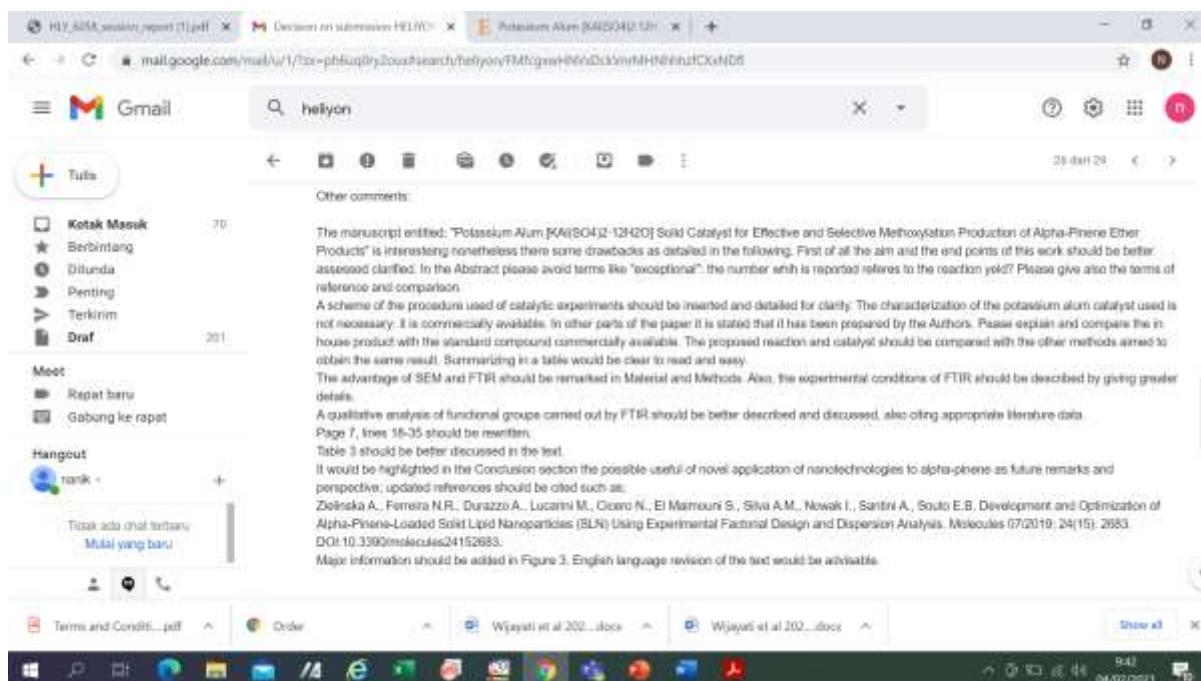
Riwayat Publikasi di Heliyon 2020-2021

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- Nama Penulis : Nanik Wijayati, Lulua Romjanah Lestari, Lisa Ayuningtyas Wulandari, F. Widhi Mahatmanti, Senda Kartika Rakainsa, Edi Cahyono, and Roswanira Abdul Wahab
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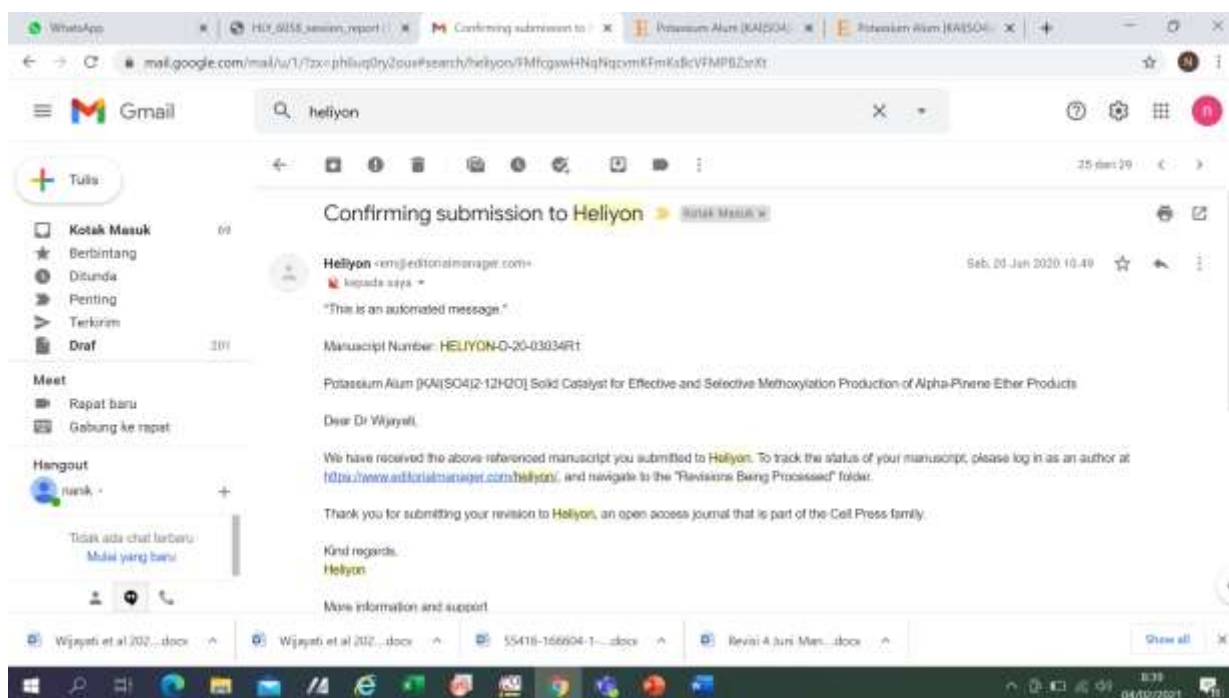
Artikel Submit

Kamis, 14 Mei 2020





Sabtu, 20 Juni 2020



Rabu, 15 Juli 2020

The image displays two screenshots of a Gmail inbox on a Windows desktop. The top screenshot shows an email from Heliyon with the subject "Decision on submission HELIYON-D-20-03034R1 to Heliyon". The email body contains the following text:

Dear Dr. Wijayati,

Thank you for submitting your manuscript to Heliyon.

We have completed the review of your manuscript and a summary is appended below. The reviewers recommend major revisions are required before publication can be considered.

If you are able to address all reviewer comments in full, I invite you to resubmit your manuscript. We ask that you respond to each reviewer comment by either outlining how the criticism was addressed in the revised manuscript or by providing a rebuttal to the criticism. This should be carried out in a point-by-point fashion as illustrated here: <https://www.egil.com/heliyon/links-for-authors#Revisions>

To allow the editors and reviewers to easily assess your revised manuscript, we also ask that you upload a version of your manuscript highlighting any revisions made. You may wish to use Microsoft Word's Track Changes tool or, for LaTeX files, the latexdiff Perl script (<https://dan.cryptgen.com/diff>).

The bottom screenshot shows the same email with the "Editor and Reviewer comments" section expanded. The comments are as follows:

Kind regards,
Francisco Epifano
Section Editor
Heliyon

Editor and Reviewer comments

Editor's comments: the manuscript contains several mistakes of the format. Authors are encouraged to definitively solve the problems. Moreover the language, grammar, and style are still not acceptable

Reviewer #3: Methods: ok

Results: ok

Interpretation: ok

Other comments: The reference citation in the main text seems confused in formatting, such as author name and number are both applied in many places.

Rabu, 5 Agustus 2020

The screenshot shows a Gmail interface on a Windows desktop. The browser tabs include 'Heliyon', 'HIV_S038_avivire_report', 'Confirming submission to...', 'Potassium Alum (KAlSO4)', and 'Potassium Alum (KAlSO4)'. The email address in the address bar is 'mail.google.com/mail/u/1/?ui=ph&ui=ph&ui=search/heliyon/FMfcgwiXLLWjKZiWSDmSWkM0hRzzL0h'. The search bar contains 'heliyon'. The left sidebar shows folders: 'Kotak Masuk' (24), 'Berbintang', 'Ditunda', 'Penting', 'Terakhir', 'Draf' (201), 'Meet', 'Rapat baru', 'Gabung ke rapat', and 'Hangout' (rank -). The main email content is as follows:

Confirming submission to Heliyon Kotak Masuk

Heliyon <em@heliyonmanager.com>
hazada oya

Feb 5 Agri 2020 17:33

"This is an automated message."

Manuscript Number: HELIYON-D-20-0303HR2

Potassium Alum [KAlSO₄·12H₂O] Solid Catalyst for Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products

Dear Dr. Wijayati,

We have received the above referenced manuscript you submitted to Heliyon. To track the status of your manuscript, please log in as an author at <https://www.editorialmanager.com/heliyon/>, and navigate to the "Revisions Being Processed" folder.

Thank you for submitting your revision to Heliyon, an open access journal that is part of the Cell Press family.

Kind regards,
Heliyon

More information and support

The taskbar at the bottom shows several open Word documents: 'Wijayati et al. 202...docx', 'Wijayati et al. 202...docx', '55416-166604-1...docx', and 'Revisi 4 Juni Mar...docx'. The system clock shows 8:41 on 04/08/2021.

Senin, 28 September 2020

This screenshot shows a Gmail inbox on a Windows desktop. The active email is from Heliyon, dated September 28, 2020. The subject is "Decision on submission HELIYON-D-20-03034R2 to Heliyon". The email body contains the following text:

Dear Dr. Wijayati,

Thank you for submitting your manuscript to Heliyon.

We have completed the review of your manuscript and a summary is appended below. The reviewers recommend major revisions are required before publication can be considered.

If you are able to address all reviewer comments in full, I invite you to resubmit your manuscript. We ask that you respond to each reviewer comment by either outlining how the criticism was addressed in the revised manuscript or by providing a rebuttal to the criticism. This should be carried out in a point-by-point fashion as illustrated here: <https://www.ccsj.com/heliyon/guide-for-authors#Revisions>

To allow the editors and reviewers to easily assess your revised manuscript, we also ask that you upload a version of your manuscript highlighting any revisions made. You may wish to use Microsoft Word's Track Changes tool or, for LaTeX files, the latexdiff Perl script (<https://dan.org/latexdiff/>)

The taskbar at the bottom shows several open documents, including "Wijayati et al. 202..._docs" and "Revisi 4 Juni Mar..._docs".

This screenshot shows a follow-up email from Heliyon, dated September 24, 2020. The subject is "Decision on submission HELIYON-D-20-03034R2". The email body contains the following text:

Kind regards,
Francesco Epifano
Section Editor
Heliyon

Editor and Reviewer comments:

Editor's comments: the manuscript contains several mistakes of the format. Authors are encouraged to definitively solve the problems. Moreover the language, grammar, and style are still not acceptable

Reviewer #3: Methods: ok

Results: ok

Interpretation: ok

Other comments: The reference citation in the main text seems confused in formatting, such as author name and number are both applied in many places.

The taskbar at the bottom shows open documents including "Terms and Conditions...pdf", "Order", and "Wijayati et al. 202..._docs".

Rabu, 28 Oktober 2020

The screenshot shows a Gmail interface on a Windows desktop. The browser tabs include 'Whishiya', 'HIV_S038_avant_report', 'Confirming submission to...', 'Potassium Alum (KAlSO4)', and 'Potassium Alum (KAlSO4)'. The Gmail search bar contains 'heliyon'. The left sidebar shows folders: 'Tulis', 'Kotak Masuk' (24), 'Berbintang', 'Ditunda', 'Penting', 'Terakhir', 'Draf' (201), 'Meet', 'Rapat baru', 'Gabung ke rapat', and 'Hangout' (rank -). The main email is from 'Heliyon' (en@edkinatmanager.com) dated 'Rab, 28 Okt 2020 13:10'. The subject is 'Confirming submission to Heliyon'. The body text reads: 'This is an automated message.'; 'Manuscript Number: HELIYON-D-20-03034R3'; 'Potassium Alum [KAlSO4]·2H2O Solid Catalyst for Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products'; 'Dear Dr. Wijayati,'; 'We have received the above referenced manuscript you submitted to the Chemistry section of Heliyon. To track the status of your manuscript, please log in as an author at <https://www.edkinatmanager.com/heliyon/>, and navigate to the "Revisions Being Processed" folder.'; 'Thank you for submitting your revision to Heliyon, an open access journal that is part of the Cell Press family.'; 'Kind regards, Heliyon'; 'More information and support'. The taskbar at the bottom shows several open Word documents and the system tray with the date '04/10/2021'.

Selasa, 29 Desember 2020

This screenshot shows a Gmail inbox on a desktop browser. The search bar contains the word "heliyon". The selected email is from "Heliyon" (heliyon@editorialmanager.com) dated "Sat, 29 Dec 2020 08:52". The subject is "Decision on submission HELIYON-D-20-03034R3 to Heliyon". The email body contains the following text:

Dear Dr. Wijayati,

Thank you for submitting your manuscript to Heliyon.

We have now received all of the editor and reviewer comments on your recent submission to Heliyon. Your paper will become acceptable for publication after implementation of minor formatting and/or administrative changes outlined below.

To submit your revised manuscript, please log in as an author at <https://www.editorialmanager.com/heliyon/>, and navigate to the "Submissions Needing Revision" folder under the Author Main Menu. When submitting your revised manuscript, please ensure that you upload your most recent document with the "Revised manuscript file - highlighting revisions made" item type.

Kind regards,

This screenshot shows the "Editor and Reviewer comments" section of the email. The subject is "Editor and Reviewer comments". The content includes:

Comments from Editorial Office:

(1) Please remove your "Author Contributions", "Conflict of Interest" and "Credit Author Statement" section from your manuscript file, as this information is handled separately.

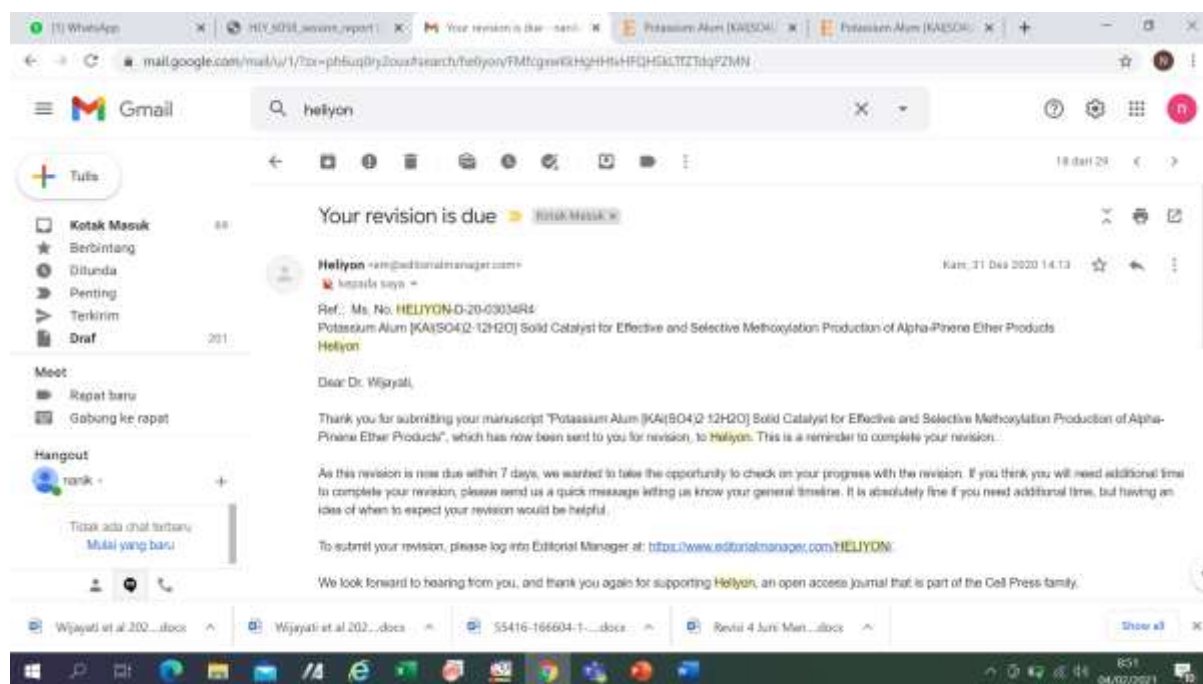
(2) Please remove "This research is supported by grant under Basic Research for Higher Education program (Grant no.102/SP2H/LT/DORPM2019) by the Directorate of Research and Public Service, Ministry of Research, Technology, and Higher Education, Republic of Indonesia." from your Acknowledgements, as this information is handled separately.

(3) Under Additional Information please complete the author contribution statement indicating which author contributed to each section. Please note that all authors must be attributed to at least one numbered section. Please note that all authors should have made substantial contributions to all of the following: (1) the conception and design of the study; the acquisition of data, or the analysis and interpretation of data (i.e. at least one of sections 1-4 below); (2) drafting the article or critically revising its important intellectual content; (3) final approval of the version submitted. Currently, it seems author Roowanita Abdul Wahab only contributed to writing and revising the paper. Please correct your Author Contribution Statement to follow the guidelines above, using only Heliyon's standard wording as provided:

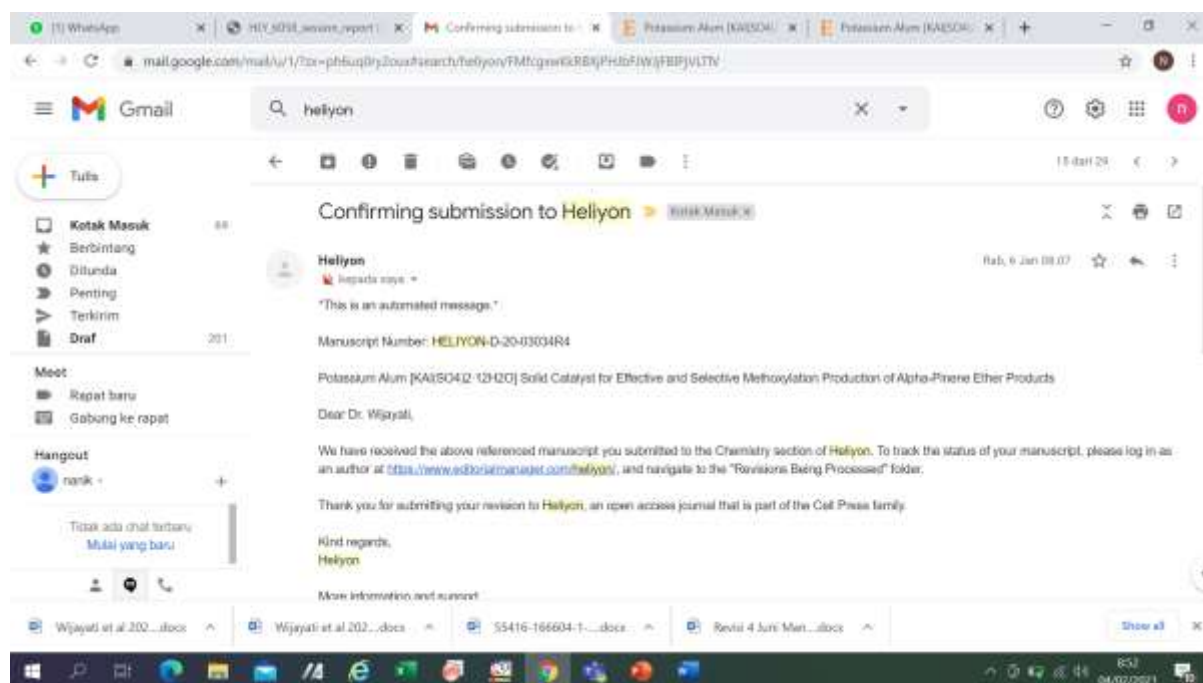
- 1 - Conceived and designed the experiments;
- 2 - Performed the experiments;
- 3 - Analyzed and interpreted the data;
- 4 - Contributed reagents, materials, analysis tools or data;
- 5 - Wrote the paper.

Please ensure that any co-author with the contribution "Wrote the paper" has also contributed to at least one other numbered section, as drafting of the article is

Kamis 31 Desember 2020

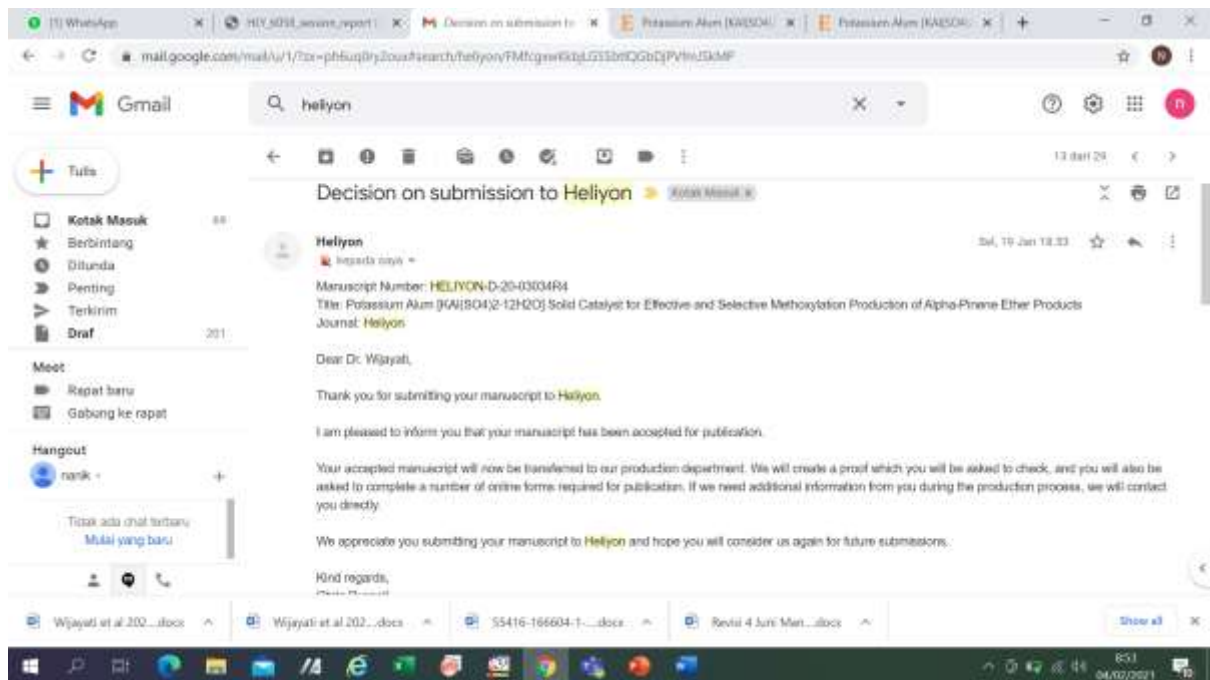


Rabu, 6 Januari 2021



Artikel Accepted

Selasa, 19 Januari 2021



The screenshot shows a Gmail interface on a Windows desktop. The browser address bar displays a Gmail URL. The search bar contains the word "heliyon". The left sidebar shows the Gmail navigation menu with categories like "Kotak Masuk", "Berbintang", "Ditunda", "Penting", "Terakhir", "Draf", "Meet", "Hangout", and "Tidak ada chat terbaru". The main content area shows an email from "Heliyon" dated "24, 19 Jan 18:33". The email subject is "Decision on submission to Heliyon". The body of the email reads: "Dear Dr. Wijayati, Thank you for submitting your manuscript to Heliyon. I am pleased to inform you that your manuscript has been accepted for publication. Your accepted manuscript will now be transferred to our production department. We will create a proof which you will be asked to check, and you will also be asked to complete a number of online forms required for publication. If we need additional information from you during the production process, we will contact you directly. We appreciate you submitting your manuscript to Heliyon and hope you will consider us again for future submissions. Kind regards,". The Windows taskbar at the bottom shows several open documents and the system tray with the date "19/01/2021".

Decision on submission to Heliyon

Heliyon

Manuscript Number: HELIYON-D-20-03034R4
Title: Potassium Alum [KAl(SO₄)₂·12H₂O] Solid Catalyst for Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products
Journal: Heliyon

Dear Dr. Wijayati,

Thank you for submitting your manuscript to Heliyon.

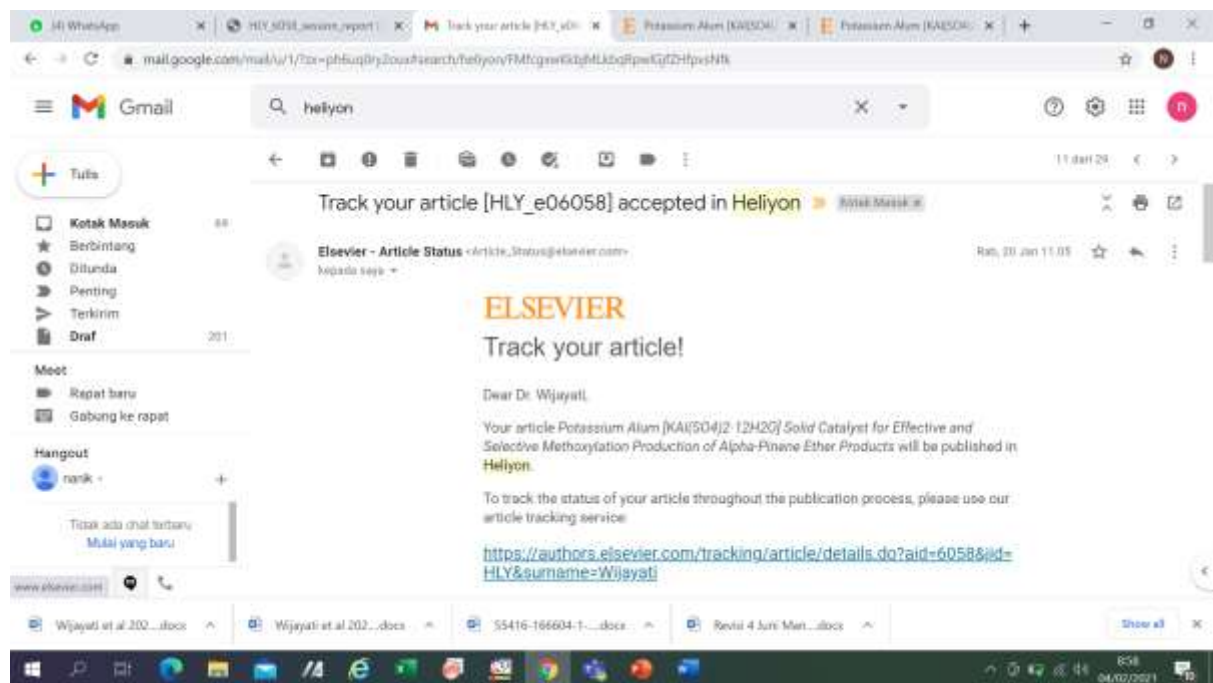
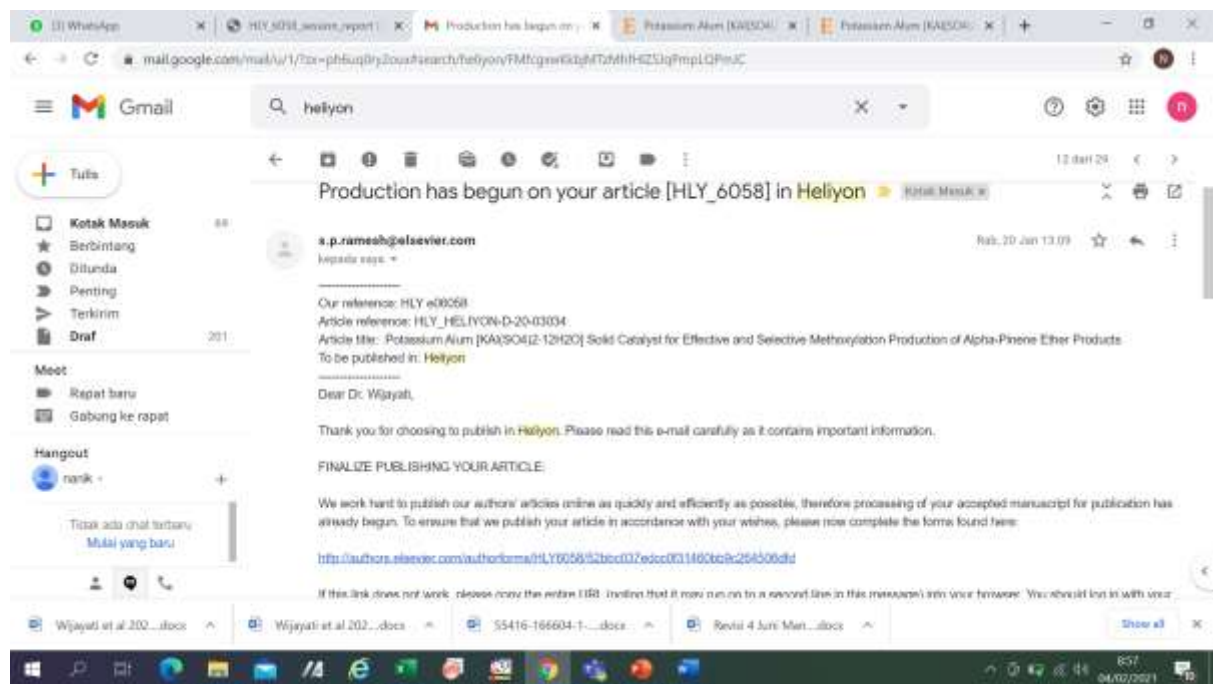
I am pleased to inform you that your manuscript has been accepted for publication.

Your accepted manuscript will now be transferred to our production department. We will create a proof which you will be asked to check, and you will also be asked to complete a number of online forms required for publication. If we need additional information from you during the production process, we will contact you directly.

We appreciate you submitting your manuscript to Heliyon and hope you will consider us again for future submissions.

Kind regards,

Rabu, 20 Januari 2021



Proof Reading in Heliyon

Kamis, 21 Januari 2021

This screenshot shows a Gmail inbox with a search filter for 'heliyon'. The selected email is titled 'Publishing Agreement completed for your article [HLY_e06058]' from Elsevier. The email content includes the Elsevier logo, a greeting to Dr. Wijayati, and a thank-you message for completing the publishing agreement form for the article 'Potassium Alum [KAl(SO4)2·12H2O] Solid Catalyst for Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products'. A yellow Heliyon journal cover is displayed on the right. The email also provides contact information for any questions.

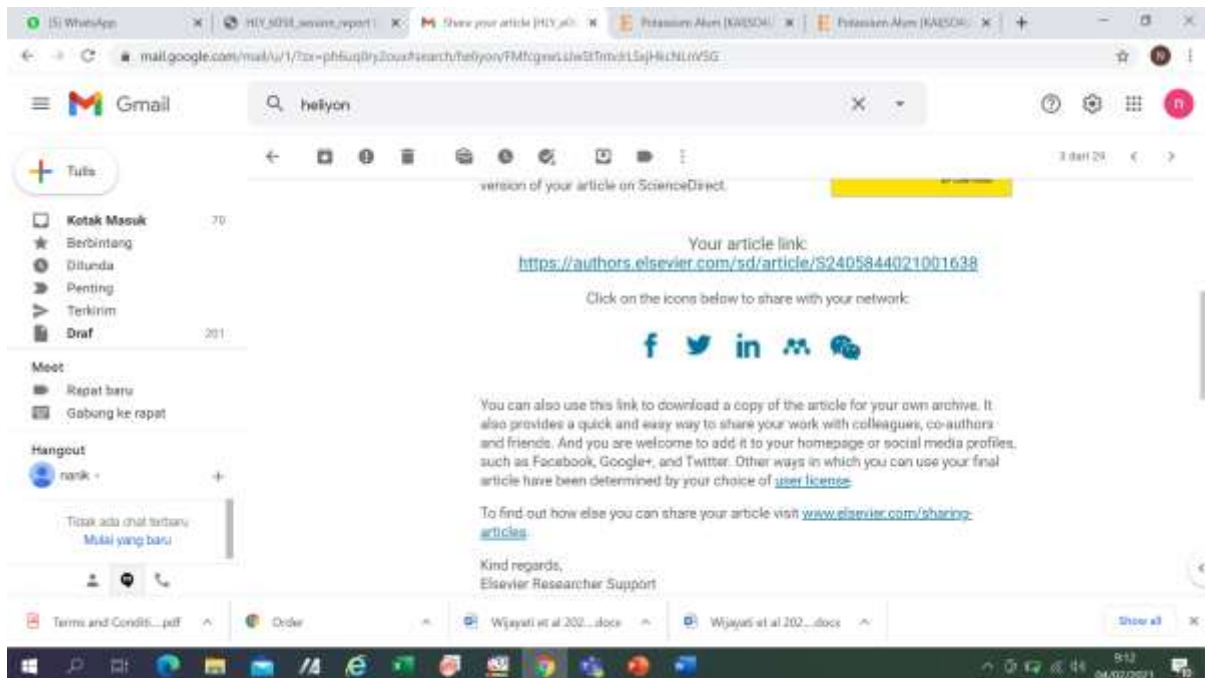
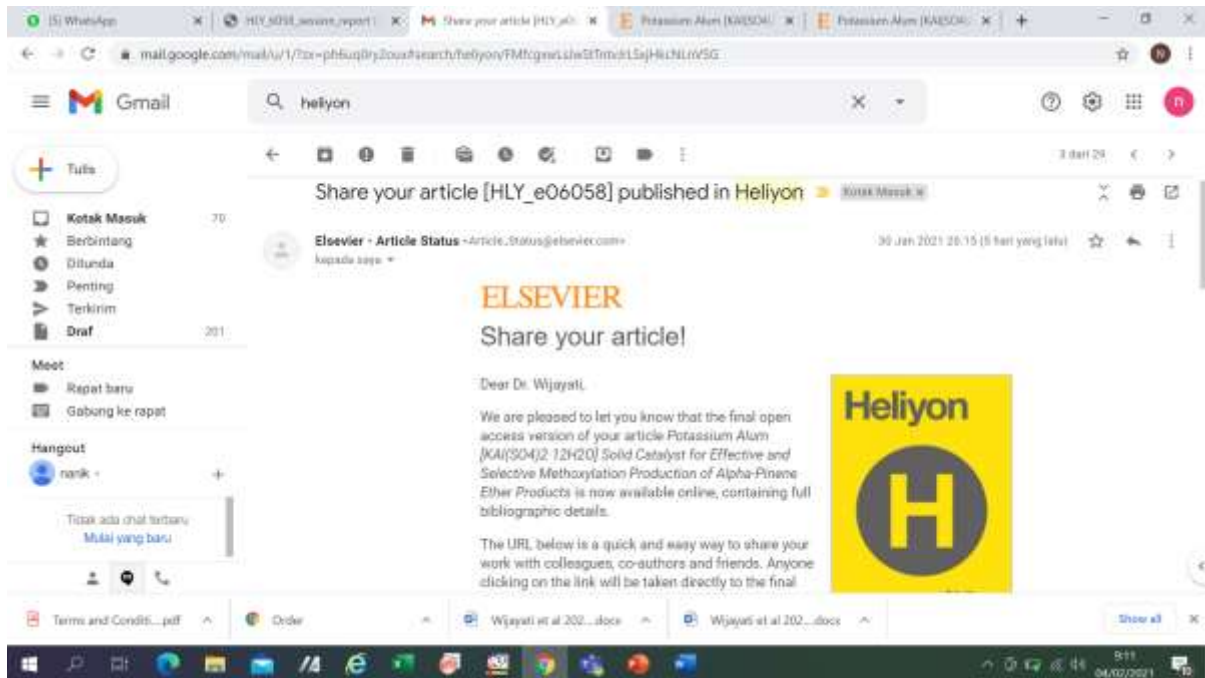
This screenshot shows a Gmail inbox with a search filter for 'heliyon'. The selected email is titled 'Proof of [HLY_8558] - new' from Elsevier. The email content informs the recipient that copy-editing changes have been highlighted and provides instructions on how to review and submit corrections within a 48-hour period. It includes the Elsevier logo, a sign-off, and the customer support email address: corrections.support@elsevier.com. A disclaimer at the bottom states that the email content is confidential and intended solely for the use of the individual or entity to whom they are addressed.

Rabu, 27 Januari 2021

The screenshot shows a Gmail interface on a Windows desktop. The browser tabs include 'Whisklyn', 'HLY 6058_avevnt_report', 'Re: HLY 6058 - Query received from production', and two instances of 'Potassium Alum (KAl(SO4)3)'. The Gmail search bar contains 'helyon'. The email being viewed is titled 'Re: HLY 6058 - Query received from production - Please check [210127-000335]' and is from 'Helyon' (helyon@pelauver.com), dated 'Rab, 27 Jan 2021 (8 hari yang lalu)'. The email content reads: 'Dear Prof. Wijayati, I trust this e-mail finds you well. We have received below queries from production, it would be of great help if you could check and provide response at your earliest possible convenience. Q1) The correction provided in section 2.3.1 is not clear. You have replaced the text "The gas pressure was set to 0.5 bar and the analysis was conducted at 20 mA for 5-10 min using AuPd as the solvent" with the text "coc" which seems to be inappropriate. Kindly check and advise what exactly has to be corrected in the text.'

Artikel Publish di Heliyon

Sabtu, 30 Januari 2021



Senin, 1 Februari 2021

The screenshot shows a Gmail interface with a search bar containing 'heliyon'. The main email is from 'Author Services <support@elsevier.com>' with the subject 'Final version of your article published'. The email body features the Elsevier logo and the text: 'Dear Dr. Wijayati, The final version of your article with full bibliographic details is now available online at: <https://doi.org/10.1016/j.heliyon.2021.e06058>. Since your article is being published open access, access to your full article is not restricted in any way. Want to tell the world about your new publication? You

Publish

The screenshot shows the ScienceDirect website page for the article. The article title is 'Potassium Alum [KAl(SO₄)₂·12H₂O] solid catalyst for effective and selective methoxylation production of alpha-pinene ether products'. The authors listed are 'Narik Wijayati^a, R. W. Lubis^b, Benjani Lestari^c, Dia Apungtyas Wulandari^d, F. Wati Melitiani^e, Senda Kartika Rakanna^f, Edi Cahyana^g, Roswina Abdul Wahab^h'. The page includes a 'Download PDF' button, a 'ScienceDirect' logo, and a 'CellPress' logo. The article is categorized as a 'Research article'.

Potassium Alum [KAl(SO₄)₂·12H₂O] Solid Catalyst for Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products

Nanik Wijayati^{a,*}, Lulua Romjanah Lestari^a, Lisa Ayuningtyas Wulandari^a, F. Widhi Mahatmanti^a, Senda Kartika Rakainsa^a, and Edi Cahyono^b, Roswanira Abdul Wahab^{c,d}

^aDepartment of Chemistry, Universitas Negeri Semarang, Semarang 50229, Central Java, Indonesia

^bPerhutani Pine Chemical Industry, Pemalang 52319, Central Java, Indonesia

^cDepartment of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Malaysia

^dEnzyme Technology and Green Synthesis Group, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

*Corresponding author, e-mail: nanikanang@gmail.com

Abstract. Methoxylation is among the technologically relevant processes for producing high-value α -pinene derivative compounds. Consequently, methoxylation of α -pinene catalyzed by potassium alum [KAl(SO₄)₂·12H₂O] is preferable on account of its lower cost and eco-friendliness. In this study, influence of the volume ratio of reactants (α -pinene:methanol = 1:4, 1:7, 1:10), mass of catalyst (0.5, 1, and 1.5 g) and temperature (50, 55, 60, 65°C) on α -pinene methoxylation by the prepared KAl(SO₄)₂·12H₂O was assessed, and the generated products were characterized by GC-MS and FT-IR. The study aimed to identify the best reaction condition that warrants the highest selectivity and percentage conversion of α -pinene by the KAl(SO₄)₂·12H₂O solid catalyst. The study discovered that KAl(SO₄)₂·12H₂O catalyzed an exceptional 98.18% methoxylation production of α -pinene derivatives, *viz.* terpinyl methyl ether (TME), fenchyl methyl ether (FME), and bornyl methyl ether (BME), with the use of 1 g of catalyst and 1:10 volume ratio of reactant, while requiring 360 min of reaction at 65°C. Reaction selectivity was maximum under the aforesaid condition to yield 59.59%, 8.87% and 7.13% of TME, FME and BME, respectively. In a nutshell, the research demonstrated the promising applicability of KAl(SO₄)₂·12H₂O for a more effective methoxylation of α -pinene to obtain reasonable yields of different ether derivatives.

Keywords: α -pinene; methoxylation; potassium alum; catalyst

1. Introduction

The organic compound α -pinene belongs to the terpene group endowed with a reactive ring following the presence of double bonds. The compound is a commonplace constituent in various coniferous tree oils, particular the pine tree [1,2]. The use of α -pinene becomes interesting and highly diverse when the compound is chemically transformed *via* various chemical processes, into an array of high value compounds [3]. Transformations of α -pinene can be conducted beforehand by using different acid catalysts, e.g. activated carbon, Al^{3+} ion exchanger clay, acid oxide, zeolite, activated clays, ion exchange resin, and $\text{TCA}/\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ [4–13]. Among the chemical reactions, methoxylation by addition of methoxide ions, is the frequent choice of reaction to modify functional groups of α -pinene, as well as its applicability. Literature have shown that the α -terpinyl methyl ether compound predominates the α -pinene methoxylation products, alongside minor products, for instance, α -terpinyl methyl ether, β -terpinyl methyl ether, terpinolene, limonene, endo-bornyl methyl ether, β -fenchyl methyl ether, exobornyl methyl ether, bornilene, and camphene [14]. The α -terpinyl methyl ether notably exudes fresh and citrus-like aroma, which makes it desirable as a component in flavors and aromas of perfumes and cosmetic products, plus as aromatic additives for topical medicines and agricultural chemicals, as well as in the food industry [5].

The conventional process of α -pinene methoxylation to produce the α -terpinyl methyl ether involves certain kinds of catalysts, including Al^{3+} ion exchanger clays, mesoporous/microporous carbon, poly(vinyl alcohol) (PVA) containing sulfonic, β -zeolite, MCM-41, PMO, and heteropolyacids immobilized on silica [4,5,14–16]. Nonetheless, it is a well-known fact that the chemical synthetic route of α -terpinyl methyl ether by the aforementioned catalysts is far from efficient, while being environmentally unfriendly [5,17]. There is much to be done with regards to improving the selectivity of the catalytic process, as well as guaranteeing a higher methoxylation production yield of this very much popular derivative of the α -pinene. This study believes that the issue can be resolved with the use of suitable heterogeneous catalysts, in order to facilitate a more benign synthesis of the ether product.

A noteworthy point to indicate here, a heterogeneously catalyzed methoxylation reaction averts the shortcomings typically observed in homogenous catalysis. This is because the former is more environmentally friendly and, its solid form advantageously permits the facile separation of the catalyst from the reaction mixture upon completion

of the reaction. Moreover, specific pore sizes of heterogeneous catalysts can selectively adsorb the reactant molecules for a rapid transformation into products [18–21]. Pertinently, adsorption of a molecule into the cavity of the catalyst occurs more rapidly when their sizes and shapes are similar and compatible [9,10]. As a matter of fact, the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is a promising heterogeneous acid catalyst to catalyze the methoxylation of α -pinene into the value-added α -terpinyl methyl ether.

The $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, or called potassium alum, or potash alum acid, exists in solid form. This solid catalyst has been commonly utilized for several kinds of reactions, such as the synthesis of mono and bis-2-amino-4H-pyrans by reaction of three or five pseudo components from 4-hydroxycoumarin. The catalyst has also been examined for the reaction of malononitrile and aldehyde in ethanol/water media at room temperature and for the Erlenmeyer synthesis, as well as for the transesterification of palm oil [19,22,23]. Considering the relatively versatility of this solid catalysts to mediate a relatively wide variety of reactions, the study believes it may be useful for the methoxylation of α -pinene to produce α -terpinyl methyl ether. Thus, the study aimed to assess the influence of the volume ratio of reactants, mass of catalysts, and reaction temperature on $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to catalyze the selective and high percentage methoxylation production of α -pinene derivatives. This study details the first attempt to carry out methoxylation of α -pinene by the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ solid catalyst. The study objectively wishes to identify the best methoxylation conditions, as well as qualitatively and quantitatively characterize the reaction products using Fourier-Transform infrared spectroscopy and gas chromatograph-mass spectrometry, respectively.

2. Materials and Methods

2.1. Materials

The compound was obtained from Sigma Aldrich, Germany and turpentine oil from KBM Perhutani Pine Chemical Industry Pemalang, Indonesia. Analytic grade methanol and potassium alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] were both procured from Merck. Potassium alum catalyst was prepared in the lab.

2.2. Instrumentations

Quantitative and qualitative analyses of the isolated α -pinene and the corresponding methoxylation products were conducted for GC 23 Agilent 6820 (Version A. 01. 03), HP-5 column and FID detector (detector temperature of 300°C), with Helium as carrier gas.

Injection temperature was 280°C. Column temperature was 70–300°C with initial temperature of 70°C for 10 minutes, increasing gradually until 280°C (5°C/min), and until 300°C (20°C/min). The GC-MS (Shimadzu QP-2010 Plus) equipped with a AOC-20i+s autosampler that operated under the following conditions: column temperature 70°C, injection temperature 200°C with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min, ion source temperature 200°C and interface temperature 240°C. In this analysis, helium (He) gas was used as the carrier with a constant flowrate of 0.1 µL/min. The study would like to note that estimation of the methoxylation products of α -pinene were based on the area beneath each peak. The percentage of each ether product were obtained by dividing the peak area of each α -pinene ether product with that of isolated α -pinene and multiplied by 100. For the qualitative analysis of the reaction products, Fourier-transform spectroscopy was performed on prepared KBr pellets and analyzed on a Perkin Elmer Spectrum Version 10.4.00 for wavenumber region between 4000–400 cm^{-1} were used to quantify the produced ether products.

For catalyst preparation, potassium alum was spray coated over AuPd plates under Argon flow for 90 s to give $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The gas pressure set to 0.5 bar, and the analysis was conducted at 20 mA for the duration of 5-10 mins in AuPd solvent. Scanning electron micrographs (SEM) of the prepared $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was obtained on a Pro X Scanning Desktop Electron Microscope with Energy Dispersive X-Ray (EDX). The catalysts were characterized by X-Ray Diffractometer (D-Max III (Rigaku) dengan radiasi $\text{Cu K}\alpha$ ($\alpha = 1.5378 \text{ \AA}$, 40kV, 30mA).

2.3. General Procedures

Fractional distillation of turpentine oil under reduced pressure was used to prepare the α -pinene starting material in the methoxylation reaction. The catalytic experiments were carried out in a stirred batch reactor with reflux, at different temperatures (50–65°C) and ambient pressure. In a typical experiment, the reactor was loaded with 20 mL of methanol and 1 g of catalyst, followed by the addition of 5 mL of α -pinene and the mixture was stirred for a further 360 min. Samples were taken periodically and analyzed by GC, GC-MS and FTIR. The $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ methoxylation of α -pinene was assessed for the variables of reaction temperature (50, 55, 60 and 65°C), mass of catalyst (0.5; 1; and 1.5 g), and volume ratio of reactants (α -pinene : methanol = 1:4, 1:7, 1:10).

3. Results and Discussions

3.1 Characterization of catalyst

The potassium alum catalyst ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) is an inexpensive, non-toxic, water-soluble, and commercially available compound that can be used in the laboratory without special precautions [19, 22,23]. Alum was characterized using FT-IR, SEM, and XRD. The following Figure 1 illustrates the SEM micrograph of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ solid catalyst prepared by this study. It appears that $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ has a micro structure that is reasonably similar to ammonium aluminum sulfate dodecahydrate [$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$], except the latter has a more rounded shape, showing sizes of between 100–200 μm . However, when heated at a higher temperatures of 1100–1200°C, the overall construct is altered and adopt an elongated oval shape [24].

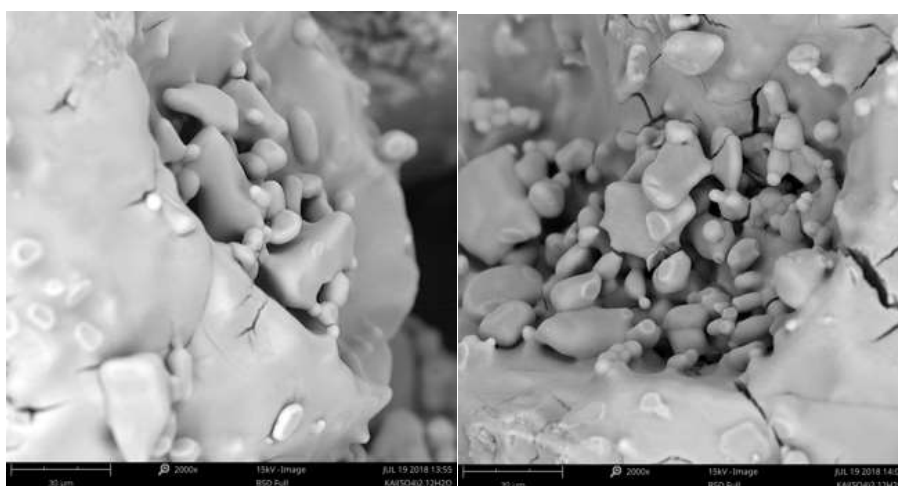


Figure 1. SEM micrograph of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ magnified 2000 x

Composition of the prepared $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was subjected to FT-IR analysis for confirmation. The emergence of absorptions at 3553–3108 cm^{-1} and 1640 cm^{-1} indicated the presence of an O—H group from water (H_2O). Peaks at 1195 cm^{-1} and 1077 cm^{-1} can be allotted to the stretching vibration of the S=O group, while peaks at 933 cm^{-1} and 737 cm^{-1} corresponded to the stretching vibrations of the S—O group and Al—O bond. Pertinently, absorption peaks in the region of 750–400 cm^{-1} are characteristic for the vibration of Al—O [25]. Results of the FT-IR analyses in study, hence affirmed the successful preparation of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is illustrated in Figure 2.

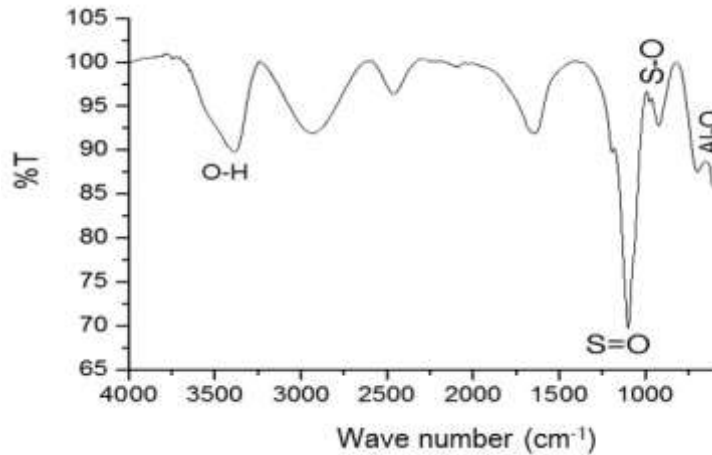


Figure 2. FT-IR spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

The crystallinity of the alum catalyst and the crystal lattice of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst were characterized using X-Ray Diffraction (XRD) technique. The XRD patterns of catalyst are presented in Figure 3. High crystallinity indicating higher catalytic properties, stability at high temperatures, wide porosity, and free of impurities [26]. The main composition of alum sample was identified to be aluminum potassium sulfate. The peak of $2\theta = 21^\circ$; 28° ; and 32° represents the characteristics of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. According to Souza *et al.* (2019), 100% of $\text{KAl}(\text{SO}_4)_2$ anhydrous showed peaks at $2\theta = 25^\circ$; 32° ; and 28° . The 100% of Al_2O_3 compound showed peak at $2\theta = 36^\circ$; 45° ; and 58° . The 68.54% of $\text{K}_2(\text{SO}_4)$ showed peak at $2\theta = 22^\circ$; 32° ; and 45° [27]. According to Abdulwahab *et al.* (2019) $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ has peak of $2\theta = 21^\circ$; 22° ; and 28° . These results are in accordance with PDF File 07.0017. The XRD test results can be concluded that the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ used has high crystallinity but the levels did not reach 100% [28].

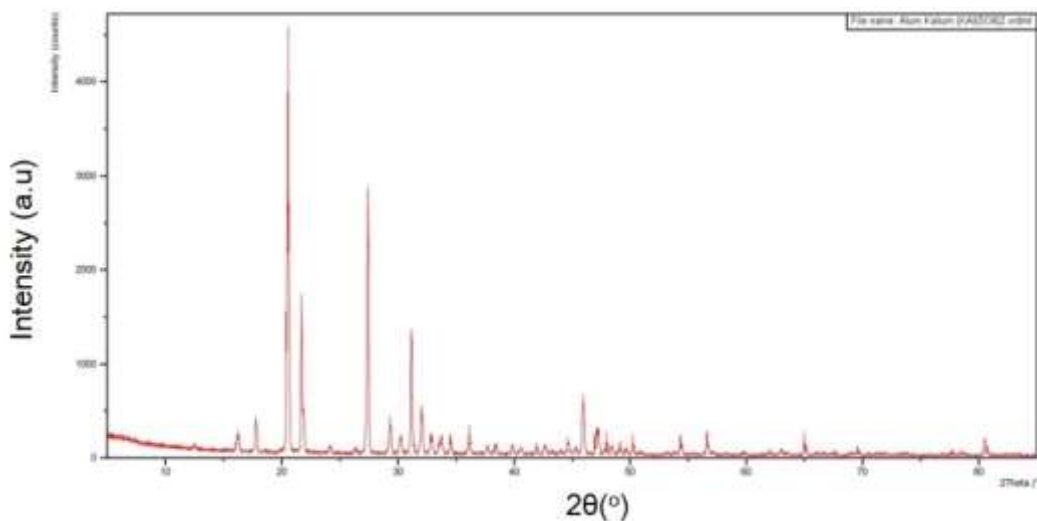


Figure 3. XRD diffractogram of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

3.2 Catalytic test

The effects of three reaction conditions on the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation of α -pinene was examined. The reaction was carried out with a volume ratio of α -pinene and methanol of 1:4, 1:7, and 1:10, 60°C temperature, and amount of potassium alum catalyst of 1 g. The conversion of α -pinene and selectivity of the reaction product with respect to the volume ratio of reactants are shown in Figure 4.

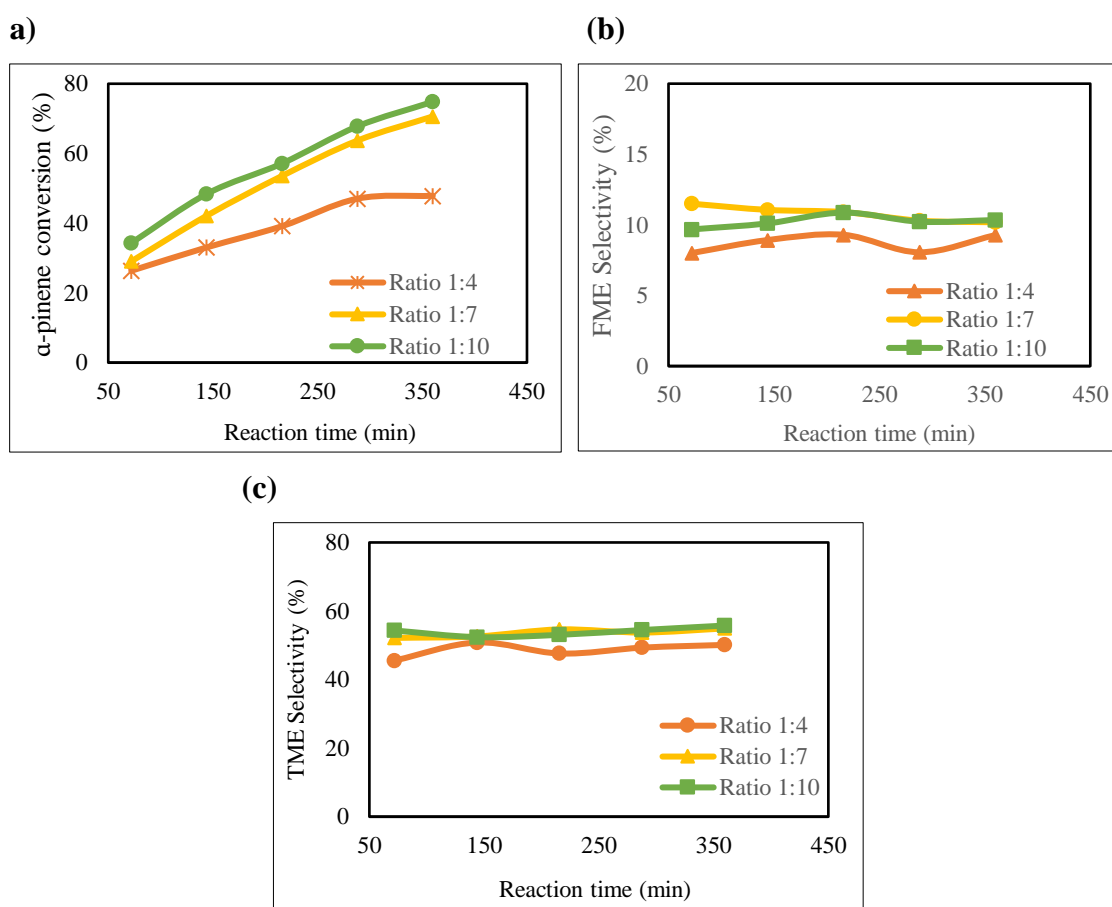


Figure 4. Influence of volume ratio of reactants on the methoxylation of α -pinene: (a) conversion of α -pinene (b) selectivity of FME (c) selectivity of TME

Observably, the concentration of α -pinene decreased from the initial concentration, which was 96.30% (Figure 4a). The volume ratio of reactants affected the outcome of the methoxylation reaction, whereby increasing concentrations of methanol was favorable in the yielding higher amounts of the ether products (Figure 4a). Concentration of products also tended to increase over an extended reaction time and the magnitude of the ratio used. The highest conversion of α -pinene was reached at 74.82% when a volume ratio of reactants 1:10 and reaction time of 360 min was employed for the methoxylation reaction.

This can be explained by the fact that methanol simultaneously acts as the reactant and solvent in the reaction, hence improving integration of the reactions and thereby, accelerating the percentage conversion into the main product, and other ether products [29]. Likewise, by-products of the methoxylation were also formed, due to the isomerization of α -pinene including camphene, limonene, and terpinolene, under the applied reaction condition [30]. The highest selectivity of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation was observed when the substrate reaction ratio was 1:10 with stirring for 360 min at 60°C , to give products terpinyl methyl ether (TME) (55.76%) and fenchyl methyl ether (FME) (10.34%) and, as presented in Figure 4b and 4c.

In addition to reaction time, increase in temperature was seen to cause a general increase in the reaction rate. This subsequently led to the improved percentage conversion of α -pinene into the ether products. It should be noted that the boiling point of methanol was $\sim 338\text{K}$ or 65°C . For this very reason, the suitable temperature for the methoxylation reaction was seen at a lower temperature of 60°C [29]. This is in accordance with the data in Figure 5a, which at temperature of 60°C the α -pinene conversion increased steadily. However, when the reaction temperature was elevated to 65°C , a notable increase in reaction time from 72 minutes to 144 minutes was observed, considering that higher temperature would result in transformation of the reactants into more products. It is pertinent to highlight here, α -pinene conversion catalyzed by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ peaked at 98.18% when the reaction temperature was 65°C .

On the same note, selectivity of the catalyst was the highest at 65°C and employing a 360 min reaction which led to production of 8.7% of FME (Figure 5b), 7.13% of BME (Figure 5c), and 59.59% of TME (Figure 5d). The high selectivity values of TME corroborated a report by Catrinescu's (2013) which explored the methoxylation of limonene through the exchange of acid-activated ions and clay. The study asserted that an increase in reaction temperature as high as 65°C did not lead to a decrease in methoxylation selectivity [31].

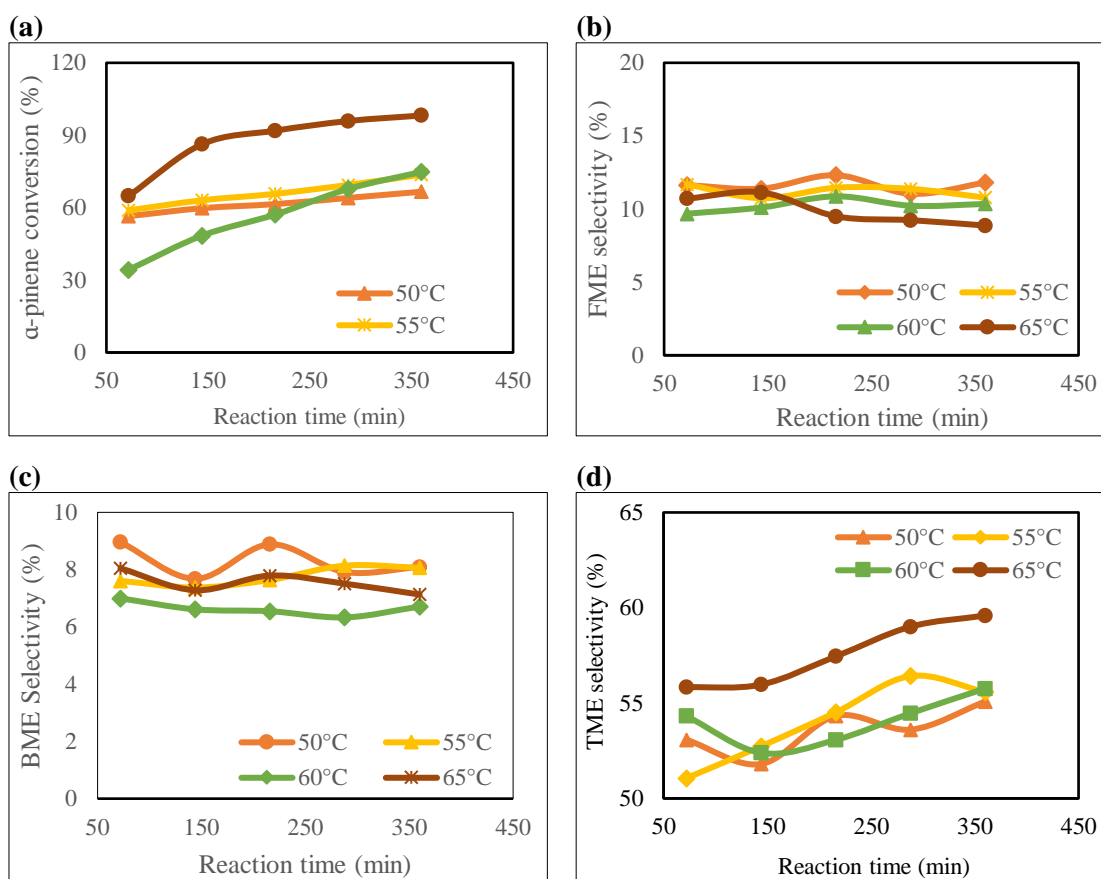


Figure 5. Effect of temperature on α -pinene methoxylation: (a) α -pinene conversion vs time (b) FME selectivity vs time (c) BME selectivity vs time (d) TME selectivity vs time

It was apparent that the concentration of α -pinene declined with increasing reaction time, implying an on-going methoxylation reaction on α -pinene and that a longer reaction time was favourably to warrant higher conversions of α -pinene into the corresponding different α -pinene ether products. Interestingly, the study also noted that the percentages of the different α -pinene ether products tended to fluctuate over the course of the methoxylation reaction, for the exception of TME, which demonstrated a consistent upward trend over time. The outcome seen here, thus insinuated the reversible nature of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation of α -pinene, and that the exact conditions of the reaction must be found in order to obtain high percentages of the desired ether products.

While the percentage of α -pinene being converted into the corresponding ether products exhibited a monotonic upward trend with longer reaction time, selectivity of the reaction, however, fluctuated over the course of the reaction. This was most likely due to the unstable temperature at certain intervals, particularly when the sampling of the

reaction mixture took place. This was probably because the reaction vessel must be open to allow sampling and led to a large drop in the overall reaction temperature. This corresponds to the findings of Hensen et al (1997) which investigated the effects of temperature on the alkoxylation of pinene. They discovered that the maximum alkoxylation conversion was reached at 60°C and t=120 min [14]. The use of a temperature of 80°C led to the reverse reaction that reformed pinene isomers in methanol as the solvent. The same trend was noted for α -pinene conversion in a related system using 100 mg of Al-SAz-1 as the catalyst [5]. As anticipated, increasing the reaction favorably increased the conversion of pinene, under otherwise identical conditions. Reaction selectivity towards the mono-ether, at constant conversion, seems to be largely unaffected by raising the reaction temperature. Likewise, increasing the temperature up to 65°C, nonetheless, did not lead to a decrease in selectivity, as observed in the previous study on limonene methoxylation [31].

Consequently, the corresponding GC chromatograms of sampled reaction mixture uncovered the main ether products being α -terpinyl methyl ether (59.59%), followed by fenchyl methyl ether (8.87%) and bornyl methyl ether (7.13%). The products are also detected when conventionally produced by alkoxylation from pinene or limonene using mineral acids [5]. This also meant that $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ solid catalyst prepared in this study was converting α -pinene into the corresponding ether products, with good success. Also, it was apparent that compositions of the α -pinene ether products increased with increasing amount of catalyst. A noteworthy aspect to highlight here, 0.5 g of the catalyst gave the highest methoxylation selectivity of α -pinene for FME and BME, while the use of 1 g of the catalyst leaned towards a higher production of TME (Table 2).

Table 2. Data on the percentage conversion (% C) and selectivity of methoxylation of α -pinene with variable amount of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst.

Alum (g)	t (min)	α -pinene (%)	%C	Reaction products					
				FME		BME		TME	
				%A	%S	%A	%S	%A	%S
0.5	72	78.70	18.28	2.12	11.60	1.46	7.99	10.04	54.92
	144	68.68	28.68	3.21	11.19	2.12	7.39	15.75	54.92
	216	61.24	36.41	4.05	11.12	2.52	6.92	19.95	54.79
	288	53.75	44.18	4.83	10.93	3.69	8.35	23.78	53.82
	360	48.02	50.13	5.45	10.87	3.62	7.22	27.14	54.14
1	72	71.92	25.32	2.48	9.79	1.93	7.62	13.46	53.16
	144	60.51	37.16	3.87	10.41	2.79	7.51	20.50	55.17
	216	52.87	45.10	4.65	10.31	3.31	7.34	24.53	54.39

	288	44.88	53.40	5.35	10.02	4.09	7.66	28.94	54.19
	360	38.05	60.49	6.05	10.00	4.11	6.79	32.96	54.49
1.5	72	56.00	41.85	4.40	10.51	3.23	7.72	22.39	53.50
	144	45.58	52.67	5.47	10.38	3.76	7.14	28.31	53.75
	216	37.42	61.14	6.23	10.19	4.18	6.84	32.58	53.29
	288	30.38	68.45	6.72	9.82	4.71	6.88	36.61	53.48
	360	24.56	74.50	7.16	9.61	5.20	6.98	39.97	53.65

Note: %C (% Conversion), %A (% Content), %S (% Selectivity), FME (α -Fenchyl Methyl Ether), BME (Bornyl Methyl Ether), and TME (Terpinyl Methyl Ether).

Representative samples of reaction mixture assessed for the mass of catalyst, temperature and volume ratio of reactants were analyzed by FT-IR, to ensure that the data of the formed methoxylation compounds supported the ones detected in the GC-MS analysis (Figure 6).

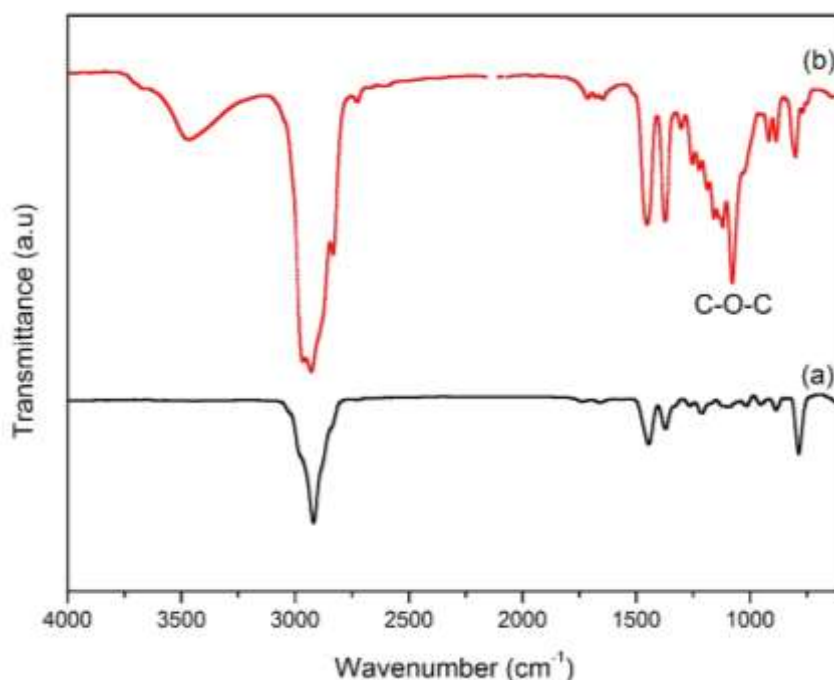
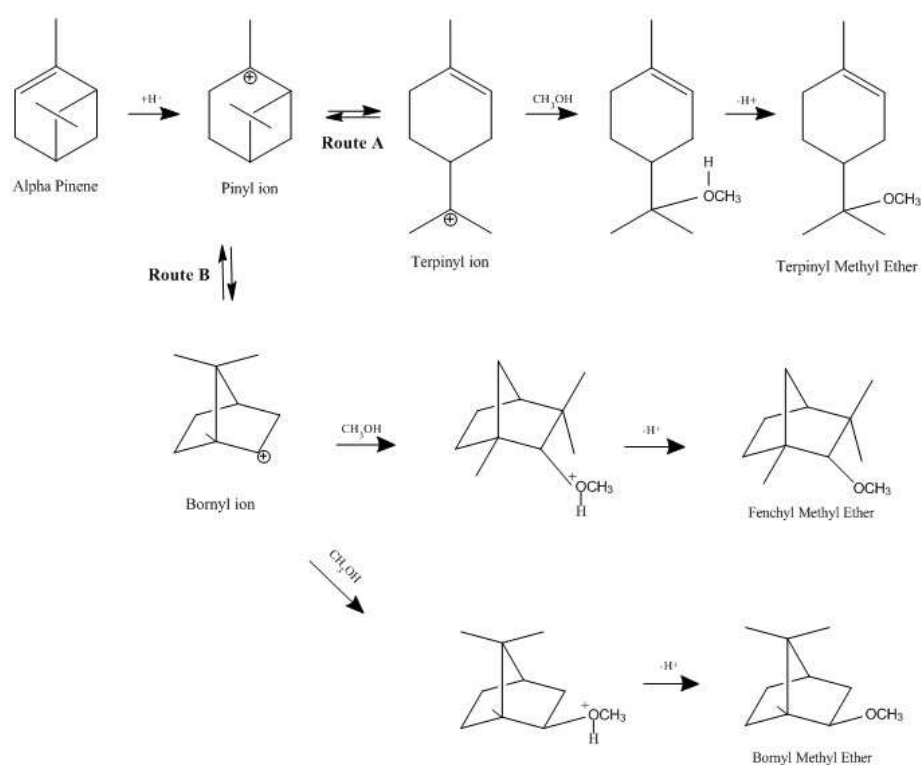


Figure 6. (a) FT-IR spectrum of α -pinene; (b) FT-IR spectrum of reaction products

The mechanisms of the predominant methoxylated products of α -pinene seen in this study are presented Scheme 1. The mechanism begins with the protonation of the double bond of α -pinene to give the pinyl ion, under an acidic condition from the hydrolysis of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst. According to literary review, the process catalyzed by acid (potassium alum) takes place through two routes, route A is obtained by bornyl ion and route B is obtained by ionized ion [4]. The alkoxylation of α -pinene initiated by protonation of the α -pinene double bond to form the pinyl ion. The reaction then proceeds via two parallel pathways depending on the pinyl ion rearrangement, one of which

resulting in bicyclic products and the other in monocyclic products. Bornyl ions and terpinyl ions present in the reaction mixture then react with methanol, and are consequently deprotonated to yield the ether products *viz.* TME, BME, and FME. Catrinecu et al (2015) also stated that pinene reacted with methanol over the acid sites available on the clay surface to form terpinyl methyl ether, TME, as the main reaction product. Other compounds were also identified in the complex reaction mixture, which include bicyclic ethers (fenchyl methyl ether and bornyl methyl ethers) [5]. Several reaction products were thought to be associated with irreversible rearrangements of the pinyl ion [15]. This was because the pinyl ion can rearrange into the bornyl ion, and after methanol addition, and when bornyl methyl ether, and fenchyl methyl ether are formed. The pinyl ion can also rearrange into the terpinyl ion upon formation terpinyl methyl ether, in which methanol was employed as the solvent.



Scheme 1. The mechanism of α -pinene methoxylation

4. Conclusion

The study successfully established the best conditions for the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation of α -pinene to give satisfactorily afford the high percentage conversion of α -pinene into its ether derivatives. It was discovered that the highest selectivity values of the α -pinene methoxylation reaction was achievable when the

methoxylation condition was carried out using 1 g of catalyst, volume ratio of reactant of 1:10, with the temperature and reaction time set to 65°C and 360 min, respectively. Most importantly, the reaction yielded 59.59% of TME, 8.87% of FME, 7.13% of BME, with an exceptional percentage conversion of α -pinene at 98.18%. Thus, the study demonstrated that $KAl(SO_4)_2 \cdot 12H_2O$ was an effective and suitable solid catalyst for α -pinene methoxylation. Further research on the catalyst is still needed to improve the selectivity of this solid catalyst, for increasing its efficiency to catalyze the methoxylation of α -pinene.

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Author Contributions

N.W. designed, performed the experiments, wrote the paper, and analyzed the data; L.R.L. and L.A.W. helped with performing the experiments and assisted in data analysis; F.W.M. and S.K.R. carried out the SEM and FT-IR analysis, and helped with the interpretations; E.C. provided the materials and RAW helped with the conception and editing of the manuscript. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest: The authors declare no conflict of interest.

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Potassium Alum [KAl(SO₄)₂·12H₂O] Solid Catalyst for

Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products

Nanik Wijayati^{a,*}, Lulua Romjanah Lestari^a, Lisa Ayuningtyas Wulandari^a, F. Widhi Mahatmanti^a, Senda Kartika Rakainsa^a, Edi Cahyono^b, and Roswanira Abdul Wahab^{c,d}

^a Department of Chemistry, Universitas Negeri Semarang, Semarang 50229, Central Java, Indonesia

^b Perhutani Pine Chemical Industry, Pemalang 52319, Central Java, Indonesia

^c Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Malaysia

^d Enzyme Technology and Green Synthesis Group, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

*Corresponding author, e-mail: nanikanang@gmail.com

Abstract. Methoxylation is ~~among the technologically relevant processes for producing a relevant technological process applied in the production of high-value~~ α -pinene derivative compounds. ~~In this study, we report~~ ~~This report investigates~~ the use of potassium alum [KAl(SO₄)₂·12H₂O] ~~as a catalyst~~ in the methoxylation of α -pinene, at 65°C, ~~being the~~. ~~The main reaction product of~~ α -terpinyl methyl ether (TME) ~~the main product. The main reaction products and~~), alongside the intermediates ~~were was~~ identified ~~by using GC-MS. The~~ ~~Furthermore, the~~ influence of various ~~reaction conditions, to maximize conditions on the maximization of~~ α -pinene conversion and selectivity, ~~selectivity~~ was ~~studied over potassium alum [KAl(SO₄)₂·12H₂O] catalyst also evaluated. When the reaction was performed for 6 h at 65°C, the~~ ~~The results show~~ conversion reached 98.18% with 59.59% selectivity towards the mono ether, TME, ~~using 65°C treatment for 6 h. Similar conversions and selectivities required up to 20 h over~~ ~~However, AISAz-1 and other solid acid catalysts require exposure for up to 20 h to achieve similar outcome.~~

Keywords: α -pinene; methoxylation; potassium alum; catalyst

1

2 1. Introduction

3 The organic compound α -pinene belongs to the terpene ~~group endowed with~~
4 ~~group, characterized by~~ a reactive ~~ring following~~ring, alongside the presence of double
5 bonds. ~~The compound~~This is a commonplace constituent ~~in of~~ various coniferous tree
6 oils, ~~particular especially~~ the pine tree [1,2]. ~~The use of α -pinene becomes,~~ possessing
7 interesting and highly diverse ~~when the compound is chemically transformed via~~
8 ~~various applications, particularly after~~ chemical ~~processes, transformation~~ into an array
9 of high value compounds [3]. ~~Transformations of α -pinene can be~~The modification is
10 initially conducted ~~beforehand by~~ using different acid catalysts, e.g. activated carbon,
11 Al^{3+} ion exchanger clay, acid oxide, zeolite, activated clays, ion exchange resin, and
12 TCA/ $ZrO_2 \cdot nH_2O$ [4–13]. ~~Among the chemical reactions~~In addition, methoxylation ~~by~~
13 through the addition of methoxide ~~ions,~~ ions is the most frequent ~~choice of and~~
14 applicable reaction ~~to modify functional groups~~ choice for the modification of α -pinene,
15 ~~as well as its applicability~~functional groups. ~~Literature have shown that the~~Previous
16 literature showed α -terpinyl methyl ether compound ~~predominates as~~ the α -pinene
17 ~~methoxylation~~predominant products, ~~alongside followed by other~~ minor ~~products~~yields,
18 ~~for instance,~~ including α -terpinyl methyl ether, β -terpinyl methyl ether, terpinolene,
19 limonene, endo-bornyl methyl ether, β -fenchyl methyl ether, exobornyl methyl ether,
20 bornilene, and camphene [14]. ~~The~~Specifically, α -terpinyl methyl ether notably exudes
21 fresh and citrus-like aroma, ~~which makes it desirable with peculiar desirability~~ as a
22 component in flavors and aromas of perfumes and cosmetic products. Also, plus there
23 have been applications as an aromatic ~~additives for~~additive in topical ~~medicines and~~
24 medicines, agricultural chemicals, ~~as well as in and~~ the food industry [5].

25 The conventional ~~process of~~ α -pinene methoxylation ~~to produce the α -terpinyl~~
26 ~~methyl ether~~process involves ~~certain kinds the use of~~ certain catalysts, including Al^{3+}
27 ion exchanger clays, mesoporous/microporous carbon, poly(vinyl alcohol) (PVA)
28 containing sulfonic, β -zeolite, MCM-41, PMO, and heteropolyacids immobilized on
29 silica [4,5,14–16]. ~~Nonetheless, it is a well known fact that~~However, the chemical
30 synthetic route ~~of for~~ α -terpinyl methyl ether ~~by the aforementioned~~ catalysts is far
31 from efficient, ~~while being and also~~ environmentally unfriendly [5,17]. ~~There~~This is
32 much due to be done with regards to improving the ~~poor~~ selectivity ~~of in~~ the catalytic
33 process, ~~as well as guaranteeing a and inability to guarantee~~ higher ~~methoxylation~~

1 production yield of this very much popular derivative of the α -pinene yield. This study
2 believes that the issue can be resolved with the use of focuses on resolving these
3 challenges by using suitable heterogeneous catalysts, ~~in order~~ to facilitate a more
4 benign synthesis of the ether products synthesis.

5 ~~A noteworthy point to indicate here~~ Interestingly, a ~~heterogeneously catalyzed~~
6 ~~methoxylation reaction this approach~~ averts the shortcomings typically observed in
7 homogenous catalysis. ~~This is because the former is,~~ featuring more environmentally
8 friendly ~~and~~ properties. Also, ~~its~~ the solid form advantageously permits the facile
9 separation of ~~the~~ catalyst from the reaction mixture upon completion of termination,
10 and the reaction. Moreover, specific pore sizes ~~of heterogeneous catalysts can~~
11 selectively adsorb the reactant ~~molecules for molecules~~. This prompts a rapid
12 transformation into products [18–21]. ~~Pertinently, adsorption of a molecule into the~~
13 ~~cavity of the catalyst occurs more rapidly when their sizes and the rapid activity results~~
14 from similarity in size and shapes are similar and compatible, alongside compatibility
15 [9,10]. ~~A matter of fact~~ In addition, the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is identified as a promising
16 heterogeneous acid ~~catalyst to catalyze the methoxylation of α -pinene into catalyst~~
17 needed for the production of value-added α -terpinyl methyl ether from α -pinene.

18 ~~The $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$~~ This is a solid state compound, ~~or also~~ called potassium
19 alum, or potash alum acid, ~~exists in solid form~~. ~~This solid catalyst has~~ Furthermore,
20 they have commonly been commonly utilized for applied in several kinds of reactions,
21 such as including the synthesis of mono and bis-2-amino-4H-pyrans ~~pyrans~~, by reaction
22 of reacting three or five pseudo components from 4-hydroxycoumarin. ~~The~~ Also, the
23 catalyst has ~~also~~ been examined for in the reaction of malonitrile and aldehyde in
24 ethanol/water media at room temperature ~~and, as well as~~ for the Erlenmeyer synthesis,
25 as well as for and the transesterification of palm oil [19,22,23]. ~~Considering~~ Due to the
26 relatively versatility of relative versatility, this ~~solid catalysts to mediate a relatively~~
27 wide variety study assumes the possible usefulness of reactions, potassium alum
28 [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] catalyst in the study ~~believes it may be useful for the~~
29 methoxylation of α -pinene to produce α -terpinyl methyl ether.

30 ~~In this work, we report the α -pinene methoxylation over potassium alum~~
31 ~~[$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] catalyst~~. The influence of various ~~reaction~~ parameters, such as,
32 volume ratio of including α -pinene to methanol/methanol volume ratio, temperature, and

1 catalyst loading on the catalytic activity of the catalyst, were also studied. This approach is known to be catalytic activity frequently
2 adopted in organic reactions involving polar reagents.

4 **2. Materials and Methods**

5 *2.1. Materials*

6 α -Pinene standard and anhydrous methanol were obtained from Sigma Aldrich,
7 while Turpentine oil was ~~obtained~~, acquired from KBM Perhutani Pine Chemical
8 ~~Industry-Industry~~, Pemalang, Indonesia. The Potassium alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] used
9 was procured from Merck.

11 *2.2. Instrumentations*

12 Quantitative and qualitative analyses of the isolated α -pinene and the
13 corresponding methoxylation products were conducted ~~for~~ with GC 23 Agilent 6820
14 (Version A. 01. 03), HP-5 column and FID detector (detector temperature of 300°C),
15 with Helium as carrier gas. ~~Injection-The injection~~ temperature was 280°C. ~~Column~~
16 ~~temperature~~, while the column was ~~70-300°C with~~ set at an initial temperature of 70°C
17 for 10 minutes, ~~increasing-increased~~ gradually ~~until-to~~ 280°C (5°C/min), and ~~until-up to~~
18 300°C ~~(C. at 20°C/min)~~. ~~The~~ Furthermore, GC-MS (Shimadzu QP-2010 Plus) equipped
19 with a AOC-20i+s autosampler ~~that-was~~ operated under the following conditions:
20 column and injection temperature of 70°C and 200°C, ~~injection temperature 200°C~~
21 respectively with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min,
22 ion source and interface temperature of 200°C and interface temperature 240°C. ~~In this~~
23 analysis, correspondingly. This analysis required the use of helium (He) gas ~~was used as~~
24 the ~~carrier with carrier~~, at a constant flowrate of 0.1 $\mu\text{L}/\text{min}$. ~~The study would like to~~
25 ~~note that estimation of~~, and the methoxylation ~~products of α pinene result~~ were
26 estimated based on the area beneath each peak. ~~The~~ Furthermore, the percentage of each
27 ether product ~~where obtained was achieved~~ by dividing the respective peak area ~~of each~~
28 ~~α pinene ether product with that of the~~ isolated α -pinene, and multiplied by 100. ~~For the~~
29 The qualitative analysis ~~of the reaction products, involved performing~~ Fourier-transform
30 spectroscopy ~~was performed~~ on prepared KBr ~~pellets-pellets~~, and ~~analyzed-subsequently~~
31 evaluated on a Perkin Elmer Spectrum Version 10.4.00 ~~for~~, in the wavenumber region
32 between ~~of~~ 4000–400 cm^{-1} ~~were used to quantify the produced ether products~~.

1 2.3. Procedures

2 2.3.1 Preparation of the catalysts

3 For catalyst preparation, potassium alum was spray coated over AuPd plates
4 under Argon flow for 90 s to ~~give-generate~~ $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The gas pressure ~~was~~ set
5 to 0.5 bar, and the analysis was conducted at ~~at~~ 20 mA for ~~the duration of~~ 5-10 mins in
6 AuPd solvent. The catalyst was ~~then~~ characterized ~~by using~~ X-Ray Diffractometer (D-
7 Max III (Rigaku) ~~), with radiation of~~ Cu $\text{K}\alpha$ ($\lambda = 1.5378 \text{ \AA}$, 40kV, 30mA). ~~The~~
8 ~~radiation. Furthermore,~~ morphology and mean crystallite size ~~of the catalyst~~ was
9 determined by scanning electron microscopy (SEM) ~~in a~~ with JEOL JFC-1600 and
10 JSM-6701F equipments. ~~Scanning electron micrographs (SEM) of the prepared~~
11 ~~$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was obtained on~~ The results were extracted from a Pro X Scanning
12 Desktop Electron ~~Microscope~~ Microscope, with Energy Dispersive X-Ray (EDX).

13
14 2.3.2 Isolation of α -pinene

15 ~~The~~ fractional distillation of turpentine oil ~~was used~~ under reduced pressure ~~was~~
16 ~~used~~ to prepare the α -pinene starting ~~material in the methoxylation reaction~~ material.
17 ~~The result of isolation process was analyzed using GC-MS and FT-IR.~~ Hasil isolasi
18 dianalisis menggunakan GC-MS dan FT-IR.

Commented [SK1]: Already translated

Commented [e2]: Translate please

19
20 2.3.3 Catalytic experiments

21 The catalytic experiments were ~~carried out~~ performed in a stirred batch reactor
22 with reflux, at different temperatures (50-65°C) and ambient pressure. ~~Before~~ Prior to
23 the reaction, a known amount of catalyst powder was thermally activated in an oven at
24 110°C, ~~in oven~~ and then placed in a desiccator at room temperature (15 min) to cool
25 and prevent rehydration. ~~After being cooled at room temperature (15 min) the catalyst~~
26 ~~powder~~ This was quickly transferred into the reaction vessel containing 20 mL dry
27 ~~methanol, methanol and~~ preheated at the reaction temperature, ~~—,~~ followed by the
28 addition and mixture of 5 mL of α -pinene ~~and the mixture was stirred by stirring for a~~
29 ~~further another~~ 360 min. ~~Samples~~. ~~Therefore, samples were taken periodically~~
30 collected periodically, and the catalyst was removed by syringe filtration. ~~The,~~ using
31 a filter ~~had with~~ no influence impact on the ~~reaction products and products~~. Also, no
32 further reaction ~~took place was reported~~ during storage. ~~The reaction products,~~ and
33 the yields were identified by using GC-MS (Shimadzu QP-2010 Plus) and quantified

Commented [SK3]: Right, it is 360 minutes

Commented [e4]: Is this 360 or 36

1 by). In addition, GC Agilent 6820 with FID detector (T 300°C), using a HP-5 column
2 with Helium as carrier gas was adopted for quantification. The chromatogram peaks of
3 chromatogram were identified by comparing retention times and gas chromatography-
4 mass spectrometry.

5 In order to optimize the reaction conditions, conditions were optimized by
6 evaluating the effect of different parameters (parameters, including reaction
7 temperature (50, 55, 60 and 65°C), catalyst loading (0.5; 1; and 1.5 g), and volume
8 ratio of reactants (α -pinene : methanol = methanol of 1:4, 1:7, 1:10) on during the
9 methoxylation of α -pinene over $KAl(SO_4)_2 \cdot 12H_2O$ catalyst was studied process. The
10 selectivity of Therefore, α -terpinyl methyl ether selectivity, and conversion of α -
11 pinene conversion were calculated by using the external standard standardized
12 method, the standard with curves was prepared by detecting different concentration of
13 the standard solution. The In addition, the conversion of α -pinene (X) and the
14 selectivity (S) of α -terpinyl methyl ether were calculated using the following formula:

$$15 \quad X = \frac{\% \text{ converted alpha pinene}}{\% \text{ initial alpha pinene}}, \quad S = \frac{\% \text{ desired product}}{\% \text{ conversion of alpha pinene}}$$
$$16 \quad X = \frac{\% \text{ converted alpha pinene}}{\% \text{ initial alpha pinene}}, \quad S = \frac{\% \text{ desired product}}{\% \text{ conversion of alpha pinene}}$$

17 3. Results and Discussions

18 3.1 Characterization of catalyst

19 The potassium alum catalyst ($KAl(SO_4)_2 \cdot 12H_2O$) is an inexpensive, non-
20 toxic, water-soluble, and commercially available compound that can be frequently used
21 in the laboratory without with no special precautions [19, 22,23]. Alum was
22 characterized using Furthermore, characterization involved FT-IR, XRD, as well as
23 SEM, and XRD. The following Figure 1 illustrates with micrograph illustrated in figure
24 1, showing reasonable similarities with the SEM micrograph of $KAl(SO_4)_2 \cdot 12H_2O$
25 solid catalyst prepared by this study. It appears that $KAl(SO_4)_2 \cdot 12H_2O$ has a micro
26 structure that is reasonably similar to of ammonium aluminum sulfate dodecahydrate
27 [$NH_4Al(SO_4)_2 \cdot 12H_2O$]. However, except the latter has comprise a more rounded
28 shape, showing sizes with a size range of between 100–200 μm . However, when heated
29 at a at At higher temperatures of 1100-1200°C, the overall construct of
30 $KAl(SO_4)_2 \cdot 12H_2O$ is altered and adopt altered, therefore generating an elongated oval
31 shape [24].
32

1 Infrared spectroscopy is often used ~~for characterization of~~ to characterize solid
2 state ~~catalysts due to its catalysts, resulting from the~~ flexible nature ~~identify during the~~
3 ~~identification of~~ surface functional groups, ~~both~~ organic ~~or and~~ inorganic. ~~The Figure 2~~
4 ~~shows the~~ spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ~~is illustrated in Figure 2.~~ ~~Peaks~~ $12\text{H}_2\text{O}$, with
5 ~~peaks~~ at 1195 cm^{-1} and 1077 cm^{-1} ~~is indicating~~ the stretching vibration of ~~the~~ $\text{S}=\text{O}$
6 group, while ~~the peaks at~~ 933 cm^{-1} and 737 cm^{-1} are related to the stretching vibrations
7 of ~~the~~ $\text{S}-\text{O}$ and $\text{Al}-\text{O}$ bonds, respectively. ~~Assignments~~ ~~The assignment~~ of various
8 bands to corresponding vibrational modes of the functional groups present in ~~alums and~~
9 ~~alums, as well as~~ the related aluminum bearing compounds are sufficiently detailed in
10 the literature. ~~A~~ Furthermore, absorption peaks in the region of $750\text{--}400\text{ cm}^{-1}$ ~~are~~
11 ~~characteristic for~~ indicate the vibration of $\text{Al}-\text{O}$ [25]. ~~Observable from~~ ~~Fig. 2, the~~ ~~2~~
12 ~~shows~~ sharp sulfate (SO_4^{2-}) bands in $468\text{--}471\text{ cm}^{-1}$, $603\text{--}608\text{ cm}^{-1}$, $657\text{--}686\text{ cm}^{-1}$, 1104--
13 1115 cm^{-1} and $1237\text{--}1247\text{ cm}^{-1}$ corresponds to symmetrical SO_4^{2-} bending mode,
14 degeneration of asymmetric bending, symmetrical bending, degenerate symmetric
15 stretching and degenerate asymmetric stretching ~~modes of~~ SO_4^{2-} modes, respectively
16 [23].

17 The crystallinity ~~of the alum catalyst and the~~ crystal lattice of ~~the~~
18 $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ~~catalyst~~ $12\text{H}_2\text{O}$ were ~~characterized~~ evaluated using X-Ray
19 Diffraction (XRD) technique. ~~The XRD, and the deduced~~ patterns ~~of catalyst~~ are
20 presented in Figure 3. ~~It is important to note here that a~~ Furthermore, high crystallinity
21 ~~indicates a high~~ implies greater catalytic properties, ~~as well as and~~ better stability at
22 high temperatures, alongside wide porosity, and ~~free of impurities~~ purity [26]. The main
23 composition of alum ~~sample~~ was identified to be aluminum potassium ~~sulfate~~ sulfate,
24 based on the characteristic peaks at $2\theta = 21^\circ$; 28° ; and 32° ~~represents the characteristics~~
25 ~~of~~ $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. ~~The~~ Based on the diffractogram in Figure 3, Al_2O_3 is represented
26 by 2θ peaks at 36° ; 46° and 58° , while the 68.54% ~~of~~ $\text{K}_2(\text{SO}_4)$ ~~showed~~ was designated
27 at 2θ ~~peaks that corresponded,~~ corresponding to 22° ; 32° ; and 45° ~~on the diffractogram~~
28 ~~(Figure 3).~~ Most importantly, the results seen here ~~The result is~~ substantially
29 corroborated by Souza *et al.* ~~which assessed,~~ where a similar compound was assessed
30 [27]. ~~The,~~ and the 2θ peaks ~~seen~~ observed at 21° , 22° ; and 28° ~~accorded~~ were
31 congruent with the PDF File 07.0017 for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. ~~The diffractogram~~
32 therefore In addition, the diffractogram affirmed the samples' high crystallinity ~~of~~

1 $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, matching a recent report ~~by of from~~ another analogous compound
2 ~~investigated~~ by Abdulwahab *et al.* (2019) [28].

3.2 Catalytic test

3.2.1 Effect of volume ratio of α -pinene and methanol

6 The effect of ~~the volume ratio of vried~~ α -pinene and methanol ~~volume ratio~~ on
7 the selectivity to α -terpinyl methyl ether was also ~~studied. At the different volume ratio~~
8 ~~of α -pinene evaluated, and methanol considered,~~ good selectivity values (about 56%, at
9 conversion of α -pinene 75%) were obtained. ~~The reaction was carried out with a~~
10 ~~volume ratio of α -pinene and methanol of. The ratios investigated were 1:4, 1:7, and~~
11 1:10, at 60°C temperature, ~~and with~~ 0.1 g of potassium alum catalyst. ~~The conversion of~~
12 ~~, while α -pinene conversion and selectivity of the reaction product with respect to the~~
13 ~~volume ratio of reactants are relative product selectivity is~~ shown in Figure 4.

14 ~~Figure 4a shows a decline in the initial concentration of α -pinene decreased from~~
15 ~~the initial concentration, which was 96.30% (Figure 4a). The. The reactant volume ratio~~
16 ~~of reactants affected ratio also influenced the outcome of the methoxylation~~
17 ~~reaction reactions, whereby increasing concentrations thus a higher concentration of~~
18 methanol ~~was favorable in the yielding higher led to greater~~ amounts of ~~the ether~~
19 ~~products yield~~ (Figure 4a). ~~Concentration of products also tended to increase. Also, the~~
20 ~~production increased over an extended reaction time and the magnitude of the ratio~~
21 ~~used. The duration, and the highest conversion of α -pinene was reached at conversion~~
22 ~~(74.82% when a volume ratio of reactants) was attained at 1:10 ratio and reaction time~~
23 of 360 min ~~was employed for the methoxylation reaction. This can be explained by is~~
24 ~~possibly due to the fact that ability for methanol to simultaneously acts act as the~~
25 reactant and ~~solvent in solvent, thus augmenting the reaction integrations, hence~~
26 ~~improving integration of the reactions and thereby, accelerating the percentage~~
27 conversion into the main ~~ether~~ product, and ~~other ether products others~~ [29].
28 ~~Likewise Furthermore, by-products of the methoxylation were also formed, due to the~~
29 ~~isomerization of formed from α -pinene isomerization, including camphene, limonene,~~
30 and terpinolene, under the ~~applied~~ reaction condition ~~applied~~ [30]. The highest
31 selectivity of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation was observed when ~~the at~~
32 ~~a substrate reaction ratio was 1:10 of 1:10, with stirring for 360 min at 60°C, to give,~~

1 Figure 4b and c show the most prominent products to be terpinyl methyl ether (TME)
2 (55.76%) and fenchyl methyl ether (FME) (10.34%)and, as presented in Figure 4b and 4e.

3 4 3.2.2 Effect of reaction temperature

5 The effect of ~~the reaction~~ temperature on the selectivity to α -terpinyl methyl ether
6 was also studied. ~~The catalysed reactions were carried out at different temperatures~~
7 ~~(investigated, by exposing the reactions to 50, 55, 60 and 65°C),~~ over 1 g of
8 ~~KAl(SO₄)₂·12H₂O catalyst while the catalyst, and constant~~ α -pinene: methanol volume
9 ~~ratio and the catalyst loading were kept constant ratio.~~ As anticipated, ~~α -pinene~~ the
10 ~~percentage~~ conversion increased with the rise in temperature, ~~under otherwise identical~~
11 ~~conditions.~~ The influence of the reaction temperature on pinene conversion and ~~This~~
12 ~~influence, alongside the~~ selectivity towards the mono-ether products is presented in Fig.
13 5a, 5b and 5c. ~~At the different temperatures considered,~~ Also, the variations were
14 ~~considered capable of generating~~ good selectivity values (of about 60% ether product, at
15 ~~conversion of from 98% α -pinene 98%) were obtained conversion.~~

16 Increase in temperature was seen to cause a general increase in the reaction rate.
17 This subsequently led to the improved percentage conversion of α -pinene into the ether
18 products. It should be noted that the ~~The~~ boiling point of methanol was 65°C. ~~For this~~
19 ~~very reason, the,~~ hence 60°C was determined as suitable temperature for the
20 methoxylation reaction was seen at a lower temperature of 60°C [29]. This is in
21 accordance with the data in Figure 5a, ~~which at temperature of 60°C the where~~ α -pinene
22 conversion steadily increased steadily at 60°C. However, ~~when the reaction temperature~~
23 ~~was elevated to 65°C,~~ a notable increase elevation in reaction time from 72 to 144
24 minutes was ~~observed~~ observed at 65°C, considering ~~that higher temperature would~~
25 ~~result in transformation~~ the possibility of the reactants into generating more
26 ~~products~~ products at higher temperature. It is pertinent to highlight here, ~~Hence, the peak~~
27 ~~conversion of~~ α -pinene conversion catalyzed by KAl(SO₄)₂·12H₂O peaked at ~~was~~
28 98.18% ~~when the reaction temperature was at~~ 65°C.

29 ~~The catalyst~~ selectivity of the catalyst was the highest at 65°C and employing a
30 C, over reaction duration of 360 min ~~reaction which led,~~ leading to the production of
31 8.7% of FME (Figure 5b), 7.13% of BME (Figure 5c), and 59.59% of TME (Figure 5d).
32 ~~The same~~ Similar trend was observed for limonene conversion in the methoxylation of
33 limonene through the exchange of acid-activated ions and clay ~~exvangers~~ [31].

1 ~~Increasing~~ Accordingly, the ~~increase in~~ temperature ~~up to 65°C, did not lead to~~
 2 ~~prevented a decrease~~ decline in selectivity, ~~as observed in the previous study on~~
 3 ~~limonene methoxylation~~ [31]. This corresponds to the findings of Hensen *et al* (1997)
 4 ~~which investigated~~, on the effects of temperature on ~~pinene alkoxylation, and the~~
 5 ~~alkoxylation of pinene. They discovered that the maximum alkoxylation conversion was~~
 6 ~~reached~~ attained at 60°C and t=120 min [14]. ~~The use~~ However, temperatures of a
 7 ~~temperature of 80°C led to the~~ have been affiliated with reverse reaction that reformed
 8 ~~reactions, characterized by the reformation of pinene isomers in methanol as the~~
 9 ~~methanol solvent. The same~~ In addition, similar trend was ~~noted for~~ observed in α -
 10 pinene conversion in a ~~related system~~ systems, using 100 mg of Al-SAz-1 as ~~the~~
 11 catalyst [5]. ~~As anticipated, increasing the reaction favorably increased the conversion~~
 12 ~~of pinene and is more favorable, under otherwise~~ compared to other identical conditions.
 13 ~~Reaction~~ The reaction selectivity ~~towards the for~~ mono-ether, ~~at constant conversion,~~
 14 seems to be largely unaffected by ~~raising the reaction~~ increase in temperature. Likewise,
 15 ~~increasing the temperature~~ up to 65°C, ~~nonetheless~~ at constant percentage conversion.
 16 ~~Also, did not lead to a decrease~~ there was no decline in selectivity, as observed in ~~the~~
 17 previous ~~study on~~ studies concerning limonene methoxylation [31].

18 Table 1 ~~presents~~ is a summary of ~~the~~ α -pinene methoxylation activity ~~of in~~ the
 19 ~~presence of various catalysts that have been investigated~~ catalysts, as shown in ~~the~~
 20 previous literatures. ~~Highest~~ The highest yield was obtained ~~over using~~ AlSAz-1 ~~in the~~
 21 ~~present work~~ under a mild reaction ~~condition~~ conditions.

22 **Table 1.** The summary of α -pinene methoxylation activity in the presence of various
 23 catalysts in a batch reactor

Catalysts	Temp °C	Reaction Time (h)	Conversion (%)	Selectivity (%)	Literature
AlSAz-1	60	1	65	65	Catrinescu <i>et al.</i> (2015) [5]
AlSAz-1	40	20	71	91	Catrinescu <i>et al.</i> (2013) [31]
CB, CMN, CNorit	60	250	55-75	50-55	Matos <i>et al.</i> (2014) [4]
PW2-S	60	27	40	60	Pito <i>et al.</i> (2010) [32]
PVSSA-20	60	24	40	60	Pito <i>et al.</i> (2009) [15]
PMO-SO3H-g	100	-	90	45	Castanheiro <i>et al.</i> (2008) [16]
Beta Zeolite	40	5	92	54	Hensen <i>et al.</i> (1997) [14]

24
 25 3.2.3 Effect of the catalyst loading

The effect of the catalyst loading on the selectivity of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to α -terpinyl methyl ether was also studied. The reaction was carried out with, using a catalyst loading of 0.5, 1, and 1.5 g, 60°C temperature, and volume ratio of α -pinene and methanol volume ratio of 1:10. The Figure 4 shows the conversion of α -pinene and selectivity of the reaction product with respect to the volume ratio of reactants are shown in Figure 4. It was observed that selectivity, where the catalytic experiments over different amount of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ treatments yield good values amount of α -terpinyl methyl ether selectivity (about 54% and with 75% α -pinene conversion of 75% conversion). These products are also detected when conventionally produced by after the conventional alkoxylation from of pinene or limonene using with mineral acids [5]. Hence, the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ solid catalyst prepared in this study was converting successfully converted α -pinene into the corresponding expected ether products, with good success. Also, it there was apparent that compositions of an upsurge in yield following an increase in the α -pinene ether products increased with increasing amount quantity of catalyst catalyst used. A noteworthy aspect to highlight here Interestingly, 0.5 g of the catalyst gave ensured the highest methoxylation selectivity of α -pinene selectivity for FME and BME, while the use of 1 g of the catalyst leaned towards a prompted higher production of TME (Table 2). Matos *et al* [4], stated that attributed this improved percentage conversion increases as to the increasing amount of catalyst, which is probably related with the corresponding increase in quantity of active centers. However, increasing the amount of catalyst from 0.2 g to 0.4 g produces just a small of catalyst caused insignificant increment in conversion, thus indicating there is no advantage in using the absence of any added advantages, following the use of higher amounts.

Table 2. Data on the percentage conversion (% C) and selectivity of methoxylation of α -pinene with variable amount of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst.

Alum (g)	t (min)	α -pinene (%)	%C	Reaction products					
				FME		BME		TME	
				%A	%S	%A	%S	%A	%S
0.5	72	78.70	18.28	2.12	11.60	1.46	7.99	10.04	54.92
	144	68.68	28.68	3.21	11.19	2.12	7.39	15.75	54.92
	216	61.24	36.41	4.05	11.12	2.52	6.92	19.95	54.79
	288	53.75	44.18	4.83	10.93	3.69	8.35	23.78	53.82
	360	48.02	50.13	5.45	10.87	3.62	7.22	27.14	54.14
1	72	71.92	25.32	2.48	9.79	1.93	7.62	13.46	53.16

	144	60.51	37.16	3.87	10.41	2.79	7.51	20.50	55.17
	216	52.87	45.10	4.65	10.31	3.31	7.34	24.53	54.39
	288	44.88	53.40	5.35	10.02	4.09	7.66	28.94	54.19
	360	38.05	60.49	6.05	10.00	4.11	6.79	32.96	54.49
1.5	72	56.00	41.85	4.40	10.51	3.23	7.72	22.39	53.50
	144	45.58	52.67	5.47	10.38	3.76	7.14	28.31	53.75
	216	37.42	61.14	6.23	10.19	4.18	6.84	32.58	53.29
	288	30.38	68.45	6.72	9.82	4.71	6.88	36.61	53.48
	360	24.56	74.50	7.16	9.61	5.20	6.98	39.97	53.65

Note: %C (% Conversion), %A (% Content), %S (% Selectivity), FME (α -Fenchyl Methyl Ether), BME (Bornyl Methyl Ether), and TME (Terpinyl Methyl Ether).

The Scheme 1 shows the mechanisms of the predominant methoxylated products of α -pinene seen in this study are presented Scheme 1. The mechanism begins with the protonation of the products. This is initiated by double bond of α -pinene protonation, to give the yield pinyl ions, under an acidic condition from created through the hydrolysis of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst. According to literary review, the process catalyzed acid catalysis by acid (potassium alum) takes place through alum ensues via two routes, route including A is obtained by terpinyl ion and route B is B, obtained by terpinyl and bornyl ion-ion, respectively [4]. The alkoxylation of α -pinene process was initiated by protonation of the α -pinene double bond to form bond, therefore forming the pinyl ion. The This reaction then proceeds via is proceeded through two parallel pathways depending pathways, dependent on the pinyl ion-product rearrangement, one of which resulting in including bicyclic products and the other in monocyclic products. Bornyl ions type. Furthermore, the bornyl and terpinyl ions present in the reaction mixture then are react with methanol, and are consequently deprotonated to yield the ether products ethers viz. TME, BME, and FME. Catrinescu *et al* (2015) also stated that reported on the reaction of pinene reacted with methanol over the acid sites available on the clay surface surface, to form terpinyl methyl ether, TME, as the main reaction product. Other Meanwhile, other compounds were also identified in the complex reaction mixture, which include bicyclic ethers (fenchyl methyl ether and bornyl methyl ethers), encompassing the fenchyl and bornyl methyl varieties [5]. Several Moreover, several reaction products were thought to be associated with the irreversible rearrangements of the pinyl ion [15]. This was because the pinyl ion can, resulting from the intrinsic ability to rearrange into the bornyl ion, and after methanol addition, and when. This leads to the formation of bornyl methyl ether, and fenchyl methyl ether are formed ether, following the addition of methanol. The Therefore, pinyl ion can also rearrange is

1 ~~further rearranged~~ into the terpinyl ion ~~upon formation after the generation of~~ terpinyl
2 methyl ether, ~~in which using~~ methanol ~~was employed as the a~~ solvent.

4. Conclusion

5 ~~Potassium Potassium~~ alum [KAl(SO₄)₂·12H₂O] ~~catalyzed~~ was successfully used as
6 acid catalysts in the ~~methoxilation methoxylation~~ of α-pinene. ~~The main product of α-~~
7 ~~pinene methoxylation was, to produce~~ a-terpinyl methyl ether (TME) ~~as the main~~
8 ~~product. The~~ This process also ~~forms causes~~ the formation of fenchyl methyl ether
9 (FME), bornyl methyl ether (BME), limonene, and terpinolene as by-products. ~~In order~~
10 ~~to optimize the~~ The optimized reaction ~~conditions, condition was evaluated from~~ the
11 effect of various parameters, ~~such as, volume ratio of including~~ α-pinene to
12 ~~methanol methanol~~ volume ratio, reaction temperature, and catalyst loading of
13 KAl(SO₄)₂·~~12H₂O~~ ~~were carried out~~ 12H₂O. ~~It was discovered that~~ Furthermore, the
14 highest selectivity values ~~of the α pinene methoxylation reaction~~ was achievable when
15 ~~the methoxylation condition was carried out~~ achieved using 1 g of catalyst, volume
16 ratio ~~of reactant~~ of 1:10, ~~with the temperature as well as temperature~~ and reaction time
17 set ~~to at~~ 65°C and 6 h, respectively. The ~~reaction yielded final yield comprises~~ 59.59%
18 ~~of TME, 8.87% of FME, 7.13% of BME, with from~~ an exceptional ~~percentage~~
19 ~~conversion of α-pinene at~~ percentage conversion of 98.18%.

Author Contributions

22 Nanik Wijayati designed the methodology and supervised the project; Lulua Romjanah
23 Lestari performed the experiments, and wrote the original draft; Lisa Ayuningtyas
24 Wulandari assisted in ~~performing the experiments, maintain experimental procedures~~
25 ~~and maintaining~~ the research data; F. Widhi Mahatmanti analyzed ~~the data~~ and
26 interpreted the SEM and FT-IR ~~analysis analysis~~ data; Senda Kartika Rakainsa ; Edi
27 Cahyono provided the materials; Roswanira Abdul Wahab helped with the conception
28 and ~~editing of the manuscript~~ manuscript editing. All authors have read and agreed to
29 the published version of the manuscript.

31 **Conflict of Interest:** The authors declare no conflict of interest.

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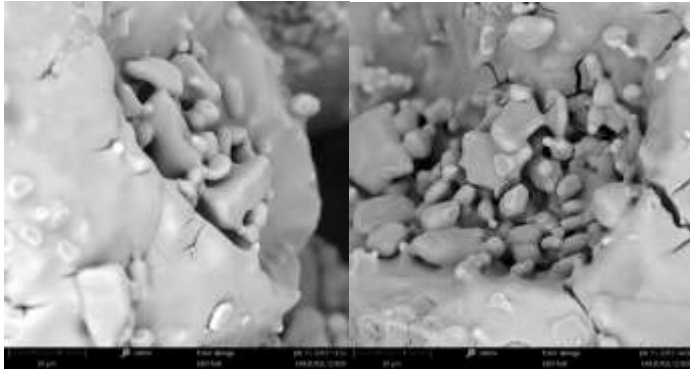
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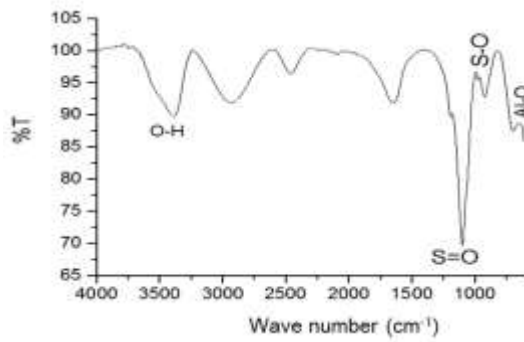
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1
2 **Figures**
3



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6 **Figure 1.** Scanning Electron Microscope (SEM) micrograph of $KAl(SO_4)_2 \cdot 12H_2O$
7 magnified 2000 x
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10
11 **Figure 2.** Fourier Transform-Infrared (FT-IR) spectrum of $KAl(SO_4)_2 \cdot 12H_2O$
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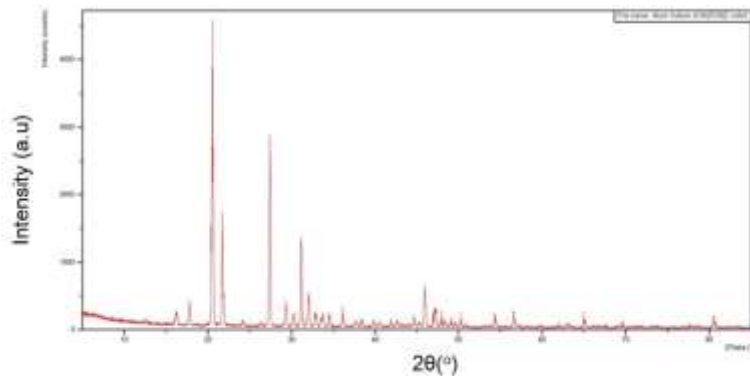
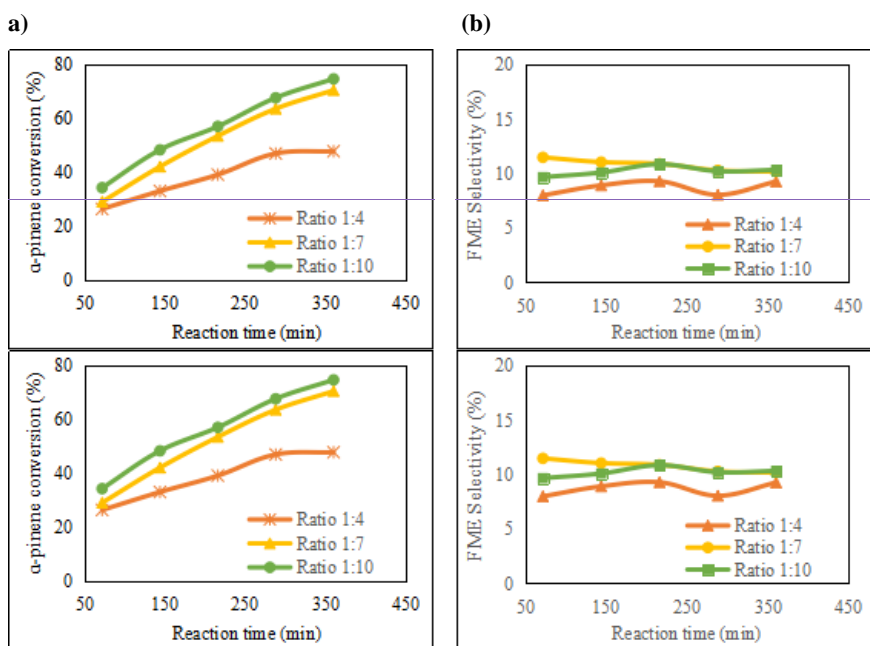
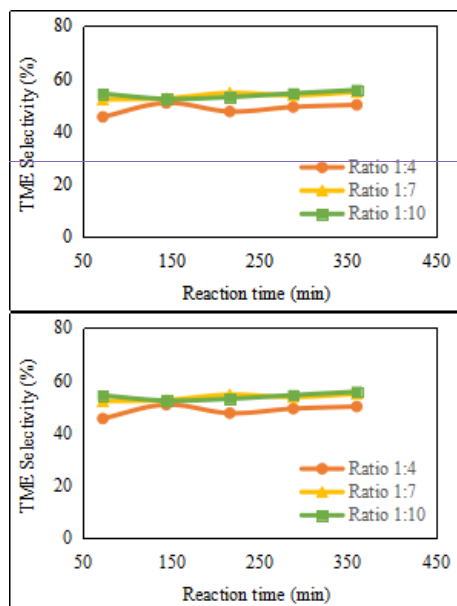


Figure 3. X-Ray Diffraction (XRD) diffractogram of $KAl(SO_4)_2 \cdot 12H_2O$

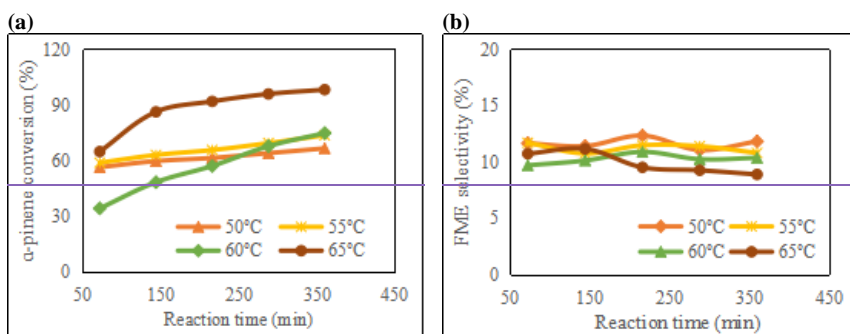
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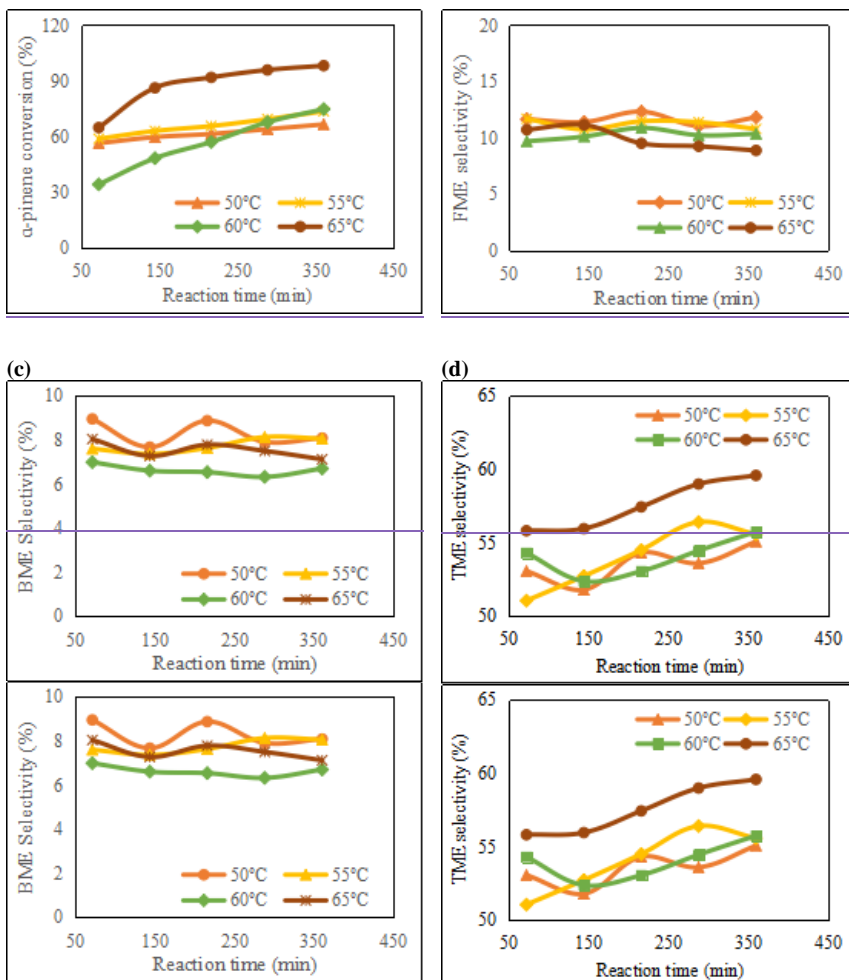


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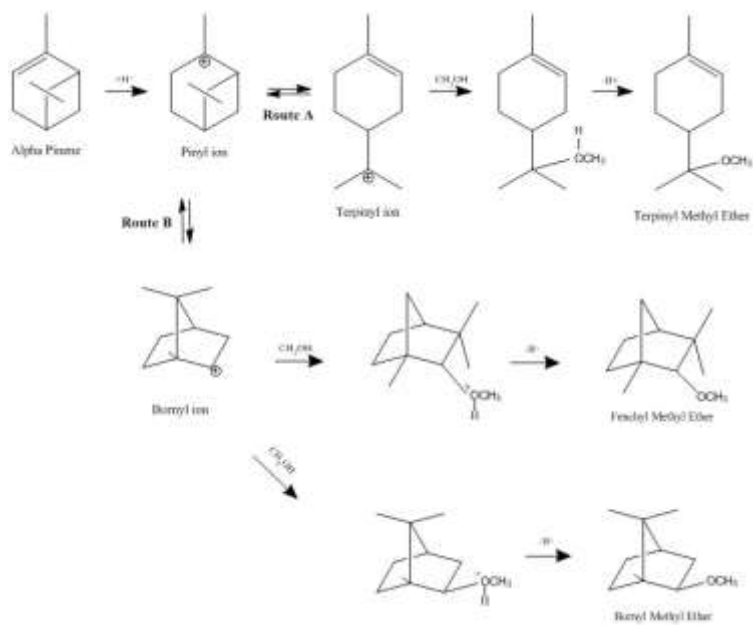
1 **Figure 4.** Influence of volume ratio of reactants on the methoxylation of α -pinene: (a)
2 conversion of α -pinene (b) selectivity of Fenchyl Methyl Ether (FME) (c) selectivity of
3 Terpinyl Methyl Ether (TME)
4
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1 **Figure 5.** Effect of temperature on α -pinene methoxylation: (a) α -pinene conversion vs
 2 time (b) Fenchyl Methyl Ether (FME) selectivity vs time (c) Bornyl Methyl Ether
 3 (BME) selectivity vs time (d) Terpinyl Methyl Ether (TME) selectivity vs time
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Scheme 1. The mechanism of α -pinene methoxylation

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1 **Potassium Alum [KAl(SO₄)₂·12H₂O] Solid Catalyst for**
2 **Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products**

3
4 Nanik Wijayati^{a,*}, Lulua Romjanah Lestari^a, Lisa Ayuningtyas Wulandari^a, F. Widhi
5 Mahatmanti^a, Senda Kartika Rakainsa^a, Edi Cahyono^b, and Roswanira Abdul Wahab^{c,d}

6
7 ^aDepartment of Chemistry, Universitas Negeri Semarang, Semarang 50229, Central Java,
8 Indonesia

9 ^bPerhutani Pine Chemical Industry, Pemalang 52319, Central Java, Indonesia

10 ^cDepartment of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310,
11 UTM Johor Bahru, Malaysia

12 ^dEnzyme Technology and Green Synthesis Group, Universiti Teknologi Malaysia,
13 81310 UTM Johor Bahru, Malaysia

14
15 *Corresponding author, e-mail: nanikanang@gmail.com

16
17 **Abstract.** Methoxylation is a relevant technological process applied in the production of
18 high-value α -pinene derivative compounds. This report investigates the use of potassium
19 alum [KAl(SO₄)₂·12H₂O] as a catalyst in the methoxylation of α -pinene, at 65°C. The
20 main reaction product of α -terpinyl methyl ether (TME), alongside the intermediates was
21 identified using GC–MS. Furthermore, the influence of various conditions on the
22 maximization of α -pinene conversion and selectivity was also evaluated. The results show
23 conversion reached 98.18% with 59.59% selectivity towards the mono ether, TME, using
24 65°C treatment for 6 h. However, AISAz-1 and other solid acid catalysts require exposure
25 for up to 20 h to achieve similar outcome.

26
27
28 Keywords: α -pinene; methoxylation; potassium alum; catalyst

1. Introduction

The organic compound α -pinene belongs to the terpene group, characterized by a reactive ring, alongside the presence of double bonds. This is a commonplace constituent of various coniferous tree oils, especially the pine tree [1,2], possessing interesting and highly diverse applications, particularly after chemical transformation into an array of high value compounds [3]. The modification is initially conducted using different acid catalysts, e.g. activated carbon, Al^{3+} ion exchanger clay, acid oxide, zeolite, activated clays, ion exchange resin, and $\text{TCA/ZrO}_2 \cdot n\text{H}_2\text{O}$ [4–13]. In addition, methoxylation through the addition of methoxide ions is the most frequent and applicable reaction choice for the modification of functional groups. Previous literature showed α -terpinyl methyl ether compound as the predominant product, followed by other minor yields, including α -terpinyl methyl ether, β -terpinyl methyl ether, terpinolene, limonene, endobornyl methyl ether, β -fenchyl methyl ether, exobornyl methyl ether, bornilene, and camphene [14]. Specifically, α -terpinyl methyl ether notably exudes fresh and citrus-like aroma, with peculiar desirability as a component in flavors and aromas of perfumes and cosmetic products. Also, there have been applications as an aromatic additive in topical medicines, agricultural chemicals, and the food industry [5].

The conventional α -pinene methoxylation process involves the use of certain catalysts, including Al^{3+} ion exchanger clays, mesoporous/microporous carbon, poly(vinyl alcohol) (PVA) containing sulfonic, β -zeolite, MCM-41, PMO, and heteropolyacids immobilized on silica [4,5,14–16]. However, the chemical synthetic route for α -terpinyl methyl ether is far from efficient, and also environmentally unfriendly [5,17]. This is due to poor selectivity in the catalytic process, and inability to guarantee higher yield. This study focuses on resolving these challenges by using suitable heterogeneous catalysts, to facilitate a more benign synthesis.

Interestingly, this approach averts the shortcomings typically observed in homogenous catalysis, featuring more environmentally friendly properties. Also, the solid form advantageously permits the facile separation of catalyst from the reaction mixture upon termination, and the specific pore sizes selectively adsorb the reactant molecules. This prompts a rapid transformation into products [18–21], and the rapid activity results from similarity in size and shape, alongside compatibility [9,10]. In addition, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is identified as a promising heterogeneous acid catalyst needed for the production of value-added α -terpinyl methyl ether from α -pinene.

1 This is a solid state compound, also called potassium alum, or potash alum acid.
2 Furthermore, they have commonly been applied in several reactions, including the
3 synthesis of mono and bis-2-amino-4H-pyrans, by reacting three or five pseudo
4 components from 4-hydroxycoumarin. Also, the catalyst has been examined in the
5 reaction of malononitrile and aldehyde in ethanol/water media at room temperature, as
6 well as for the Erlenmeyer synthesis, and the transesterification of palm oil [19,22,23].
7 Due to the relative versatility, this study assumes the possible usefulness of potassium
8 alum $[KAl(SO_4)_2 \cdot 12H_2O]$ catalyst in the methoxylation of α -pinene to produce α -terpinyl
9 methyl ether.

10 The influence of various parameters, including α -pinene to methanol volume ratio,
11 temperature, and catalyst loading on catalyst activity were also studied. This approach
12 is frequently adopted in organic reactions involving polar reagents.

14 2. Materials and Methods

15 2.1. Materials

16 α -Pinene standard were obtained from Sigma Aldrich, while Turpentine oil was
17 acquired from KBM Perhutani Pine Chemical Industry, Pematang, Indonesia. The
18 methanol for analysis and potassium alum $[KAl(SO_4)_2 \cdot 12H_2O]$ were procured from
19 Merck.

21 2.2. Instrumentations

22 Quantitative and qualitative analyses of the isolated α -pinene and the corresponding
23 methoxylation products were conducted with GC 23 Agilent 6820 (Version A. 01. 03),
24 HP-5 column and FID detector (detector temperature of 300°C), with Helium as carrier
25 gas. The injection temperature was 280°C, while the column was set at an initial
26 temperature of 70°C for 10 minutes, increased gradually to 280°C (5°C/min), and up to
27 300°C, at 20°C/min. Furthermore, GC-MS (Shimadzu QP-2010 Plus) equipped with a
28 AOC-20i+s autosampler was operated under the following conditions: column and
29 injection temperature of 70°C and 200°C, respectively with split injection mode, pressure
30 13.7 kPa, flow column 0.50 mL/min, ion source and interface temperature of 200°C and
31 240°C, correspondingly. This analysis required the use of helium (He) gas as the carrier,
32 at a constant flow rate of 0.1 μ L/min, and the methoxylation result were estimated based
33 on the area beneath each peak. Furthermore, the percentage of each ether product was

1 achieved by dividing the respective peak area with the isolated α -pinene, and multiplied
2 by 100. The qualitative analysis involved performing Fourier-transform spectroscopy on
3 prepared KBr pellets, and subsequently evaluated on a Perkin Elmer Spectrum Version
4 10.4.00, in the wavenumber region of 4000–400 cm^{-1} .

5 6 2.3. Procedures

7 2.3.1 Preparation of the catalysts

8 For catalyst preparation, potassium alum was spray coated over AuPd plates under
9 Argon flow for 90 s to generate $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The gas pressure was set to 0.5 bar,
10 and the analysis was conducted at 20 mA for 5-10 mins in AuPd solvent. The catalyst
11 was then characterized using X-Ray Diffractometer(D-Max III (Rigaku), with $\text{Cu K}\alpha$ (α
12 = 1.5378 Å, 40kV, 30mA) radiation. Furthermore, morphology and mean crystallite size
13 was determined by scanning electron microscopy (SEM) with JEOL JFC-1600 and JSM-
14 6701F equipments. The results were extracted from a Pro X Scanning Desktop Electron
15 Microscope, with Energy Dispersive X-Ray (EDX).

16 17 2.3.2 Isolation of α -pinene

18 The fractional distillation of turpentine oil was used under reduced pressure to
19 prepare the α -pinene starting material. The result of isolation was analyzed using GC-MS
20 and FT-IR.

21 22 2.3.3 Catalytic experiments

23 The catalytic experiments were performed in a stirred batch reactor with reflux, at
24 different temperatures (50 – 65°C) and ambient pressure. Prior to the reaction, a known
25 amount of catalyst powder was thermally activated in an oven at 110°C, and then placed
26 in a desiccator at room temperature (15 min) to cool and prevent rehydration. This was
27 quickly transferred into the reaction vessel containing 20 mL dry methanol and
28 preheated at the reaction temperature, followed by the addition and mixture of 5 mL α -
29 pinene by stirring for another 360 min. Therefore, samples were collected periodically,
30 and the catalyst was removed by syringe filtration, using a filter with no impact on the
31 products. Also, no further reaction was reported during storage, and the yields were
32 identified using GC-MS (Shimadzu QP-2010 Plus). In addition, GC Agilent 6820 with
33 FID detector (T 300°C), using a HP-5 column with Helium as carrier gas was adopted

1 for quantification. The chromatogram peaks were identified by comparing retention
2 times and gas chromatography-mass spectrometry.

3 The reaction conditions were optimized by evaluating the effect of different
4 parameters, including reaction temperature (50, 55, 60 and 65°C), catalyst loading (0.5;
5 1; and 1.5 g), and volume ratio of reactants (α -pinene : methanol of 1:4, 1:7, 1:10) during
6 the methoxylation process. Therefore, α -terpinyl methyl ether selectivity, and α -pinene
7 conversion were calculated using the external standardized method, with curves
8 prepared by detecting different concentration of the standard solution. In addition, the
9 conversion of α -pinene (X) and the selectivity (S) of α -terpinyl methyl ether were
10 calculated using the following formula:

$$11 \quad X = \frac{\% \text{ converted alpha pinene}}{\% \text{ initial alpha pinene}}, \quad S = \frac{\% \text{ desired product}}{\% \text{ conversion of alpha pinene}}$$

13 3. Results and Discussions

14 3.1 Characterization of catalyst

15 The potassium alum catalyst ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) is an inexpensive, non-toxic,
16 water-soluble, and commercially available compound frequently used in the laboratory
17 with no special precautions [19, 22,23]. Furthermore, characterization involved FT-IR,
18 XRD, as well as SEM, with micrograph illustrated in figure 1, showing reasonable
19 similarities with the micro structure of ammonium aluminum sulfate dodecahydrate
20 $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$. However, the latter comprise a more rounded shape, with a size
21 range of between 100–200 μm . At higher temperatures of 1100–1200°C, the overall
22 construct of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is altered, therefore generating an elongated oval shape
23 [24].

24 Infrared spectroscopy is often used to characterize solid state catalysts, resulting
25 from the flexible nature during the identification of surface functional groups, both
26 organic and inorganic. Figure 2 shows the spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, with peaks at
27 1195 cm^{-1} and 1077 cm^{-1} indicating the stretching vibration of S=O group, while 933 cm^{-1}
28 and 737 cm^{-1} are related to the stretching vibrations of S–O and Al –O bonds,
29 respectively. The assignment of various bands to corresponding vibrational modes of the
30 functional groups present in alums, as well as the related aluminum bearing compounds
31 are sufficiently detailed in the literature. Furthermore, absorption peaks in the region of
32 $750\text{-}400 \text{ cm}^{-1}$ indicate the vibration of Al–O [25]. Fig. 2 shows sharp sulfate (SO_4^{2-})

1 bands in 468–471 cm^{-1} , 603–608 cm^{-1} , 657–686 cm^{-1} , 1104–1115 cm^{-1} and 1237–1247
2 cm^{-1} corresponds to symmetrical SO_4^{2-} bending mode, degeneration of asymmetric
3 bending, symmetrical bending, degenerate symmetric stretching and degenerate
4 asymmetric stretching modes, respectively [23].

5 The crystallinity and crystal lattice of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ were evaluated using X-
6 Ray Diffraction (XRD) technique, and the deduced patterns are presented in Figure 3.
7 Furthermore, high crystallinity implies greater catalytic properties, and better stability at
8 high temperatures, alongside wide porosity, and purity [26]. The main composition of
9 alum was identified to be aluminum potassium sulfate, based on the characteristic peaks
10 at $2\Theta = 21^\circ$; 28° ; and 32° . Based on the diffractogram in Figure 3, Al_2O_3 is represented
11 by 2Θ peaks at 36° ; 46° and 58° , while the 68.54% $\text{K}_2(\text{SO}_4)$ was designated at 2Θ ,
12 corresponding to 22° ; 32° ; and 45° . The result is substantially corroborated by Souza *et*
13 *al.*, where a similar compound was assessed [27], and the 2Θ peaks observed at 21° , 22° ;
14 and 28° were congruent with the PDF File 07.0017 for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. In addition,
15 the diffractogram affirmed the samples' high crystallinity, matching a recent report from
16 another analogous compound investigated by Abdulwahab *et al.* (2019) [28].

17 18 3.2 Catalytic test

19 3.2.1 Effect of volume ratio of α -pinene and methanol

20 The effect of varied α -pinene and methanol volume ratio on the selectivity to α -
21 terpinyl methyl ether was also evaluated, and good selectivity values (about 56%, at
22 conversion of α -pinene 75%) were obtained. The ratios investigated were 1:4, 1:7, and
23 1:10, at 60°C temperature, with 0.1 g of potassium alum catalyst, while α -pinene
24 conversion and relative product selectivity is shown in Figure 4.

25 Figure 4a shows a decline in the initial concentration of α -pinene decreased from
26 96.30%. The reactant volume ratio also influenced the outcome of methoxylation
27 reactions, thus a higher concentration of methanol led to greater amounts of ether yield
28 (Figure 4a). Also, the production increased over extended reaction duration, and the
29 highest α -pinene conversion (74.82%) was attained at 1:10 ratio and reaction time of 360
30 min. This is possibly due to the ability for methanol to simultaneously act as a reactant
31 and solvent, thus augmenting the integrations, and accelerating the percentage conversion
32 into the main ether product, and others [29]. Furthermore, by-products were formed from
33 α -pinene isomerization, including camphene, limonene, and terpinolene, under the

1 reaction condition applied [30]. The highest selectivity of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
2 catalyzed methoxylation was observed when at a substrate reaction ratio of 1:10, with
3 stirring for 360 min at 60°C. Figure 4b and c show the most prominent products to be
4 terpinyl methyl ether (TME) (55.76%) and fenchyl methyl ether (FME) (10.34%).

5 6 3.2.2 Effect of reaction temperature

7 The effect of temperature on the selectivity to α -terpinyl methyl ether was also
8 investigated, by exposing the reactions to 50, 55, 60 and 65 °C, over 1 g of
9 $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst, and constant α -pinene: methanol volume ratio. As
10 anticipated, the percentage conversion increased with the rise in temperature. This
11 influence, alongside the selectivity towards mono-ether products is presented in Fig. 5a,
12 b and c. Also, the variations were considered capable of generating good selectivity
13 values of about 60% ether product, from 98% α -pinene conversion.

14 The boiling point of methanol was 65°C, hence 60°C was determined as suitable
15 for the methoxylation reaction [29]. This is in accordance with the data in Figure 5a,
16 where α -pinene conversion steadily increased at 60°C. However, a notable elevation in
17 reaction time from 72 to 144 minutes was observed at 65°C, considering the possibility
18 of generating more products at higher temperature. Hence, the peak conversion of α -
19 pinene by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was 98.18% at 65°C.

20 The catalyst selectivity was highest at 65°C, over reaction duration of 360 min,
21 leading to the production of 8.7% FME (Figure 5b), 7.13% BME (Figure 5c), and 59.59%
22 TME (Figure 5d). Similar trend was observed in the methoxylation of limonene through
23 acid-activated ions and clay exchangers [31]. Accordingly, the increase in temperature
24 prevented a decline in selectivity [31]. This corresponds to the findings of Hensen *et al*
25 (1997), on the effects of temperature on pinene alkoxylation, and the maximum
26 conversion was attained at 60°C and t=120 min [14]. However, temperatures of 80°C have
27 been affiliated with reverse reactions, characterized by the reformation of pinene isomers
28 in the methanol solvent. In addition, similar trend was observed in α -pinene conversion
29 in related systems, using 100 mg of Al-SAz-1 as catalyst [5], and is more favorable,
30 compared to other identical conditions. The reaction selectivity for mono-ether, seems to
31 be largely unaffected by increase in temperature, up to 65°C, at constant percentage
32 conversion. Also, there was no decline in selectivity, as observed in previous studies
33 concerning limonene methoxylation [31].

Table 1 is a summary of the α -pinene methoxylation activity in the presence of various catalysts, as shown in previous literatures. The highest yield was obtained using AlSAz-1 under mild reaction conditions.

Table 1. The summary of α -pinene methoxylation activity in the presence of various catalysts in a batch reactor

Catalysts	Temp °C	Reaction Time (h)	Conversion (%)	Selectivity (%)	Literature
AlSAz-1	60	1	65	65	Catrinescu <i>et al.</i> (2015) [5]
AlSAz-1	40	20	71	91	Catrinescu <i>et al.</i> (2013) [31]
CB, CMN, CNorit	60	250	55-75	50-55	Matos <i>et al.</i> (2014) [4]
PW2-S	60	27	40	60	Pito <i>et al.</i> (2010) [32]
PVSSA-20	60	24	40	60	Pito <i>et al.</i> (2009) [15]
PMO-SO3H-g	100	-	90	45	Castanheiro <i>et al.</i> (2008) [16]
Beta Zeolite	40	5	92	54	Hensen <i>et al.</i> (1997) [14]

3.2.3 Effect of the catalyst loading

The selectivity of $KAl(SO_4)_2 \cdot 12H_2O$ for α -terpinyl methyl ether was also studied, using a catalyst loading of 0.5, 1, and 1.5 g, 60°C temperature, and α -pinene and methanol volume ratio of 1:10. Figure 4 shows the conversion and product selectivity, where the different treatments yield good amount of α -terpinyl methyl ether (about 54% with 75% α -pinene conversion). These products are also detected after the conventional alkoxylation of pinene or limonene with mineral acids [5]. Hence, the $KAl(SO_4)_2 \cdot 12H_2O$ solid catalyst prepared in this study successfully converted α -pinene into the expected ether products. Also, there was an upsurge in yield following an increase in the quantity of catalyst used. Interestingly, 0.5 g ensured the highest methoxylation α -pinene selectivity for FME and BME, while 1 g prompted higher production of TME (Table 2). Matos *et al* [4] attributed this improved percentage conversion to the corresponding increase in quantity of active centers. However, 0.2 g to 0.4 g of catalyst caused insignificant increment in conversion, indicating the absence of any added advantages, following the use of higher amounts.

Table 2. Data on the percentage conversion (% C) and selectivity of methoxylation of α -pinene with variable amount of the $KAl(SO_4)_2 \cdot 12H_2O$ catalyst.

Alum (g)	t (min)	α -pinene (%)	%C	Reaction products					
				FME		BME		TME	
				%A	%S	%A	%S	%A	%S

0.5	72	78.70	18.28	2.12	11.60	1.46	7.99	10.04	54.92
	144	68.68	28.68	3.21	11.19	2.12	7.39	15.75	54.92
	216	61.24	36.41	4.05	11.12	2.52	6.92	19.95	54.79
	288	53.75	44.18	4.83	10.93	3.69	8.35	23.78	53.82
	360	48.02	50.13	5.45	10.87	3.62	7.22	27.14	54.14
1	72	71.92	25.32	2.48	9.79	1.93	7.62	13.46	53.16
	144	60.51	37.16	3.87	10.41	2.79	7.51	20.50	55.17
	216	52.87	45.10	4.65	10.31	3.31	7.34	24.53	54.39
	288	44.88	53.40	5.35	10.02	4.09	7.66	28.94	54.19
	360	38.05	60.49	6.05	10.00	4.11	6.79	32.96	54.49
1.5	72	56.00	41.85	4.40	10.51	3.23	7.72	22.39	53.50
	144	45.58	52.67	5.47	10.38	3.76	7.14	28.31	53.75
	216	37.42	61.14	6.23	10.19	4.18	6.84	32.58	53.29
	288	30.38	68.45	6.72	9.82	4.71	6.88	36.61	53.48
	360	24.56	74.50	7.16	9.61	5.20	6.98	39.97	53.65

Note: %C (% Conversion), %A (% Content), %S (% Selectivity), FME (α -Fenchyl Methyl Ether), BME (Bornyl Methyl Ether), and TME (Terpinyl Methyl Ether).

Scheme 1 shows the mechanisms of predominant methoxylated α -pinene products., This is initiated by double bond protonation, to yield pinyl ions, under an acidic condition created through the hydrolysis of $KAl(SO_4)_2 \cdot 12H_2O$. According to literary review, acid catalysis by potassium alum ensues via two routes, including A and B, obtained by terpinyl and bornyl ion, respectively [4]. The alkoxylation process was initiated by protonation of the α -pinene double bond, therefore forming the pinyl ion. This reaction is proceeded through two parallel pathways, dependent on the product rearrangement, including bicyclic and monocyclic type. Furthermore, the bornyl and terpinyl ions present in the reaction mixture are react with methanol, and consequently deprotonated to yield ethers *viz.* TME, BME, and FME. Catrinescu *et al* (2015) also reported on the reaction of pinene with methanol over the acid sites available on the clay surface, to form terpinyl methyl ether, TME, as the main product. Meanwhile, other compounds identified in the complex include bicyclic ethers, encompassing the fenchyl and bornyl methyl varieties [5]. Moreover, several reaction products were associated with the irreversible rearrangements of pinyl ion [15], resulting from the intrinsic ability to rearrange into the bornyl ion. This leads to the formation of bornyl methyl ether, and fenchyl methyl ether, following the addition of methanol. Therefore, pinyl ion is further rearranged into the terpinyl ion after the generation of terpinyl methyl ether, using methanol as a solvent.

4. Conclusion

1 Potassium alum [KAl(SO₄)₂·12H₂O] was successfully used as acid catalysts in the
2 methoxylation of α-pinene, to produce a-terpinyl methyl ether (TME) as the main
3 product. This process also causes the formation of fenchyl methyl ether (FME), bornyl
4 methyl ether (BME), limonene, and terpinolene as by-products. The optimized reaction
5 condition was evaluated from the effect of various parameters, including α-pinene to
6 methanol volume ratio, reaction temperature, and catalyst loading of KAl(SO₄)₂·12H₂O.
7 Furthermore, the highest selectivity values was achieved using 1 g of catalyst, volume
8 ratio of 1:10, as well as temperature and reaction time set at 65°C and 6 h, respectively.
9 The final yield comprises 59.59% TME, 8.87% FME, 7.13% BME, from an exceptional
10 α-pinene percentage conversion of 98.18%. Further investigation of α-pinene chemical
11 processes is still needed. One of the novel development is by using nanotechnology
12 application for α-pinene formulation [3]. This has broadened our perspective to further
13 contribute to α-pinene research in the future.

15 **Author Contributions**

16 Nanik Wijayati designed the methodology and supervised the project; Lulua Romjanah
17 Lestari performed the experiments, and wrote the original draft; Lisa Ayuningtyas
18 Wulandari assisted in the experimental procedures and maintaining the research data; F.
19 Widhi Mahatmanti analyzed and interpreted the SEM and FT-IR analysis data; Senda
20 Kartika Rakainsa assisted in data interpretation and validation; Edi Cahyono provided the
21 materials; Roswanira Abdul Wahab helped with the conception and manuscript editing.
22 All authors have read and agreed to the published version of the manuscript.

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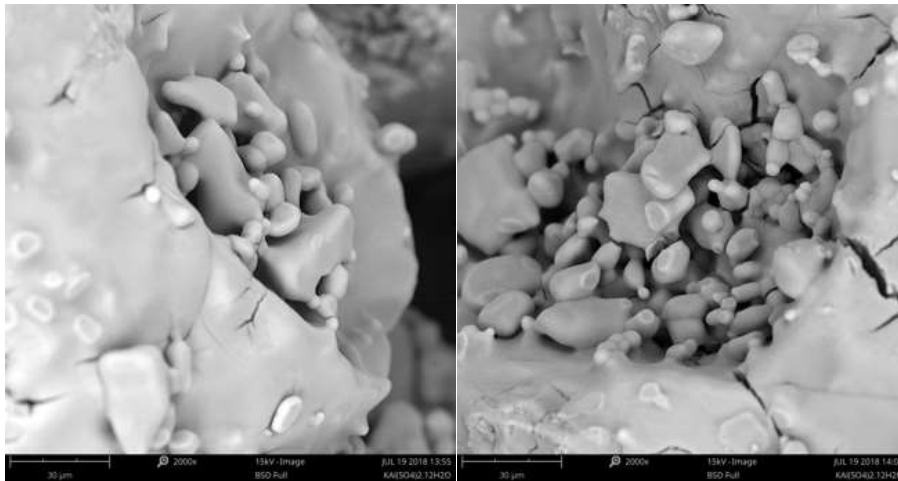
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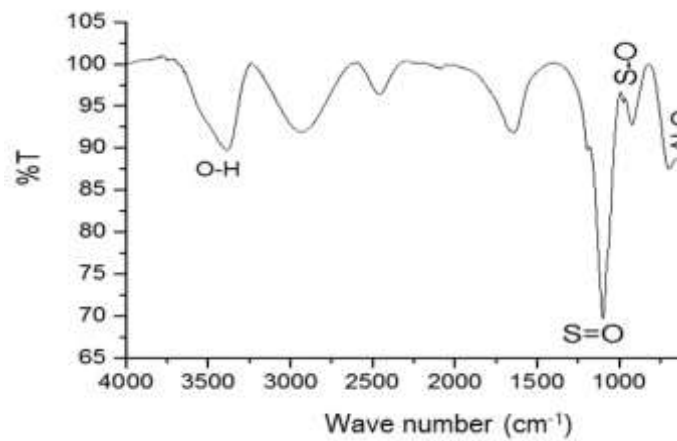
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1 **Figures**
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Figure 1. Scanning Electron Microscope (SEM) micrograph of $KAl(SO_4)_2 \cdot 12H_2O$ magnified 2000 x



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Figure 2. Fourier Transform-Infrared (FT-IR) spectrum of $KAl(SO_4)_2 \cdot 12H_2O$

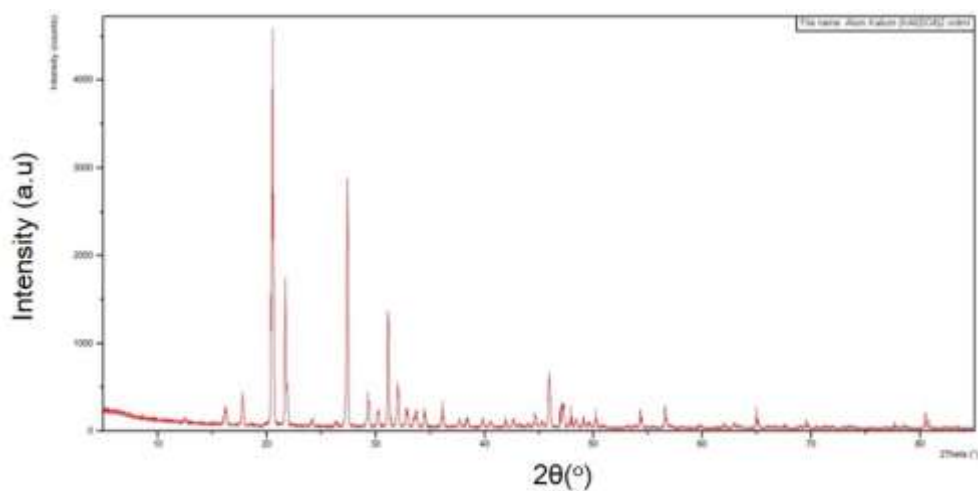


Figure 3. X-Ray Diffraction (XRD) diffractogram of $KAl(SO_4)_2 \cdot 12H_2O$

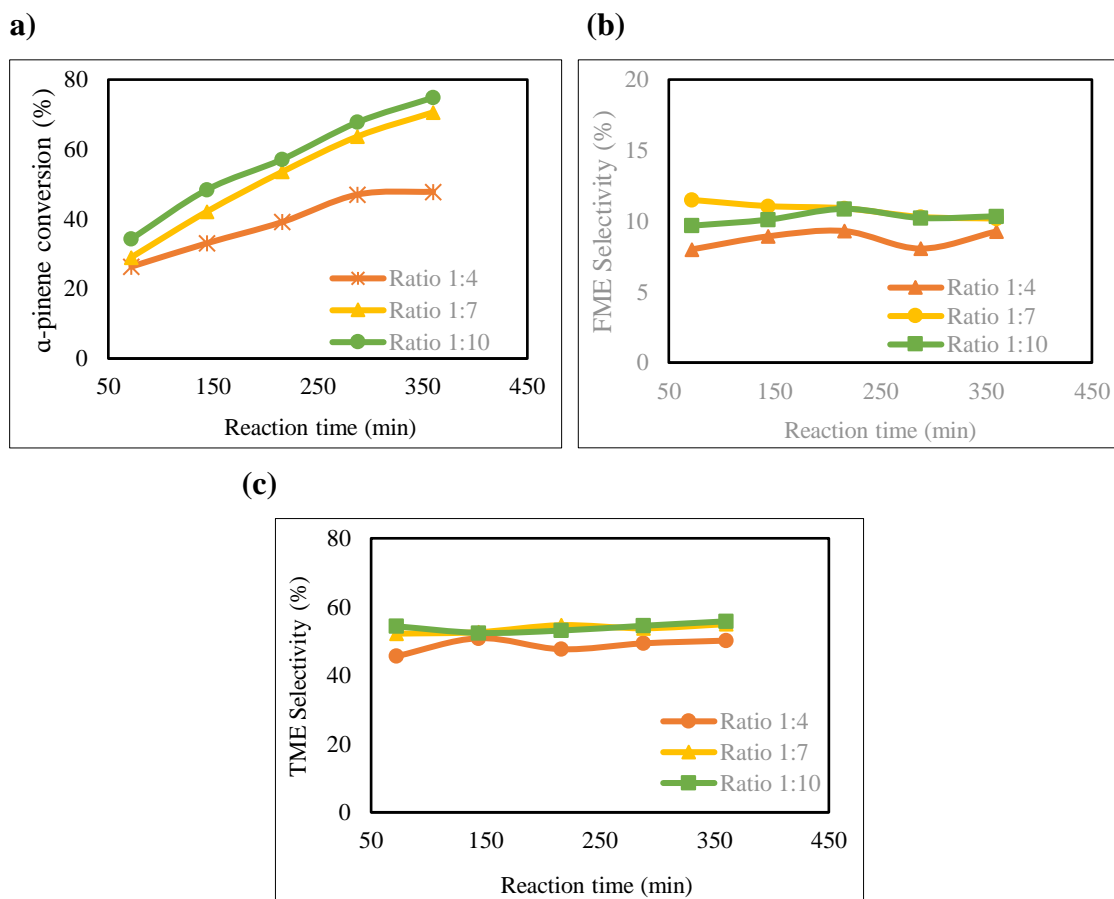
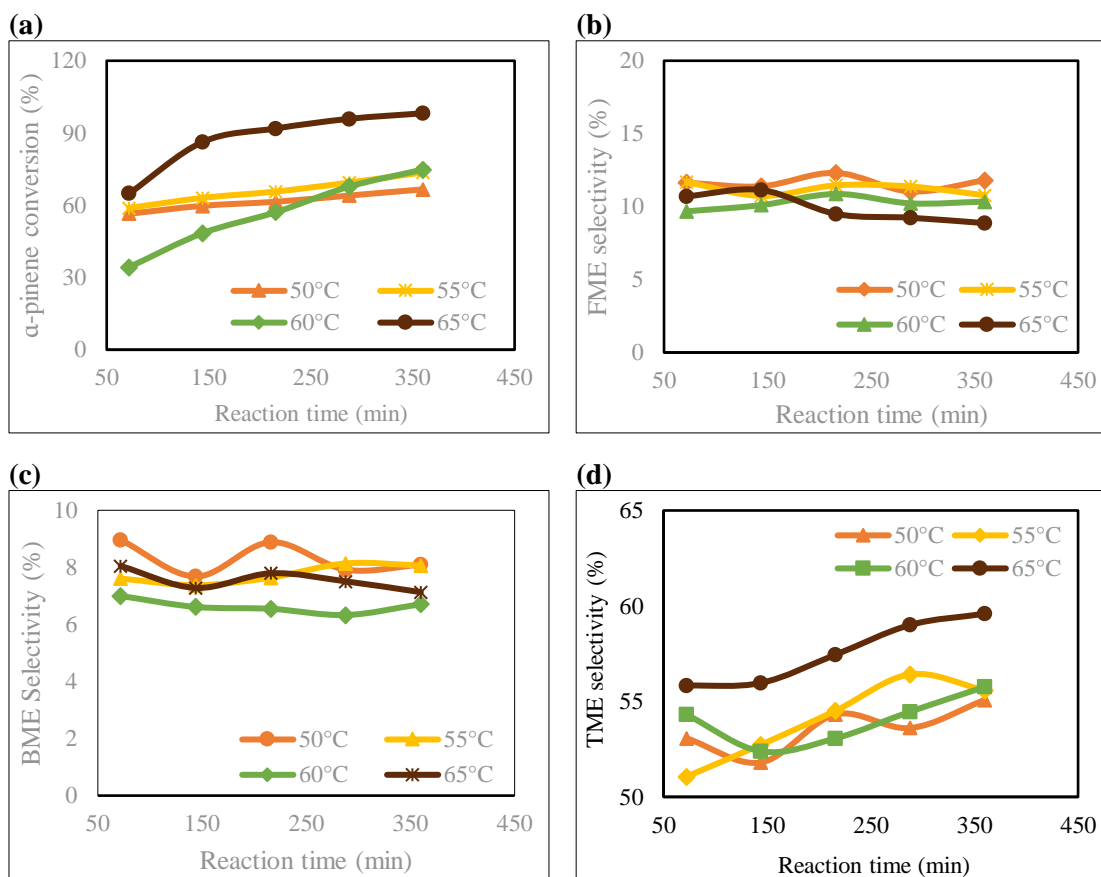
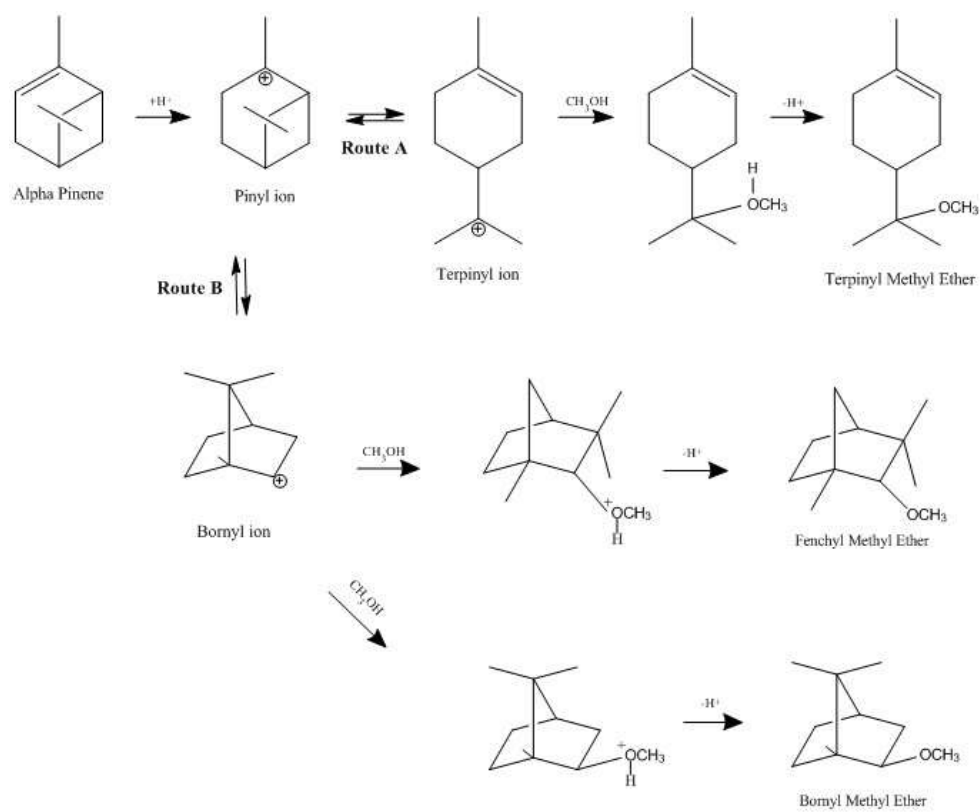


Figure 4. Influence of volume ratio of reactants on the methoxylation of α -pinene: (a) conversion of α -pinene (b) selectivity of Fenchyl Methyl Ether (FME) (c) selectivity of Terpinyl Methyl Ether (TME)



1 **Figure 5.** Effect of temperature on α -pinene methoxylation: (a) α -pinene conversion vs
 2 time (b) Fenchyl Methyl Ether (FME) selectivity vs time (c) Bornyl Methyl Ether
 3 (BME) selectivity vs time (d) Terpinyl Methyl Ether (TME) selectivity vs time
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Scheme 1. The mechanism of α -pinene methoxylation

Heliyon

Revision Report

Manuscript no. : HELIYON-D-20-03034

Title : Potassium Alum [KAl(SO₄)₂·12H₂O] Solid Catalyst for Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products

Authors : Nanik Wijayati, Lulua Romjanah Lestari, Lisa Ayuningtyas Wulandari, F. Widhi Mahatmanti, Senda Kartika Rakainsa, Edi Cahyono, and Roswanira Abdul Wahab

Reviewer no.	Reviewer's Comments	Author Response
1	<p>Point #1 on Methods: It seems an multi-factors optimization for the applicability of KAl(SO₄)₂·12H₂O as a catalyzer for methoxylation of α-pinene to obtain reasonable yields of different ether derivatives, so it is better to employ some optimal method, such as orthogonal test method, uniform test method, or response surface method, etc., to perform the optimization completely.</p> <p>Point #2 on Results: A perfect result will be obtained with the optimal procedure.</p>	<p>We regret that we cannot perform those suggested experiments due to the Covid-19 pandemic situation in our country, which causing the closure of our research facility. For now, we believe that our present methodology can quite describe the influence of various catalyst parameters to the alpha-pinene methoxylation.</p>

Reviewer no.	Reviewer's Comments	Author Response
2	<p>Point #1 on Methods: Correctly described, end points should be better assessed.</p> <p>Point #2 on Results: Properly assessed.</p> <p>Point #3 on Interpretation: Sound properly assessed.</p> <p>Point #4 (Other Comments): The manuscript entitled: "Potassium Alum [KAl(SO₄)₂·12H₂O] Solid Catalyst for Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products" is interesting nonetheless there some drawbacks as detailed in the following. First of all the aim and the end points of this work should be better assessed clarified.</p>	<p>The aim of the research has been clarified in Abstract and Introduction (page 2, line 10-12). The end points also has been clarified in Conclusion.</p>
	<p>Point #5 (Other Comments): In the Abstract please avoid terms like "exceptional": the number which is reported refers to the reaction yield? Please give also the terms of reference and comparison.</p>	<p>We have revised the abstract.</p>
	<p>Point #6 (Other Comments): A scheme of the procedure used of catalytic experiments should be inserted and detailed for clarity.</p>	<p>We have described the catalytic experiments more clearly in the Procedures (Point 2.3, page 4 and 5)</p>

Reviewer no.	Reviewer's Comments	Author Response
	<p>Point #7 (Other Comments):</p> <p>The characterization of the potassium alum catalyst used is not necessary: it is commercially available. In other parts of the paper it is stated that it has been prepared by the Authors. Please explain and compare the in house product with the standard compound commercially available.</p>	<p>This research used the commercially available potassium alum catalyst. Point 2.3.1 Preparation of Catalyst (page 4) is a procedure to prepare the catalyst before the reaction was carried out.</p>
	<p>Point #8 (Other Comments):</p> <p>The proposed reaction and catalyst should be compared with the other methods aimed to obtain the same result. Summarizing in a table would be clear to read and easy.</p>	<p>We have added in Table 1 (page 8).</p>
	<p>Point #9 (Other Comments):</p> <p>The advantage of SEM and FTIR should be remarked in Material and Methods. Also, the experimental conditions of FTIR should be described by giving greater details. A qualitative analysis of functional groups carried out by FTIR should be better described and discussed, also citing appropriate literature data.</p>	<p>We have added the advantage of FT-IR in Result and Discussion (page 5, line 24). The result of the analysis also has been described more clearly and cited the appropriate literature.</p>
	<p>Point #10 (Other Comments):</p> <p>Page 7, lines 18-35 should be rewritten.</p>	<p>We have revised it.</p>

Reviewer no.	Reviewer's Comments	Author Response
	<p>Point #11 (Other Comments):</p> <p>Table 3 should be better discussed in the text.</p>	<p>Maybe the reviewer refers to figure 3? Because there is no table 3 in our manuscript. The description of figure 3 has been added in Result and Discussion (page 6, line 5-16).</p>
	<p>Point #12 (Other Comments):</p> <p>It would be highlighted in the Conclusion section the possible useful of novel application of nanotechnologies to alpha-pinene as future remarks and perspective; updated references should be cited such as:</p> <p>Zielinska A., Ferreira N.R., Durazzo A., Lucarini M., Cicero N., El Maimouni S., Silva A.M., Nowak I., Santini A., Souto E.B. Development and Optimization of Alpha-Pinene-Loaded Solid Lipid Nanoparticles (SLN) Using Experimental Factorial Design and Dispersion Analysis. <i>Molecules</i> 07/2019; 24(15): 2683. DOI:10.3390/molecules24152683.</p>	<p>We have added the point in Conclusion.</p>
	<p>Point #13 (Other Comments):</p> <p>Major information should be added in Figure 3.</p>	<p>The description of figure 3 has been added in Result and Discussion (page 6, line 5-16).</p>
	<p>Point #14 (Other Comments):</p> <p>English language revision of the text would be advisable.</p>	<p>We have revised the English language of this manuscript and the certificate of proofreading was provided below.</p>

Certificate of Proofreading

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2013

Certificate of Proofreading

Manuscript Title

Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products

Author(s)

Nanik Wijayati, Lulua Romjanah Lestari, Lisa Ayuningtyas Wulandari, F. Widhi Mahatmanti,
Senda Kartika Rakainsa, Edi Cahyono, and Roswanira Abdul Wahab

Date Issued

June 18, 2020

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Heliyon

Revision Report

Manuscript no. : HELIYON-D-20-03034

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Reviewer no.	Reviewer's Comments	Author Response
4	An introduction is too weak, and not hypothesized why and how [KAl(SO ₄) ₂ ·12H ₂ O] better and reusable	We have revised the introduction by adding more literature sources to reinforce the advantages of [KAl(SO ₄) ₂ ·12H ₂ O] catalyst
	There are too many inappropriate phrases used	We have revised the phrases
	The purity of used chemicals is required to mention in the materials section	We have mentioned the purity of used chemicals
	Page no 4 line11-12, quantitative analysis of the product was carried out by FTIR. Which is not possible? Highly questionable.	FTIR only used in qualitative analysis, not the quantitative ones. The FTIR analysis was used to identify functional group of a compound in a certain wave number.
	Page no 4 line51-53. Not scientific again.	We have revised it
	Page no 5 line15-17. Stated that, yield were identified by GC-MS, which not correct, as GC-MS gives only	All samples collected were analyzed using a Gas Chromatograph (GC), comparing the retention times of

	<p>qualification and quantification were carried out by GC using internal or external std.</p>	<p>the compounds in the reaction mixture with those of standard compounds.</p>
	<p>Page no 5 line 35-39 given formula not correct, as we have to mention in mol%</p>	<p>The formula to determine conversion (%) and product selectivity (%) was cited from Avila <i>et al</i> (2010). The conversion of α-pinene (X) and the selectivity (S) for the desired products were defined as follows:</p> $X = \frac{\text{converted alpha pinene \%}}{\text{initial alpha pinene \%}},$ $S = \frac{\text{desired product \%}}{\text{conversion of alpha pinene \%}}$
	<p>Page no 6 line 38- it's not PDF file, it JCDF file</p>	<p>We have revised it</p>
	<p>As they have not mentioned which internal std used and how it is really calculated, the it is better to write % con and selectivity in one decimal.</p>	<p>We have revised the conversion and selectivity to one decimal</p>
	<p>Page no 7 the temperature effect is carried out in 5 °C difference, but as a thumb rule, the rate of reaction is double in every 10 °C. however, it is challenging to maintain temperature within this regime and find the kinetics</p>	<p>Based on previous reports, the experiment was performed in temperature of 60°C, thus we performed our experiment near that temperature. The outcome seen here also signified that the temperatures assessed in this study</p>

		promoted good selectivity of the methoxylation to yield ~60% of the ether products.
	I was also carried out reaction at different grams of catalyst. What is the purpose of doing this? Does authors have found our acidity of the catalyst? and any correlation of acidity to rate of reaction. Also, using a more solid catalyst, is there any mass transfer effect?	The variation of the catalyst loading is studied. This study revealed that increasing the amount of catalyst, the conversion increases with time which is probably related with the corresponding increase in active centers. However, increasing the amount of catalyst from 0.5 g to 1.5 g produces just a small increment in conversion thus indicating there is no advantage in using higher amounts. Selectivity is not affected by the changes in catalyst loading (about 60% at the highest conversion).
	How the exo and edo product characterized? Authors need to show by NMR	NMR analysis was used to analyze pure compounds. The reaction product in this study is still a mixture and we do not separate the product so we cannot differentiate between exo and endo products.
	GCMS of all the identified product need to give SI	All products were analyzed using GC-MS with SI at around 90
	Figure 2 assing all FTIR peaks and P XRD in fig -3, both figure are in poor quality	We have revised the picture
	As stated , solid catalyst can be recycled and reused, I didn't see any study on this topic, data can be provided,	We did not study about recycled and reused catalyst, because based on research that has been done by previous

	catalyst used can be characterized by PXRD, SEM with edax, ICP methods	researchers, it has shown that using catalyst for the second time has decreased its activity (Castanheiro <i>et al</i> , 2008).
	Leaching study of catalyst need to perform	In order to optimize the reaction conditions, the effect of different parameters (volume ratio of α -pinene and methanol, temperature, and catalyst loading) on the methoxylation of α -pinene over $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was studied.

Potassium Alum [KAl(SO₄)₂·12H₂O] Solid Catalyst for Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products

Nanik Wijayati^{a,*}, Lulua Romjanah Lestari^a, Lisa Ayuningtyas Wulandari^a, F. Widhi Mahatmanti^a, Senda Kartika Rakainsa^a, Edi Cahyono^b, and Roswanira Abdul Wahab^{c,d}

^aDepartment of Chemistry, Universitas Negeri Semarang, Semarang 50229, Central Java, Indonesia

^bPerhutani Pine Chemical Industry, Pemalang 52319, Central Java, Indonesia

^cDepartment of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Malaysia

^dEnzyme Technology and Green Synthesis Group, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

*Corresponding author, e-mail: nanikanang@gmail.com

Abstract. Methoxylation is a relevant technological process applied in the production of high-value α -pinene derivatives. This report investigates the use of potassium alum [KAl(SO₄)₂·12H₂O] as a catalyst in the methoxylation of α -pinene. In this study, the methoxylation reaction was optimized for the highest conversion of α -pinene and selectivity, assessed for the factors, catalyst loading (0.5; 1.0; and 1.5 g), volume ratio of α -pinene: methanol (1:4, 1:7, 1:10), reaction temperature (50, 55, 60 and 65°C), and reaction time (72, 144, 216, 288, 360 min). The highest selectivity of KAl(SO₄)₂·12H₂O in the methoxylation of α -pinene was achieved under an optimal condition of 1 g of catalyst, volume ratio of 1:10, as well as the reaction temperature and incubation time of 65°C and 6 h, respectively. GC–MS results revealed the yields of the methoxylated products from the 98.2% conversion of α -pinene, to be 59.6%, 8.9%, and 7.1% for α -terpinyl methyl ether (TME), fenchyl methyl ether (FME), bornyl methyl ether (BME), respectively. It was apparent that a lower KAl(SO₄)₂·12H₂O loading (0.5–1.5 g) was more economical for the methoxylation reaction. The findings seen here indicated the suitability of the KAl(SO₄)₂·12H₂O to catalyze the methoxylation of α -pinene to produce an commercially important ethers.

Keywords: α -pinene; methoxylation; potassium alum; catalyst

1. Introduction

α -Pinene is the main constituent of turpentine, the essential oil obtained from pine gum, in live *Pinus* trees, making cuts in the trunk openings of the wood (similar to the extraction of latex for rubber in rubber trees) so the resin present in the resinous channels exudes under pressure [1-2]. Turpentine is a valuable and renewable natural resource widely used in the medical industry, for the synthesis of new important chemicals for use as cosmetic, flavours, fragrances, and pharmaceuticals sectors as well as in the synthesis of chemical intermediates [3]. Thus, α -Pinene is considered a versatile building block for the synthesis of high-value added chemicals, mainly through catalytic processes, such as hydration [4-9], isomerization [10-11], epoxidation and pinene oxide isomerization [12-14], esterification [15-16], and etherification [17-22], among others can be applied to obtain a wide variety of added value products.

The main product of the acid-catalysed methoxylation of α -pinene is α -terpinyl methyl ether, which smells grape fruit-like and might be used as flavour and fragrance and as additive for pharmaceuticals and food industry [23]. Traditionally, sulfuric acid has been used in this reaction, as catalyst [17]. However, solid catalysts have many advantages over liquid acids, such as they do less harm to the environment, can be easily separated from liquid phase and can be reusable. The α -pinene methoxylation has been carried out over beta zeolite [18], sulfonic-modified mesoporous silica /MCM-41, PMO [19], poly(vinyl alcohol) containing sulfonic acid groups [20], Heteropolyacids Immobilized in Silica [21] and microporous and mesoporous carbons [22] and clays mineral [23] reported good selectivities, of ca. 60%, at almost complete conversion.

Potassium Alum ($KAl(SO_4)_2 \cdot 12H_2O$), which is natural materials that cost significantly less than the catalysts listed above, is versatile and environmentally friendly catalysts to promote a wide variety of organic reactions. This study introduces the term "dreamland catalyst" to denote a heterogeneous catalyst which is a cheap, water-soluble, mild, efficient, safe, stable, non-toxic, reliable, incorruptible, recyclable and commercially available compound that can be used in the laboratory without special precautions (easy to use). Moreover, the catalyst has been commonly applied in several other synthetic reactions with good success, for example, including in the transesterification of palm oil [24], acylals [25], Azlactone [26]; coumarins [27], amides [28], β -acetamido ketones [29], novel bis[spiro(quinazoline-oxindole)] derivatives [30], and bispyrazole derivatives [31]. It was therefore decided to investigate alum

($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in catalyzing certain synthetic reactions, this study assumed that this catalyst may be effective to catalyze the methoxylation of α -pinene to produce α -terpinyl methyl ether.

In this work we report the synthesis of α -terpinyl methyl ether via the methoxylation of α -pinene over Potassium Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) catalysts. The influence of various reaction parameters, such as, reaction times, α -pinene to methanol volume ratio, temperature, and catalyst loading on catalyst activity of the active catalyst, is also studied. The parameters were chosen in this study as they are also commonly assessed in similar organic reactions involving polar reagents. It is worth to mention here that the optimal condition for the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation must be found.

2. Materials and Methods

2.1. Materials

α -Pinene standard (98%) was obtained from Sigma Aldrich, while turpentine oil was acquired from KBM Perhutani Pine Chemical Industry, Pemalang, Indonesia. Methanol and potassium alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] for analysis were procured from Merck (Germany).

2.2. Instrumentations

Quantitative and qualitative analyses of the isolated α -pinene and the corresponding methoxylation products were conducted using the GC 23 Agilent 6820 (Version A. 01. 03, South Korea), HP-5 column and FID detector (detector temperature of 300°C), with helium as the carrier gas. The injection temperature was set to 280°C , while the column was maintained at an initial temperature of 70°C for 10 minutes and was increased gradually to 280°C ($5^\circ\text{C}/\text{min}$), and ramped up to 300°C at $20^\circ\text{C}/\text{min}$. Analysis of the methoxylation products was done on a GC-MS (Shimadzu QP-2010 Plus, Japan) equipped with an AOC-20i+s autosampler that was operated under the following conditions: column and injection temperature of 70°C and 200°C , respectively with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min, ion source and interface temperature of 200°C and 240°C , correspondingly. Here, helium (He) gas was used as the carrier at a constant flow rate of $0.1\mu\text{L}/\text{min}$. The percentage of the methoxylation process was estimated from the area beneath each peak. Furthermore, the percentage of

each ether product was achieved by dividing the respective peak area with the isolated α -pinene and multiplied by 100. The qualitative analysis on the produced ether products were done on a Fourier-Transform Infrared Spectrophotometer (Perkin Elmer Spectrum Version 10.4.00, US). Each sample was prepared on KBr pellets and the analysis was done in the wavenumber region of 4000–400 cm^{-1} .

2.3. Procedures

2.3.1 Preparation of the catalysts

Potassium alum was spray-coated over AuPd plates for 90 s under argon flow to produce the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The gas pressure was set to 0.5 bar and the analysis was conducted at 20 mA for 5-10 mins using AuPd as the solvent. The catalyst was characterized on an X-Ray diffractometer (D-Max III (Rigaku) with a Cu $\text{K}\alpha$ radiation source ($\lambda = 1.5378 \text{ \AA}$, 40kV, 30mA). Morphology and mean crystallite size were determined by scanning electron microscopy (SEM) performed on a JEOL JFC-1600 and JSM-6701F equipment. The crystallinity index was estimated using previously described method [32]. FT-IR analysis that was performed within the spectral region of 4000 to 400 cm^{-1} under room temperature.

2.3.2 Isolation of α -pinene

Fractional distillation of turpentine oil was performed under reduced pressure to prepare and concentrate α -pinene as the starting material for the methoxylation process. The isolated α -pinene was analyzed by GC-MS where the column and injection temperature of 70°C and 200°C, respectively with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min, ion source and interface temperature of 200°C and 240°C, correspondingly.

2.3.3 Catalytic experiments

The catalytic experiments were performed in a stirred batch reactor under reflux at different temperatures (50–65°C) and ambient pressure. A known amount of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was thermally activated in an oven at 110°C and then left to cool in a desiccator at room temperature (15 min) to prevent rehydration. The catalyst was quickly transferred into the reaction vessel containing 20 mL dry methanol and was preheated (50–65°C) before the addition of α -pinene (5 mL), followed by continuous

stirring for 360 min. The samples were then collected periodically, and the catalyst was removed using a syringe filter with no impact on the products. It is worth mentioning here that no reaction was observed during storage. The α -pinene methoxylation reaction yields were identified by a GC–MS (Shimadzu QP-2010 Plus) and then quantified on an HP-5 column with helium as carrier gas using the GC Agilent 6820 with a FID detector (T= 300°C). All samples collected were analyzed using a Gas Chromatograph (GC), comparing the retention times of the compounds in the reaction mixture with those of standard compounds.

The reaction conditions were optimized by evaluating the effects of parameters, reaction temperature (50, 55, 60 and 65°C), catalyst loading (0.5; 1; and 1.5 g), and volume ratio of reactants (α -pinene:methanol of 1:4, 1:7, 1:10) during the methoxylation process. In this study, external standard was used to estimate the α -terpinyl methyl ether selectivity, and the percentage conversion of α -pinene by preparing the corresponding standard curves. The conversion of α -pinene (X) and the selectivity (S) for the desired products were defined as follows [5]:

$$X = \frac{\text{converted alpha pinene \%}}{\text{initial alpha pinene \%}} , \quad S = \frac{\text{desired product \%}}{\text{conversion of alpha pinene \%}}$$

3. Results and Discussions

3.1 Characterization of catalyst

Potassium Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) is an inexpensive, non-toxic, water-soluble, and commercially available compound frequently used in the laboratory with no special precautions [24-31]. Data on the characterization of the produced $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ by scanning electron microscopy (SEM), FT-IR, and XRD, are illustrated in Figure 1, Figure 2, and Figure 3, respectively. The micrographs of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ showed reasonable similarities with the microstructure of ammonium aluminum sulfate dodecahydrate [$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$]. However, the latter are reportedly to be of a more rounded shape, with a size range of between 100–200 μm at higher temperatures of 1100-1200°C (Figure 1). However, the overall construct of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is altered, and adopts an overall more elongated oval shape, thus corroborated the findings of an earlier study [33].

Infrared spectroscopy is often used to characterize solid-state catalysts to identify both the organic and inorganic surface functional groups. Figure 2 shows the spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, with the peaks at 1195 cm^{-1} and 1077 cm^{-1} ascribed to the stretching vibration of a $\text{S}=\text{O}$ group, while peaks at 933 cm^{-1} and 737 cm^{-1} were the result of the stretching vibrations of $\text{S}-\text{O}$ and $\text{Al}-\text{O}$ bonds, respectively. Peaks that emerged in the region of $750-400\text{ cm}^{-1}$ indicated the vibration of $\text{Al}-\text{O}$ [34]. Figure 2 illustrates characteristic sharp sulfate (SO_4^{2-}) peaks at $468-471\text{ cm}^{-1}$, $603-608\text{ cm}^{-1}$, $657-686\text{ cm}^{-1}$, $1104-1115\text{ cm}^{-1}$ and $1237-1247\text{ cm}^{-1}$ that corresponded to the symmetrical bending mode of SO_4^{2-} degeneration of asymmetric bending, symmetrical bending, degenerate symmetric stretching and degenerate asymmetric stretching. [24].

Figure 3 depicts the crystallinity and crystal lattice of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, evaluated by XRD. It is important to indicate here, a high crystallinity insinuates appreciable catalytic properties, and better stability at high temperatures, alongside extensive porosity and purity of the sample [35]. The main composition of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was affirmed to be aluminum potassium sulfate, based on the characteristic peaks at $2\theta = 21^\circ$; 28° ; and 32° . Based on the diffractogram in Figure 3, Al_2O_3 was represented by peaks at 36° , 46° and 58° , while the 68.54% of $\text{K}_2(\text{SO}_4)$ corresponded to 22° ; 32° ; and 45° . The results seen here corroborate previous investigation for a similar compound [36], and the 2θ peaks observed at 21° , 22° ; and 28° were consistent with the JCDF File 07.0017 for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Thus, the diffractogram affirmed the prepared catalyst show high crystallinity, matching a recent report from another analogous compound [37].

3.2 Catalytic test

In order to optimise the reaction conditions, the effect of different parameters (volume ratio of α -pinene and methanol, temperature, and catalyst loading,) on the methoxylation of α -pinene over $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was studied.

3.2.1 Effect of volume ratio of α -pinene and methanol

The effect of the volume ratio of α -pinene to methanol (α -pinene:methanol; 1:4, 1:7, 1:10) on the selectivity of α -terpinyl methyl ether by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was also evaluated. In this investigation, the reactions were done at 60°C using a 0.1 g of potassium alum catalyst. The study noted that the catalysts yielded good selectivity values ($\sim 56\%$

with a 75% conversion of α -pinene) of the methoxylation. Results of the α -pinene conversion and relative product selectivity are shown in Figure 4.

The volume ratio of the reactant was found to influence the outcome of the methoxylation reaction, as higher concentrations of methanol in the mixture led to a higher ether yield (Figure 4a). Also, the percentage of the produced ether products increased with longer reaction time. The highest α -pinene conversion (74.8%) was attained with the use of 1:10 ratio of α -pinene:methanol and a reaction time of 360 min. The outcome seen here possibly resulted from the surplus presence of methanol molecules to simultaneously act as a reactant and solvent. This augmented the integration of the reactants and accelerated the conversion of α -pinene into the main ether product, α -terpinyl methyl ether and other ether by-products. In this study, the by-products were formed were from the isomerization of α -pinene under the methoxylation process, including camphene, limonene, and terpinolene, as similarly described by an earlier study [17-22].

Similarly, the highest selectivity of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation was observed at 1:10 ratio of α -pinene:methanol, with stirring for 360 min at 60°C. This also goes to show that the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was capable of carrying out selective methoxylation of the α -pinene to produce ether. Figure 4b and c show the most prominent products to be terpinyl methyl ether (TME) (55.8%) and fenchyl methyl ether (FME) (10.3%).

3.2.2 Effect of reaction temperature

The effect of temperature (50, 55, 60 and 65°C) on the selective production of α -terpinyl methyl ether by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was also investigated, under a constant catalyst loading, and volume ratio of α -pinene:methanol. As anticipated, the percentage conversion increased with the rise in temperature, which resulted in the concomitant increase in methoxylation selectivity towards mono-ether products (Figure 5a-d). Figure 5a revealed that the conversion of α -pinene steadily increased at 60°C. It is worth to indicate here, since the boiling point of methanol was 65°C; hence a lower temperature of 60°C was the suitable reaction temperature for the methoxylation process [21]. However, a notable elevation in reaction time from 72 to 144 minutes was observed at 65°C, wherein the best methoxylation temperature on α -pinene by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ occurred at 65°C for a 98.2% conversion. The outcome seen here also signified that the

temperatures assessed in this study promoted good selectivity of the methoxylation reaction to yield ~60% of the ether products.

The highest selectivity was at 65°C over a reaction time of 360 min, to produce 8.7% of FME (Figure 5b), 7.1% BME (Figure 5c), and 59.6% TME (Figure 5d). Likewise, another study documented a similar trend for the methoxylation of limonene through acid-activated ions and clay exchangers, whereby a higher reaction temperature prevented the decline in catalyst selectivity [38]. Another work saw the alkoxylation of pinene yielded the maximum conversion of the reactant when the reaction temperature and duration were set to 60°C and t=120 min, respectively [21].

Nonetheless, higher temperatures approaching 80°C or higher were found to be counterproductive and promoted the reverse reaction that reformed the pinene isomers in the methanol solvent. The same outcome was also corroborated by an earlier study that investigated a similar reaction using 100 mg of Al-SA_z-1 as the catalyst [23]. Also, a decline in selectivity was not observed during the methoxylation of limonene [38], where the reaction selectivity for mono-ether was largely unaffected when the reaction temperature was increased up to 65°C. Table 1 shows the comparative study of α -pinene methoxylation process in the presence of various catalysts. The highest percentage conversion was obtained using the catalysts, AlSA_z-1.

Table 1. Comparative summary of α -pinene methoxylation in the presence of various catalysts in a batch reactor

Catalysts	Temp (°C)	Reaction Time (h)	Conversion (%)	Selectivity (%)	Literature
AlSA _z -1	60	1	65	65	[5]
AlSA _z -1	40	20	71	91	[32]
CB, CMN, CNorit	60	250	55-75	50-55	[4]
PW2-S	60	27	40	60	[33]
PVSSA-20	60	24	40	60	[15]
PMO-SO ₃ H-g	100	-	90	45	[16]
Beta Zeolite	40	5	92	54	[14]
KAl(SO ₄) ₂ ·12H ₂ O	65	6	98	60	-

3.2.3 Effect of the catalyst loading

The selectivity of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to produce α -terpinyl methyl ether was also studied, using three catalyst loadings of 0.5, 1, and 1.5 g, while other reaction conditions were held constant at 60°C , and α -pinene:methanol volume ratio at 1:10. Table 2 shows the conversion and product selectivity, where the different treatments yielded reasonably good amount of TME ($\sim 54\%$, 75% α -pinene conversion). The $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ solid catalyst prepared in this study successfully converted the α -pinene into the expected ether products. Also, there was an upsurge in the yields of the reaction products following an increase catalyst quantity in the reaction mixture. Interestingly, 0.5 g of the catalyst gave the highest methoxylation α -pinene selectivity for FME and BME, while 1 g prompted higher production of TME. The improved percentage conversion seen here was the likelihood of the higher availability of catalyst active centers to carry out the conversion reaction [22]. The yields of TME in the methoxylation reaction appeared comparable for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ loadings between 0.2–0.4 g, thus evidently indicating the futile use of the catalyst at higher loadings. A lower $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is more economical to produce the ethers in this study.

Table 2. Data on the conversion (% C) and selectivity of methoxylation of α -pinene with a variable of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst loading.

Alum (g)	t (min)	Conversion (% C)	Selectivity of reaction products (%S)		
			TME	BME	FME
0.5	72	18.3	54.9	7.8	11.6
	144	28.7	54.9	7.4	11.2
	216	36.4	54.8	6.9	11.1
	288	44.2	53.8	8.4	10.9
	360	50.1	54.1	7.2	10.9
1.0	72	25.3	53.2	7.6	9.8
	144	37.2	55.2	7.5	10.4
	216	45.1	54.4	7.3	10.3
	288	53.4	54.2	7.7	10.0
	360	60.5	54.5	6.8	10.0
1.5	72	41.9	53.5	7.7	10.5
	144	52.7	53.8	7.2	10.4
	216	61.1	53.3	6.8	10.2
	288	68.5	53.5	6.9	9.8
	360	74.5	53.7	7.0	9.6

Note: %C (% Conversion), %S (% Selectivity), TME (Terpinyl Methyl Ether), BME (Bornyl Methyl Ether), and FME (α -Fenchyl Methyl Ether).

Scheme 1 shows the reaction mechanism of α -pinene methoxylation with potassium alum $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst. According to literary review, acid catalysis by potassium alum ensues via two routes, including A and B, obtained by terpinyl and bornyl ion, respectively [21-22]. The alkoxylation process was initiated by protonation of the α -pinene double bond to create the pinyl ion. This reaction proceeded through two parallel pathways, dependent on the product rearrangement which include bicyclic and monocyclic type. The bornyl and terpinyl ions present in the reaction mixture then react with methanol, and consequently deprotonate to yield the ethers *viz.* TME, BME, and FME. Previous investigation also reported on the reaction of pinene with methanol over the acid sites available on the clay surface, to form terpinyl methyl ether, TME, as the main product [23].

Meanwhile, other compounds identified in the complex include bicyclic ethers, encompassing the fenchyl and bornyl methyl varieties [23]. Formation of several reaction products in the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation process was associated with the irreversible rearrangements of pinyl ion [20], resulting from the intrinsic ability to rearrange into the bornyl ion. This leads to the formation of bornyl methyl ether, and fenchyl methyl ether, following the addition of methanol. Therefore, pinyl ion is further rearranged into the terpinyl ion after the generation of terpinyl methyl ether, using methanol as a solvent. In all, the collective results seen in this study advocated the feasibility of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ for a reasonably satisfactory methoxylation of α -pinene into α -terpinyl methyl ether (TME) as the main product, with relatively good selectivity.

4. Conclusion

In this study, we have successfully demonstrated that the potassium alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] is a potentially effective acid catalyst in the methoxylation of α -pinene, to give α -terpinyl methyl ether (TME) as the main product with fenchyl methyl ether (FME), bornyl methyl ether (BME), limonene, and terpinolene as the by-products. Results revealed that the highest selectivity of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to catalyze the methoxylation of α -pinene was achieved under an optimal condition of 1 g of catalyst, volume ratio of 1:10, as well as the reaction temperature and reaction time of 65°C and 6 h, respectively. This gave the final yield of the ether products as 59.6%, 8.9%, and 7.1% for TME, FME, BME, respectively, following a 98.2% conversion of α -pinene. Further research into the use of nanocatalysts for improving processes using α -pinene chemical

as the starting material may prove useful in improving the product yields and selectivity of the methoxylation process. In a nutshell, the results obtained in this study affirmed the suitability of $KAl(SO_4)_2 \cdot 12H_2O$ to selectively catalyze the methoxylation of α -pinene to produce TME.

Author Contributions

Nanik Wijayati designed the methodology and supervised the project; Lulua Romjanah Lestari performed the experiments, and wrote the original draft; Lisa Ayuningtyas Wulandari assisted in the experimental procedures and maintaining the research data; F. Widhi Mahatmanti analyzed and interpreted the SEM, FT-IR and XRD analysis data; Senda Kartika Rakainsa assisted in data interpretation and validation; Edi Cahyono provided the materials; Roswanira Abdul Wahab helped with the conception and manuscript editing. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest: The authors declare no conflict of interest.

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Figures

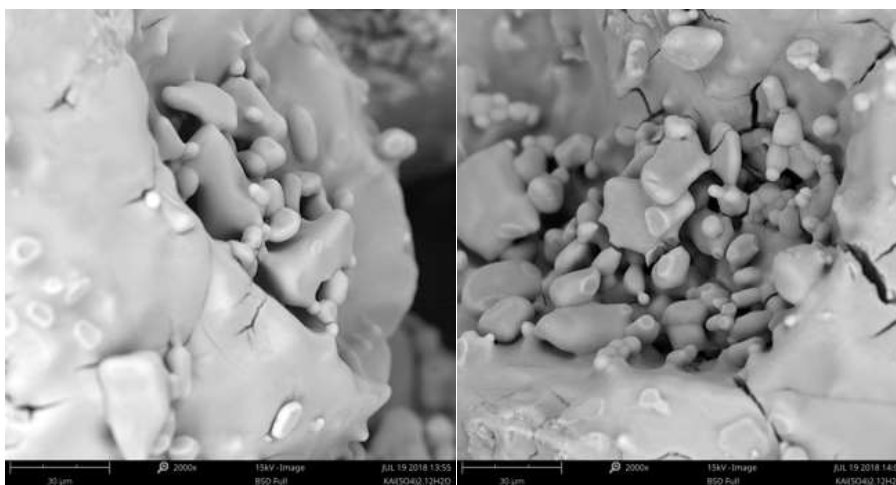


Figure 1. Scanning Electron Microscope (SEM) micrograph of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ magnified 2000 x

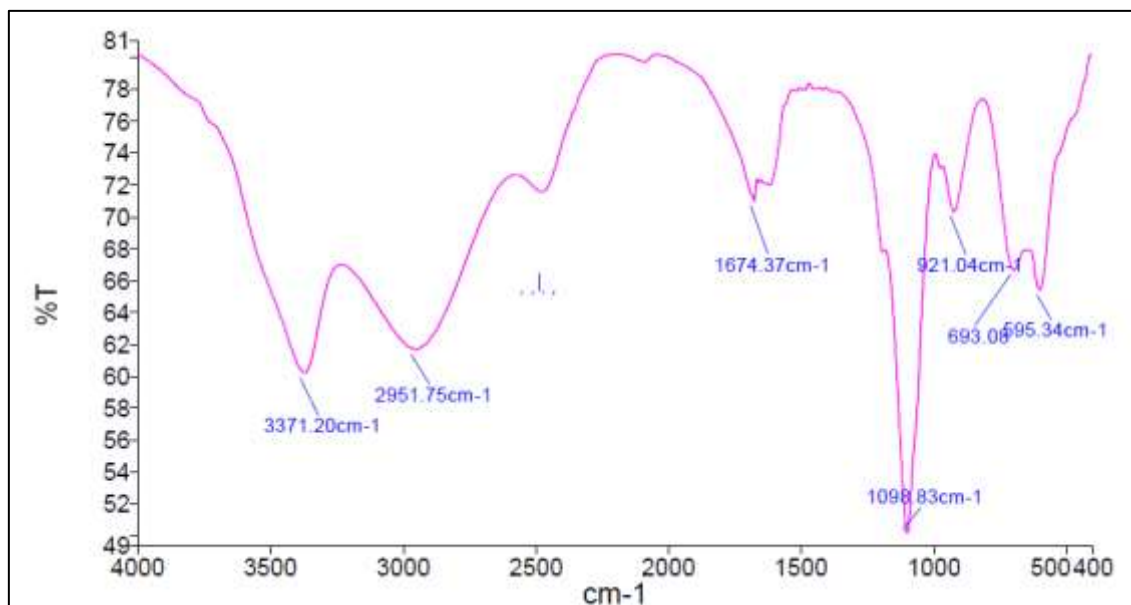


Figure 2. Fourier Transform-Infrared (FT-IR) spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

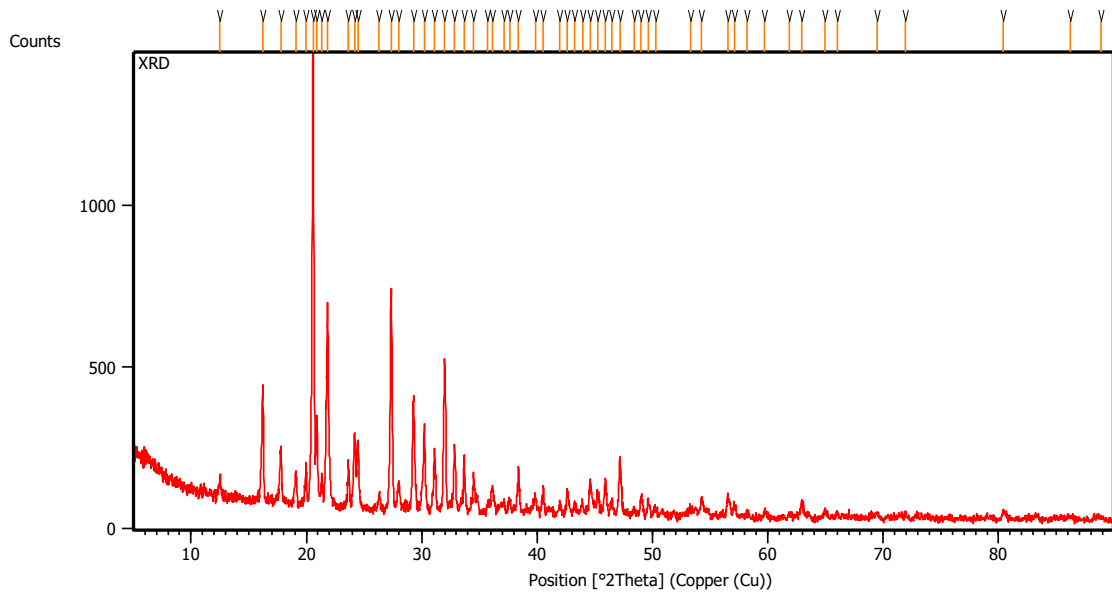


Figure 3. X-ray diffractogram of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

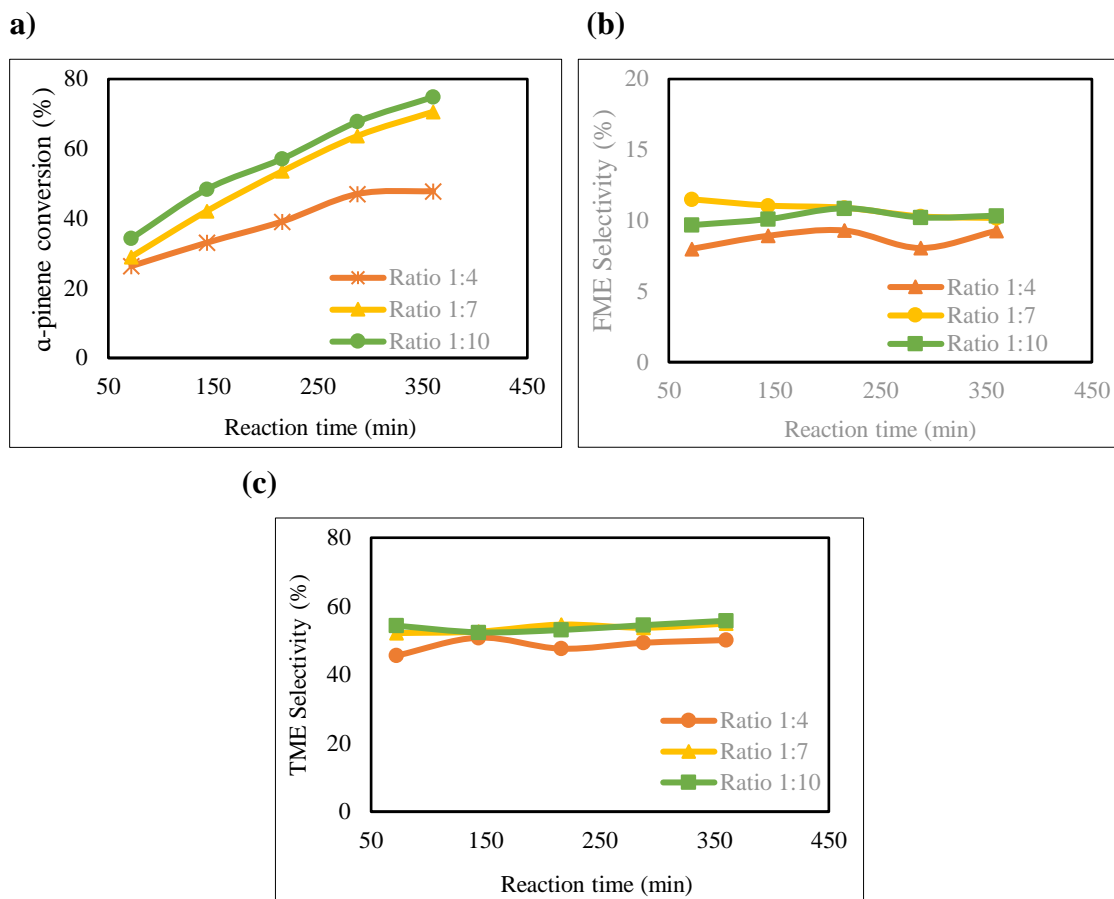


Figure 4. Influence of volume ratio of reactants on the methoxylation of α -pinene: (a) conversion of α -pinene (b) selectivity of Fenchyl Methyl Ether (FME) (c) selectivity of Terpinyl Methyl Ether (TME)

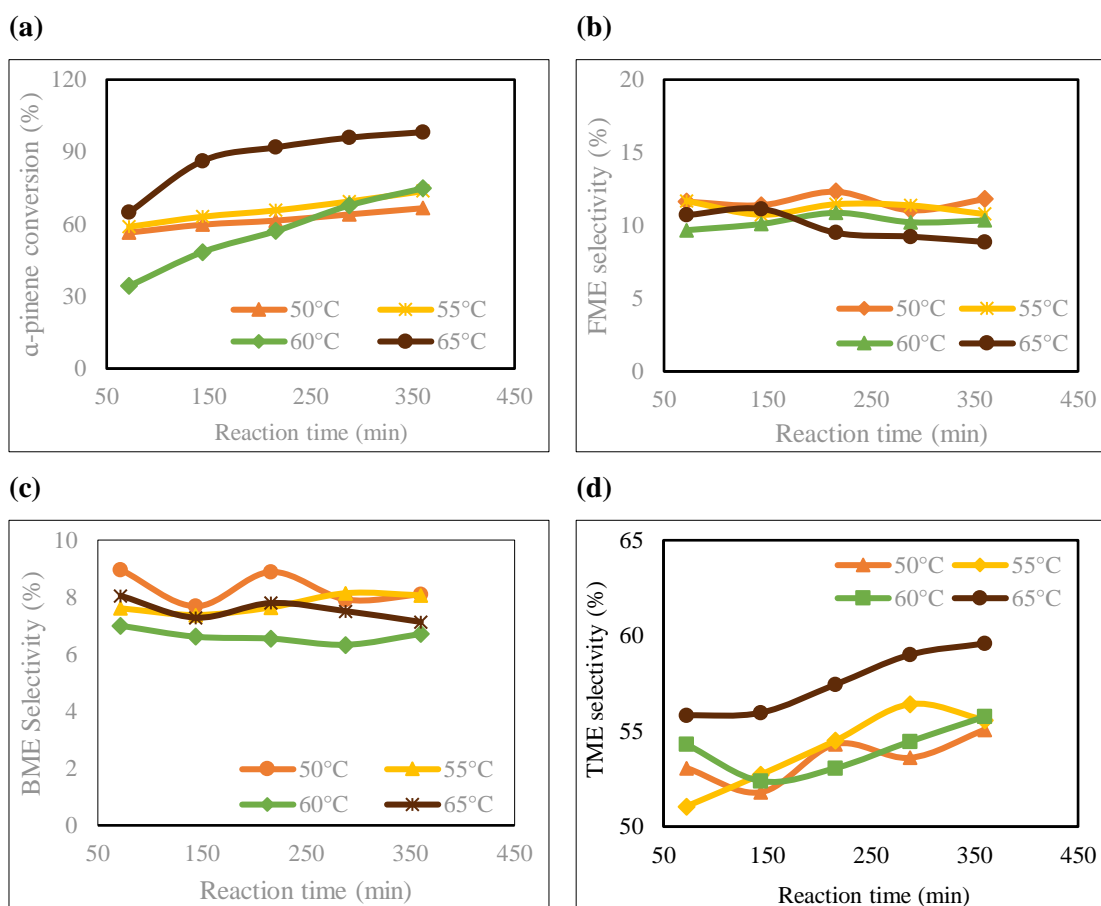
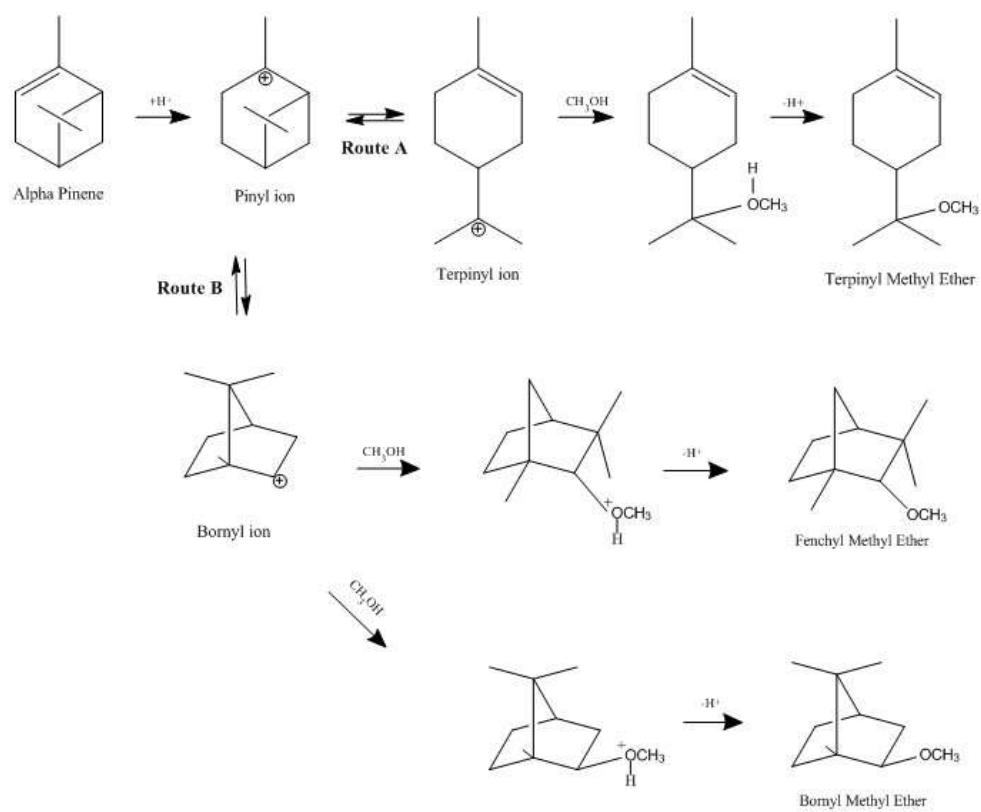


Figure 5. Effect of temperature on α -pinene methoxylation: (a) α -pinene conversion vs time (b) Fenchyl Methyl Ether (FME) selectivity vs time (c) Bornyl Methyl Ether (BME) selectivity vs time (d) Terpinyl Methyl Ether (TME) selectivity vs time



Scheme 1. The mechanism of α -pinene methoxylation

Heliyon

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- 1 - Conceived and designed the experiments;
- 2 - Performed the experiments;
- 3 - Analyzed and interpreted the data;
- 4 - Contributed reagents, materials, analysis tools or data;
- 5 - Wrote the paper.

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Potassium Alum [KAl(SO₄)₂·12H₂O] Solid Catalyst for Effective and Selective Methoxylation Production of Alpha-Pinene Ether Products

Nanik Wijayati^{a,*}, Lulua Romjanah Lestari^a, Lisa Ayuningtyas Wulandari^a, F. Widhi Mahatmanti^a, Senda Kartika Rakainsa^a, Edi Cahyono^b, and Roswanira Abdul Wahab^{c,d}

^aDepartment of Chemistry, Universitas Negeri Semarang, Semarang 50229, Central Java, Indonesia

^bPerhutani Pine Chemical Industry, Pemalang 52319, Central Java, Indonesia

^cDepartment of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Malaysia

^dEnzyme Technology and Green Synthesis Group, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

*Corresponding author, e-mail: nanikanang@gmail.com

Abstract. Methoxylation is a relevant technological process applied in the production of high-value α -pinene derivatives. This report investigates the use of potassium alum [KAl(SO₄)₂·12H₂O] as a catalyst in the methoxylation of α -pinene. In this study, the methoxylation reaction was optimized for the highest conversion of α -pinene and selectivity, assessed for the factors, catalyst loading (0.5; 1.0; and 1.5 g), volume ratio of α -pinene: methanol (1:4, 1:7, 1:10), reaction temperature (50, 55, 60 and 65°C), and reaction time (72, 144, 216, 288, 360 min). The highest selectivity of KAl(SO₄)₂·12H₂O in the methoxylation of α -pinene was achieved under an optimal condition of 1 g of catalyst, volume ratio of 1:10, as well as the reaction temperature and incubation time of 65°C and 6 h, respectively. GC–MS results revealed the yields of the methoxylated products from the 98.2% conversion of α -pinene, to be 59.6%, 8.9%, and 7.1% for α -terpinyl methyl ether (TME), fenchyl methyl ether (FME), bornyl methyl ether (BME), respectively. It was apparent that a lower KAl(SO₄)₂·12H₂O loading (0.5–1.5 g) was more economical for the methoxylation reaction. The findings seen here indicated the suitability of the KAl(SO₄)₂·12H₂O to catalyze the methoxylation of α -pinene to produce an commercially important ethers.

Keywords: α -pinene; methoxylation; potassium alum; catalyst

1. Introduction

α -Pinene is the main constituent of turpentine, the essential oil obtained from pine gum, in live *Pinus* trees, making cuts in the trunk openings of the wood (similar to the extraction of latex for rubber in rubber trees) so the resin present in the resinous channels exudes under pressure [1-2]. Turpentine is a valuable and renewable natural resource widely used in the medical industry, for the synthesis of new important chemicals for use as cosmetic, flavours, fragrances, and pharmaceuticals sectors as well as in the synthesis of chemical intermediates [3]. Thus, α -Pinene is considered a versatile building block for the synthesis of high-value added chemicals, mainly through catalytic processes, such as hydration [4-9], isomerization [10-11], epoxidation and pinene oxide isomerization [12-14], esterification [15-16], and etherification [17-22], among others can be applied to obtain a wide variety of added value products.

The main product of the acid-catalysed methoxylation of α -pinene is α -terpinyl methyl ether, which smells grape fruit-like and might be used as flavour and fragrance and as additive for pharmaceuticals and food industry [23]. Traditionally, sulfuric acid has been used in this reaction, as catalyst [17]. However, solid catalysts have many advantages over liquid acids, such as they do less harm to the environment, can be easily separated from liquid phase and can be reusable. The α -pinene methoxylation has been carried out over beta zeolite [18], sulfonic-modified mesoporous silica /MCM-41, PMO [19], poly(vinyl alcohol) containing sulfonic acid groups [20], heteropolyacids immobilized in silica [21] and microporous and mesoporous carbons [22] and clays mineral [23] reported good selectivities, of ca. 60%, at almost complete conversion.

Potassium Alum ($KAl(SO_4)_2 \cdot 12H_2O$), which is natural materials that cost significantly less than the catalysts listed above, is versatile and environmentally friendly catalysts to promote a wide variety of organic reactions. This study introduces the term "dreamland catalyst" to denote a heterogeneous catalyst which is a cheap, water-soluble, mild, efficient, safe, stable, non-toxic, reliable, incorruptible, recyclable and commercially available compound that can be used in the laboratory without special precautions (easy to use). Moreover, the catalyst has been commonly applied in several other synthetic reactions with good success, for example, including in the transesterification of palm oil [24], acylals [25], Azlactone [26]; coumarins [27], amides [28], β -acetamido ketones [29], novel bis[spiro(quinazoline-oxindole)] derivatives [30], and bispyrazole derivatives [31]. It was therefore decided to investigate alum

($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in catalyzing certain synthetic reactions, this study assumed that this catalyst may be effective to catalyze the methoxylation of α -pinene to produce α -terpinyl methyl ether.

In this work we report the synthesis of α -terpinyl methyl ether via the methoxylation of α -pinene over Potassium Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) catalysts. The influence of various reaction parameters, such as, reaction times, α -pinene to methanol volume ratio, temperature, and catalyst loading on catalyst activity of the active catalyst, is also studied. The parameters were chosen in this study as they are also commonly assessed in similar organic reactions involving polar reagents. It is worth to mention here that the optimal condition for the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation must be found.

2. Materials and Methods

2.1. Materials

α -Pinene standard (98%) was obtained from Sigma Aldrich, while turpentine oil was acquired from KBM Perhutani Pine Chemical Industry, Pematang, Indonesia. Methanol and potassium alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] for analysis were procured from Merck (Germany).

2.2. Instrumentations

Quantitative and qualitative analyses of the isolated α -pinene and the corresponding methoxylation products were conducted using the GC 23 Agilent 6820 (Version A. 01. 03, South Korea), HP-5 column and FID detector (detector temperature of 300°C), with helium as the carrier gas. The injection temperature was set to 280°C , while the column was maintained at an initial temperature of 70°C for 10 minutes and was increased gradually to 280°C ($5^\circ\text{C}/\text{min}$), and ramped up to 300°C at $20^\circ\text{C}/\text{min}$. Analysis of the methoxylation products was done on a GC-MS (Shimadzu QP-2010 Plus, Japan) equipped with an AOC-20i+s autosampler that was operated under the following conditions: column and injection temperature of 70°C and 200°C , respectively with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min, ion source and interface temperature of 200°C and 240°C , correspondingly. Here, helium (He) gas was used as the carrier at a constant flow rate of $0.1\mu\text{L}/\text{min}$. The percentage of the methoxylation process was estimated from the area beneath each peak. Furthermore, the percentage of

each ether product was achieved by dividing the respective peak area with the isolated α -pinene and multiplied by 100. The qualitative analysis on the produced ether products were done on a Fourier-Transform Infrared Spectrophotometer (Perkin Elmer Spectrum Version 10.4.00, US). Each sample was prepared on KBr pellets and the analysis was done in the wavenumber region of 4000–400 cm^{-1} .

2.3. Procedures

2.3.1 Preparation of the catalysts

Potassium alum was spray-coated over AuPd plates for 90 s under argon flow to produce the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The gas pressure was set to 0.5 bar and the analysis was conducted at 20 mA for 5-10 mins using AuPd as the solvent. The catalyst was characterized on an X-Ray diffractometer (D-Max III (Rigaku) with a Cu $\text{K}\alpha$ radiation source ($\lambda = 1.5378 \text{ \AA}$, 40kV, 30mA). Morphology and mean crystallite size were determined by scanning electron microscopy (SEM) performed on a JEOL JFC-1600 and JSM-6701F equipment. The crystallinity index was estimated using previously described method [32]. FT-IR analysis that was performed within the spectral region of 4000 to 400 cm^{-1} under room temperature.

2.3.2 Isolation of α -pinene

Fractional distillation of turpentine oil was performed under reduced pressure to prepare and concentrate α -pinene as the starting material for the methoxylation process. The isolated α -pinene was analyzed by GC-MS where the column and injection temperature of 70°C and 200°C, respectively with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min, ion source and interface temperature of 200°C and 240°C, correspondingly.

2.3.3 Catalytic experiments

The catalytic experiments were performed in a stirred batch reactor under reflux at different temperatures (50–65°C) and ambient pressure. A known amount of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was thermally activated in an oven at 110°C and then left to cool in a desiccator at room temperature (15 min) to prevent rehydration. The catalyst was quickly transferred into the reaction vessel containing 20 mL dry methanol and was preheated (50–65°C) before the addition of α -pinene (5 mL), followed by continuous

stirring for 360 min. The samples were then collected periodically, and the catalyst was removed using a syringe filter with no impact on the products. It is worth mentioning here that no reaction was observed during storage. The α -pinene methoxylation reaction yields were identified by a GC–MS (Shimadzu QP-2010 Plus) and then quantified on an HP-5 column with helium as carrier gas using the GC Agilent 6820 with a FID detector (T= 300°C). All samples collected were analyzed using a Gas Chromatograph (GC), comparing the retention times of the compounds in the reaction mixture with those of standard compounds.

The reaction conditions were optimized by evaluating the effects of parameters, reaction temperature (50, 55, 60 and 65°C), catalyst loading (0.5; 1; and 1.5 g), and volume ratio of reactants (α -pinene:methanol of 1:4, 1:7, 1:10) during the methoxylation process. In this study, external standard was used to estimate the α -terpinyl methyl ether selectivity, and the percentage conversion of α -pinene by preparing the corresponding standard curves. The conversion of α -pinene (X) and the selectivity (S) for the desired products were defined as follows [5]:

$$X = \frac{\text{converted alpha pinene \%}}{\text{initial alpha pinene \%}}, \quad S = \frac{\text{desired product \%}}{\text{conversion of alpha pinene \%}}$$

3. Results and Discussions

3.1 Characterization of catalyst

Potassium Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) is an inexpensive, non-toxic, water-soluble, and commercially available compound frequently used in the laboratory with no special precautions [24-31]. Data on the characterization of the produced $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ by scanning electron microscopy (SEM), FT-IR, and XRD, are illustrated in Figure 1, Figure 2, and Figure 3, respectively. The micrographs of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ showed reasonable similarities with the microstructure of ammonium aluminum sulfate dodecahydrate [$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$]. However, the latter are reportedly to be of a more rounded shape, with a size range of between 100–200 μm at higher temperatures of 1100–1200°C (Figure 1). However, the overall construct of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is altered, and adopts an overall more elongated oval shape, thus corroborated the findings of an earlier study [33].

Infrared spectroscopy is often used to characterize solid-state catalysts to identify both the organic and inorganic surface functional groups. Figure 2 shows the spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, with the peaks at 1195 cm^{-1} and 1077 cm^{-1} ascribed to the stretching

vibration of a S=O group, while peaks at 933 cm^{-1} and 737 cm^{-1} were the result of the stretching vibrations of S—O and Al—O bonds, respectively. Peaks that emerged in the region of 750–400 cm^{-1} indicated the vibration of Al—O [34]. Figure 2 illustrates characteristic sharp sulfate (SO_4^{2-}) peaks at 468–471 cm^{-1} , 603–608 cm^{-1} , 657–686 cm^{-1} , 1104–1115 cm^{-1} and 1237–1247 cm^{-1} that corresponded to the symmetrical bending mode of SO_4^{2-} degeneration of asymmetric bending, symmetrical bending, degenerate symmetric stretching and degenerate asymmetric stretching [24].

Figure 3 depicts the crystallinity and crystal lattice of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, evaluated by XRD. It is important to indicate here, a high crystallinity insinuates appreciable catalytic properties, and better stability at high temperatures, alongside extensive porosity and purity of the sample [35]. The main composition of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was affirmed to be aluminum potassium sulfate, based on the characteristic peaks at $2\theta = 21^\circ$; 28° ; and 32° . Based on the diffractogram in Figure 3, Al_2O_3 was represented by peaks at 36° , 46° and 58° , while the 68.54% of $\text{K}_2(\text{SO}_4)$ corresponded to 22° ; 32° ; and 45° . The results seen here corroborate previous investigation for a similar compound [36], and the 2θ peaks observed at 21° , 22° ; and 28° were consistent with the JCDF File 07.0017 for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Thus, the diffractogram affirmed the prepared catalyst show high crystallinity, matching a recent report from another analogous compound [37].

3.2 Catalytic test

In order to optimise the reaction conditions, the effect of different parameters (volume ratio of α -pinene and methanol, temperature, and catalyst loading,) on the methoxylation of α -pinene over $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was studied.

3.2.1 Effect of volume ratio of α -pinene and methanol

The effect of the volume ratio of α -pinene to methanol (α -pinene:methanol; 1:4, 1:7, 1:10) on the selectivity of α -terpinyl methyl ether by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was also evaluated. In this investigation, the reactions were done at 60°C using a 0.1 g of potassium alum catalyst. The study noted that the catalysts yielded good selectivity values ($\sim 56\%$ with a 75% conversion of α -pinene) of the methoxylation. Results of the α -pinene conversion and relative product selectivity are shown in Figure 4.

The volume ratio of the reactant was found to influence the outcome of the methoxylation reaction, as higher concentrations of methanol in the mixture led to a

higher ether yield (Figure 4a). Also, the percentage of the produced ether products increased with longer reaction time. The highest α -pinene conversion (74.8%) was attained with the use of 1:10 ratio of α -pinene:methanol and a reaction time of 360 min. The outcome seen here possibly resulted from the surplus presence of methanol molecules to simultaneously act as a reactant and solvent. This augmented the integration of the reactants and accelerated the conversion of α -pinene into the main ether product, α -terpinyl methyl ether and other ether by-products. In this study, the by-products were formed were from the isomerization of α -pinene under the methoxylation process, including camphene, limonene, and terpinolene, as similarly described by an earlier study [17-22].

Similarly, the highest selectivity of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation was observed at 1:10 ratio of α -pinene:methanol, with stirring for 360 min at 60°C. This also goes to show that the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was capable of carrying out selective methoxylation of the α -pinene to produce ether. Figure 4b and c show the most prominent products to be terpinyl methyl ether (TME) (55.8%) and fenchyl methyl ether (FME) (10.3%).

3.2.2 Effect of reaction temperature

The effect of temperature (50, 55, 60 and 65°C) on the selective production of α -terpinyl methyl ether by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was also investigated, under a constant catalyst loading, and volume ratio of α -pinene:methanol. As anticipated, the percentage conversion increased with the rise in temperature, which resulted in the concomitant increase in methoxylation selectivity towards mono-ether products (Figure 5a-d). Figure 5a revealed that the conversion of α -pinene steadily increased at 60°C. It is worth to indicate here, since the boiling point of methanol was 65°C; hence a lower temperature of 60°C was the suitable reaction temperature for the methoxylation process [21]. However, a notable elevation in reaction time from 72 to 144 minutes was observed at 65°C, wherein the best methoxylation temperature on α -pinene by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ occurred at 65°C for a 98.2% conversion. The outcome seen here also signified that the temperatures assessed in this study promoted good selectivity of the methoxylation reaction to yield ~60% of the ether products.

The highest selectivity was at 65°C over a reaction time of 360 min, to produce 8.7% of FME (Figure 5b), 7.1% BME (Figure 5c), and 59.6% TME (Figure 5d).

Likewise, another study documented a similar trend for the methoxylation of limonene through acid-activated ions and clay exchangers, whereby a higher reaction temperature prevented the decline in catalyst selectivity [38]. Another work saw the alkoxylation of pinene yielded the maximum conversion of the reactant when the reaction temperature and duration were set to 60°C and t=120 min, respectively [21].

Nonetheless, higher temperatures approaching 80°C or higher were found to be counterproductive and promoted the reverse reaction that reformed the pinene isomers in the methanol solvent. The same outcome was also corroborated by an earlier study that investigated a similar reaction using 100 mg of Al-SAz-1 as the catalyst [23]. Also, a decline in selectivity was not observed during the methoxylation of limonene [38], where the reaction selectivity for mono-ether was largely unaffected when the reaction temperature was increased up to 65°C. Table 1 shows the comparative study of α -pinene methoxylation process in the presence of various catalysts. The highest percentage conversion was obtained using the catalysts, AlSAz-1.

Table 1. Comparative summary of α -pinene methoxylation in the presence of various catalysts in a batch reactor

Catalysts	Temp (°C)	Reaction Time (h)	Conversion (%)	Selectivity (%)	Literature
Beta Zeolite	40	5	92	54	[17]
PMO-SO ₃ H-g	100	-	90	45	[19]
PVSSA-20	60	24	40	60	[20]
PW2-S	60	27	40	60	[21]
CB, CMN, CNorit	60	250	55-75	50-55	[22]
AlSAz-1	60	1	65	65	[23]
AlSAz-1	40	20	71	91	[38]
KAl(SO ₄) ₂ ·12H ₂ O	65	6	98	60	-

3.2.3 Effect of the catalyst loading

The selectivity of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to produce α -terpinyl methyl ether was also studied, using three catalyst loadings of 0.5, 1, and 1.5 g, while other reaction conditions were held constant at 60°C , and α -pinene:methanol volume ratio at 1:10. Table 2 shows the conversion and product selectivity, where the different treatments yielded reasonably good amount of TME (~54%, 75% α -pinene conversion). The $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ solid catalyst prepared in this study successfully converted the α -pinene into the expected ether products. Also, there was an upsurge in the yields of the reaction products following an increase catalyst quantity in the reaction mixture. Interestingly, 0.5 g of the catalyst gave the highest methoxylation α -pinene selectivity for FME and BME, while 1 g prompted higher production of TME. The improved percentage conversion seen here was the likelihood of the higher availability of catalyst active centers to carry out the conversion reaction [22]. The yields of TME in the methoxylation reaction appeared comparable for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ loadings between 0.5–1.5 g, thus evidently indicating the futile use of the catalyst at higher loadings. A lower $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is more economical to produce the ethers in this study.

Table 2. Data on the conversion (% C) and selectivity of methoxylation of α -pinene with a variable of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst loading.

Alum (g)	t (min)	Conversion (% C)	Selectivity of reaction products (%S)		
			TME	BME	FME
0.5	72	18.3	54.9	7.8	11.6
	144	28.7	54.9	7.4	11.2
	216	36.4	54.8	6.9	11.1
	288	44.2	53.8	8.4	10.9
	360	50.1	54.1	7.2	10.9
1.0	72	25.3	53.2	7.6	9.8
	144	37.2	55.2	7.5	10.4
	216	45.1	54.4	7.3	10.3
	288	53.4	54.2	7.7	10.0
	360	60.5	54.5	6.8	10.0
1.5	72	41.9	53.5	7.7	10.5
	144	52.7	53.8	7.2	10.4
	216	61.1	53.3	6.8	10.2
	288	68.5	53.5	6.9	9.8
	360	74.5	53.7	7.0	9.6

Note: %C (% Conversion), %S (% Selectivity), TME (Terpinyl Methyl Ether), BME (Bornyl Methyl Ether), and FME (α -Fenchyl Methyl Ether).

Scheme 1 shows the reaction mechanism of α -pinene methoxylation with potassium alum $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst. According to literary review, acid catalysis by potassium alum ensues via two routes, including A and B, obtained by terpinyl and bornyl ion, respectively [21-22]. The alkoxylation process was initiated by protonation of the α -pinene double bond to create the pinyl ion. This reaction proceeded through two parallel pathways, dependent on the product rearrangement which include bicyclic and monocyclic type. The bornyl and terpinyl ions present in the reaction mixture then react with methanol, and consequently deprotonate to yield the ethers *viz.* TME, BME, and FME. Previous investigation also reported on the reaction of pinene with methanol over the acid sites available on the clay surface, to form terpinyl methyl ether, TME, as the main product [23].

Meanwhile, other compounds identified in the complex include bicyclic ethers, encompassing the fenchyl and bornyl methyl varieties [23]. Formation of several reaction products in the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation process was associated with the irreversible rearrangements of pinyl ion [20], resulting from the intrinsic ability to rearrange into the bornyl ion. This leads to the formation of bornyl methyl ether, and fenchyl methyl ether, following the addition of methanol. Therefore, pinyl ion is further rearranged into the terpinyl ion after the generation of terpinyl methyl ether, using methanol as a solvent. In all, the collective results seen in this study advocated the feasibility of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ for a reasonably satisfactory methoxylation of α -pinene into α -terpinyl methyl ether (TME) as the main product, with relatively good selectivity.

4. Conclusion

In this study, we have successfully demonstrated that the potassium alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] is a potentially effective acid catalyst in the methoxylation of α -pinene, to give α -terpinyl methyl ether (TME) as the main product with fenchyl methyl ether (FME), bornyl methyl ether (BME), limonene, and terpinolene as the by-products. Results revealed that the highest selectivity of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to catalyze the methoxylation of α -pinene was achieved under an optimal condition of 1 g of catalyst, volume ratio of 1:10, as well as the reaction temperature and reaction time of 65°C and 6 h, respectively. This gave the final yield of the ether products as 59.6%, 8.9%, and 7.1% for TME, FME, BME, respectively, following a 98.2% conversion of α -pinene. Further research into the use of nanocatalysts for improving processes using α -pinene chemical

as the starting material may prove useful in improving the product yields and selectivity of the methoxylation process. In a nutshell, the results obtained in this study affirmed the suitability of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to selectively catalyze the methoxylation of α -pinene to produce TME.

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Figures

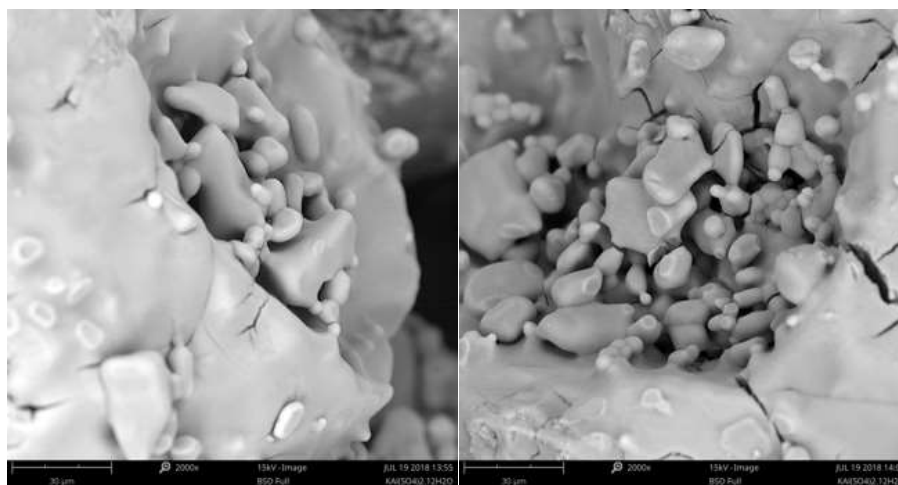


Figure 1. Scanning Electron Microscope (SEM) micrograph of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ magnified 2000 x

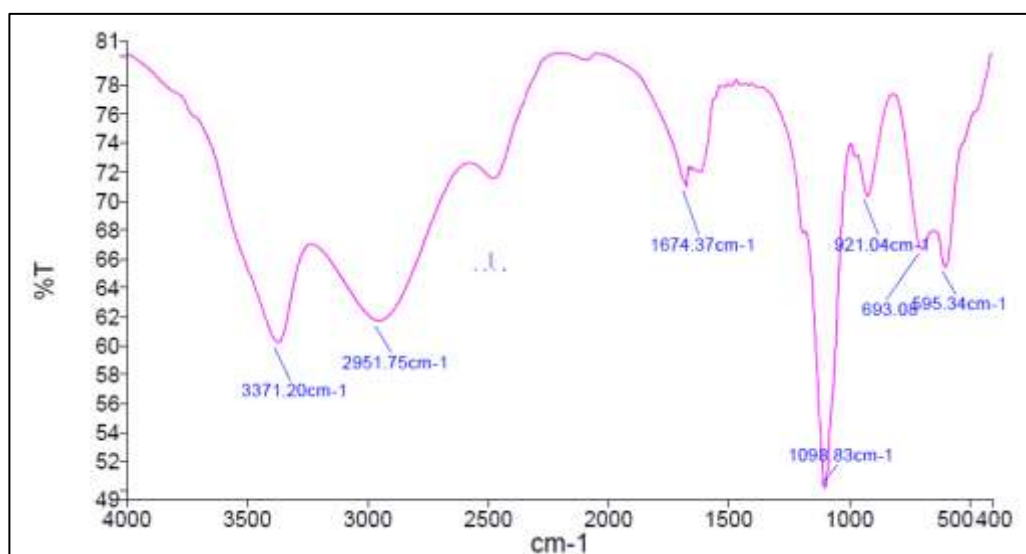


Figure 2. Fourier Transform-Infrared (FT-IR) spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

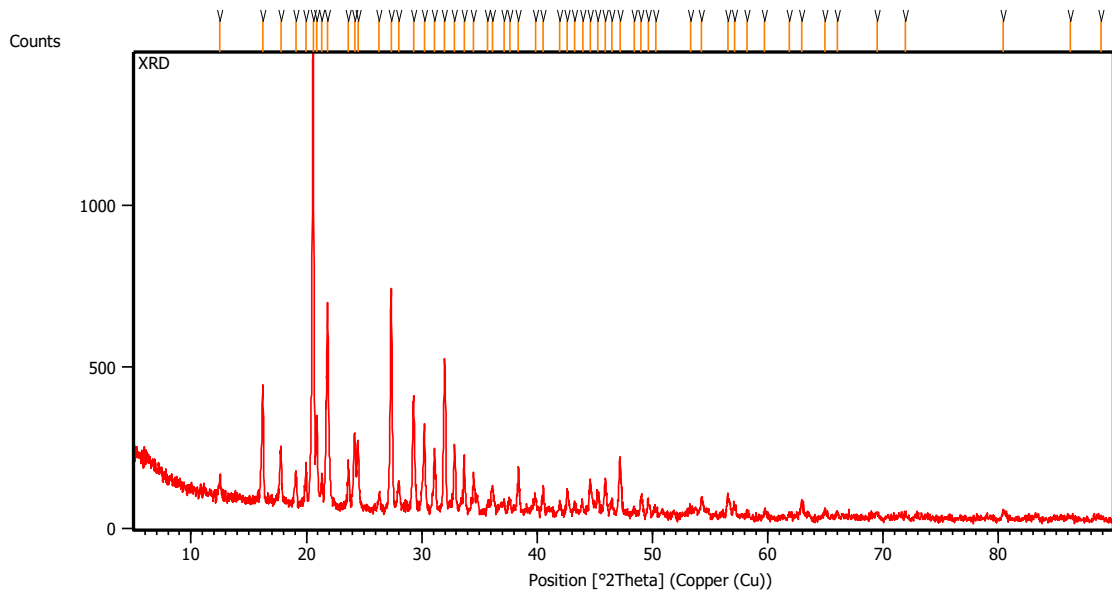


Figure 3. X-ray diffractogram of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

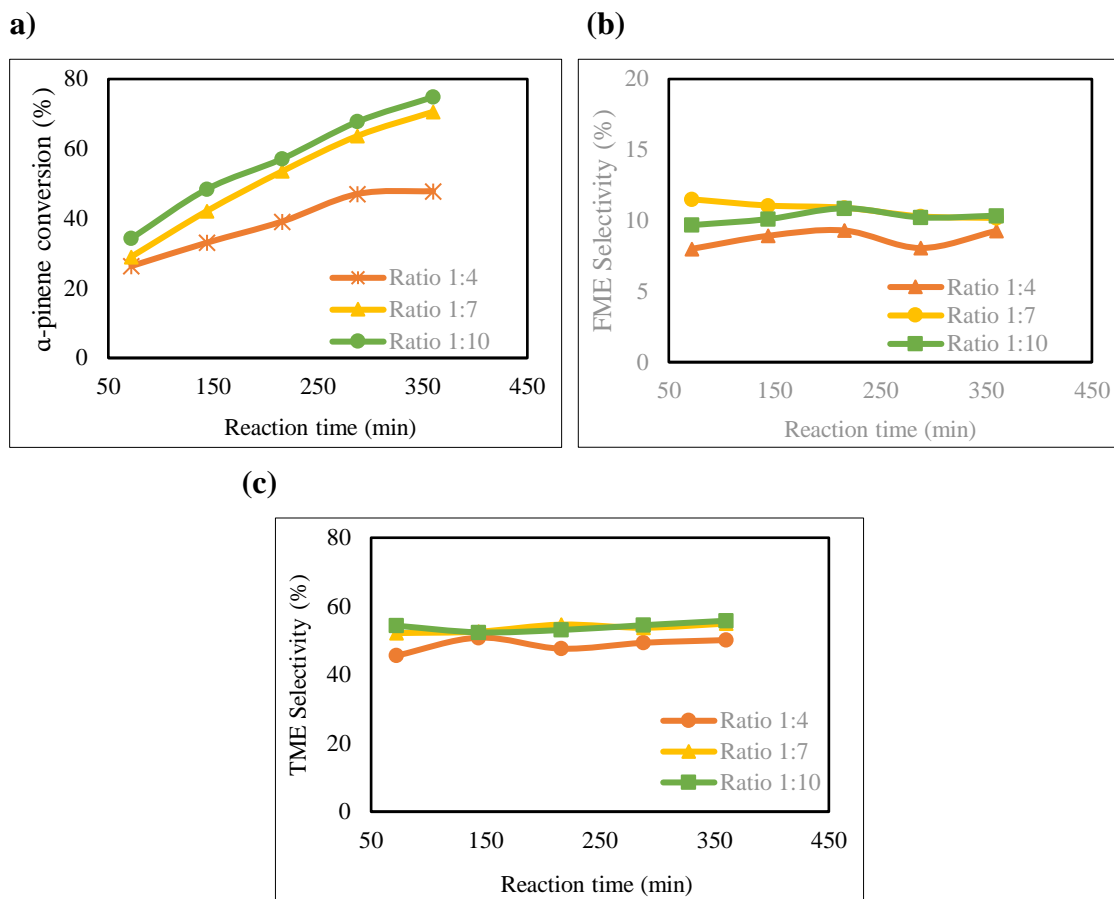


Figure 4. Influence of volume ratio of reactants on the methoxylation of α -pinene: (a) conversion of α -pinene (b) selectivity of Fenchyl Methyl Ether (FME) (c) selectivity of Terpinyl Methyl Ether (TME)

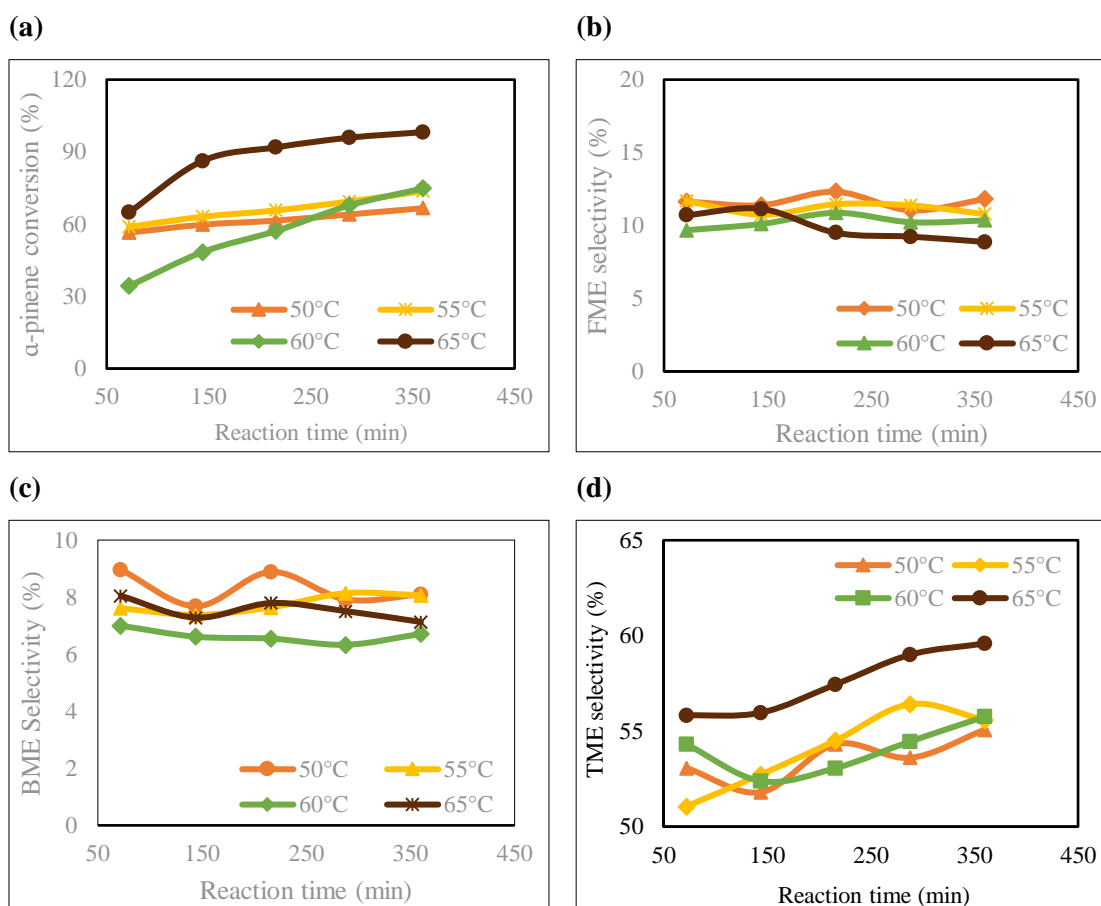
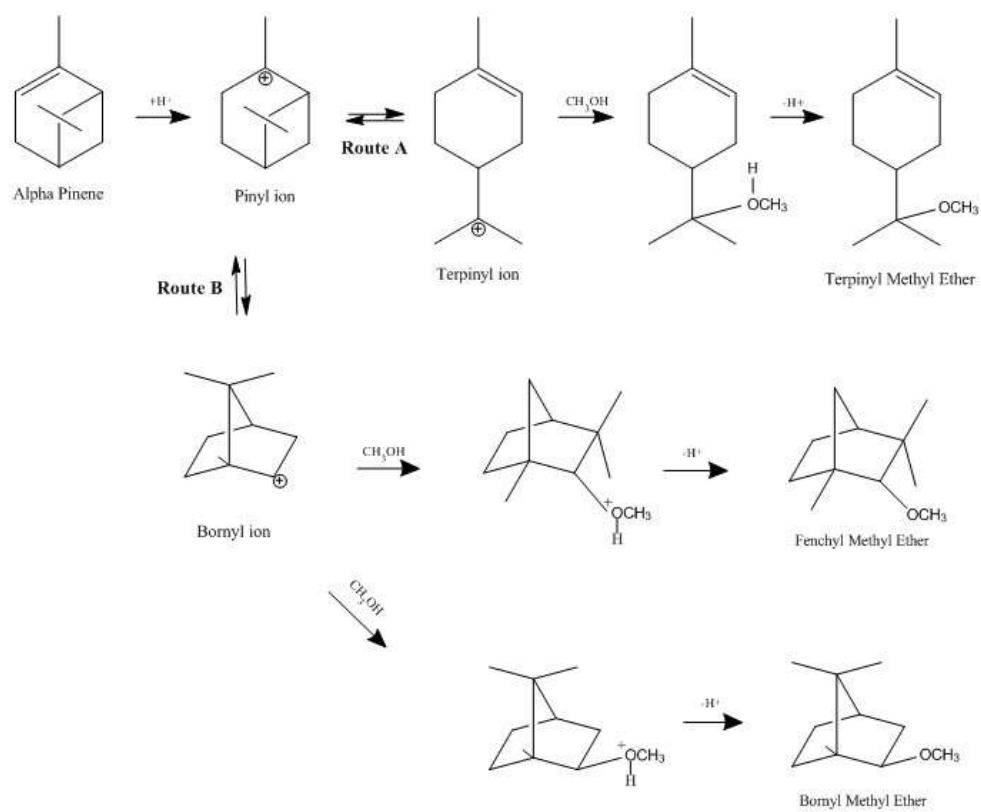


Figure 5. Effect of temperature on α -pinene methoxylation: (a) α -pinene conversion vs time (b) Fenchyl Methyl Ether (FME) selectivity vs time (c) Bornyl Methyl Ether (BME) selectivity vs time (d) Terpinyl Methyl Ether (TME) selectivity vs time



Scheme 1. The mechanism of α -pinene methoxylation

Research article

Potassium Alum [KAl(SO₄)₂·12H₂O] solid catalyst for effective and selective methoxylation production of alpha-pinene ether products

 The corrections made in this section will be reviewed and approved by a journal production editor.

Q3 Nanik Wijayati^{a,*} nanikanang@gmail.com, Lulua Romjanah Lestari^a, Lisa Ayuningtyas Wulandari^a, F. Widhi Mahatmanti^a, Senda Kartika Rakainsa^a, Edi Cahyono^b, Roswanira Abdul Wahab^{c,d}

^aDepartment of Chemistry, Universitas Negeri Semarang, Semarang 50229, Central Java, Indonesia

^bPerhutani Pine Chemical Industry, Pemalang 52319, Central Java, Indonesia

^cDepartment of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Malaysia

^dEnzyme Technology and Green Synthesis Group, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

*Corresponding author.

Abstract

Methoxylation is a relevant technological process applied in the production of high-value α -pinene derivatives. This report investigates the use of potassium alum [KAl(SO₄)₂ · 12H₂O] as a catalyst in the methoxylation of α -pinene. In this study, the methoxylation reaction was optimized for the highest conversion of α -pinene and selectivity, assessed for the factors, catalyst loading (0.5; 1.0; and 1.5 g), volume ratio of α -pinene: methanol (1:4, 1:7, 1:10), reaction temperature (50, 55, 60 and 65 °C), and reaction time (72, 144, 216, 288, 360 min). The highest selectivity of KAl(SO₄)₂·12H₂O in the methoxylation of α -pinene was achieved under an optimal condition of 1 g of catalyst loading, volume ratio of 1:10, as well as the reaction temperature and incubation time of 65 °C and 6 h, respectively. GC-MS results revealed the yields of the methoxylated products from the 98.2% conversion of α -pinene, to be 59.6%, 8.9%, and 7.1% for α -terpinyl methyl ether (TME), fenchyl methyl ether (FME), bornyl methyl ether (BME), respectively. It was apparent that a lower KAl(SO₄)₂·12H₂O loading (0.5–1.5 g) was more economical for the methoxylation reaction. The findings seen here indicated the suitability of the KAl(SO₄)₂ · 12H₂O to catalyze the methoxylation of α -pinene to produce an commercially important ethers.

Keywords: α -Pinene; Methoxylation; Potassium alum; Catalyst

1 Introduction

α -Pinene is the main constituent of turpentine, the essential oil obtained from pine gum, in live Pinus trees, making cuts in the trunk openings of the wood (similar to the extraction of latex for rubber in rubber trees *Hevea brasiliensis*) so the resin present in the resinous channels exudes under pressure [1, 2]. Turpentine is a valuable and renewable natural resource widely used in the medical industry, for the synthesis of new important chemicals for use as cosmetic, flavours, fragrances, and pharmaceuticals sectors as well as in the synthesis of chemical intermediates [3]. Thus, α -Pinene is considered a versatile building block for the synthesis of high-value added chemicals, mainly through catalytic processes, such as hydration [4, 5, 6, 7, 8, 9], isomerization [10, 11], epoxidation and pinene oxide isomerization [12,

13, 14], esterification [15, 16], and etherification [17, 18, 19, 20, 21, 22], among others can be applied to obtain a wide variety of added value products.

The main product of the acid-catalysed methoxylation of α -pinene is α -terpinyl methyl ether, which smells grape fruit-like and might be used as flavour and fragrance and as additive for pharmaceuticals and food industry [23]. Traditionally, sulfuric acid has been used in this reaction, as catalyst [17]. However, solid catalysts have many advantages over liquid acids, such as they do less harm to the environment, can be easily separated from liquid phase and can be reusable. The α -pinene methoxylation has been carried out over beta zeolite [18], sulfonic-modified mesoporous silica/MCM-41, PMO [19], poly(vinyl alcohol) containing sulfonic acid groups [20], heteropolyacids immobilized in silica [21] and microporous and mesoporous carbons [22] and clays mineral [23] reported good selectivities, of ca. 60%, at almost complete conversion.

Potassium Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), which ~~is natural materials that~~ cost significantly less than the catalysts listed above, is versatile and environmentally friendly catalysts to promote a wide variety of organic reactions. This study introduces the term "dreamland catalyst" to denote a heterogeneous catalyst which is a cheap, water-soluble, mild, efficient, safe, stable, non-toxic, reliable, incorruptible, recyclable and commercially available compound that can be used in the laboratory without special precautions (easy to use). Moreover, the catalyst has been commonly applied in several other synthetic reactions with good success, for example, including in the transesterification of palm oil [24], acylals [25], Azlactone [26]; coumarins [27], amides [28], β -acetamido ketones [29], novel bis[spiro(quinazoline-oxindole)] derivatives [30], and bispyrazole derivatives [31]. It was therefore decided to investigate alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in catalyzing certain synthetic reactions, this study assumed that this catalyst may be effective to catalyze the methoxylation of α -pinene to produce α -terpinyl methyl ether.

In this work we report the synthesis of α -terpinyl methyl ether via the methoxylation of α -pinene over Potassium Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) catalysts. The influence of various reaction parameters, such as, reaction times, α -pinene to methanol volume ratio, temperature, and catalyst loading on catalyst activity of the active catalyst, is also studied. The parameters were chosen in this study as they are also commonly assessed in similar organic reactions involving polar reagents. It is worth to mention here that the optimal condition for the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation must be found.

2 Materials and methods

2.1 Materials

α -Pinene standard (98%) was obtained from Sigma Aldrich, while turpentine oil was acquired from KBM Perhutani Pine Chemical Industry, Pemalang, Indonesia. Methanol and potassium alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] for analysis were procured from Merck (Germany).

2.2 Instrumentations

Quantitative and qualitative analyses of the isolated α -pinene and the corresponding methoxylation products were conducted using the GC 23 Agilent 6820 (Version A. 01. 03, South Korea), HP-5 column and FID detector (detector temperature of 300 °C), with helium as the carrier gas. The injection temperature was set to 280 °C, while the column was maintained at an initial temperature of 70 °C for 10 min and was increased gradually to 280 °C (5°C/min), and ramped up to 300 °C at 20°C/min. Analysis of the methoxylation products was done on a GC-MS (Shimadzu QP-2010 Plus, Japan) equipped with an AOC-20i + s autosampler that was operated under the following conditions: column and injection temperature of 70 °C and 200 °C, respectively with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min, ion source and interface temperature of 200 °C and 240 °C, correspondingly. Here, helium (He) gas was used as the carrier at a constant flow rate of 0.1 $\mu\text{L}/\text{min}$. The percentage of the methoxylation process was estimated from the area beneath each peak. Furthermore, the percentage of each ether product was achieved by dividing the respective peak area with the isolated α -pinene and multiplied by 100. The qualitative analysis on the produced ether products were done on a Fourier-Transform Infrared Spectrophotometer (PerkinElmer Spectrum Version 10.4.00, US). Each sample was prepared on KBr pellets and the analysis was done in the wavenumber region of ~~Please be informed that we have add Heliyon taxonomy term in the keywords section as per the journal standard style. Unfortunately, will not be able to make changes to the keywords as we require these terms to locate your paper on the website. Hope this is~~

2.3 Procedures

2.3.1 Preparation of the catalysts

~~Potassium alum was~~ The $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was thermally activated in an oven at 110 °C and then left to cool in a desiccator at room temperature (15 min) to prevent rehydration before used. The morphology of alum was determined by scanning electron microscopy (SEM) performed on a JEOL JFC-1600 and JSM-6701F equipment. Alum catalyst was spray-coated over AuPd plates for 9010 minutes s under argon flow to produce generate conductive layers the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The gas pressure was set to 0.5 bar and the analysis was conducted at 20 mA for 5–10 min using AuPd as the solvent coa. The catalyst was characterized on an X-Ray diffractometer (D-Max III (Rigaku) with a Cu K α radiation source ($\alpha = 1.5378 \text{ \AA}$, 40kV, 30mA). Morphology and mean crystallite size were determined by scanning electron microscopy (SEM) performed on a JEOL JFC-1600 and JSM-6701F equipment. The crystallinity index was estimated using previously described method [32]. FT-IR analysis that was performed within the spectral region of 4000 to 400 cm⁻¹ under room temperature.

2.3.2 Isolation of α -pinene

Fractional distillation of turpentine oil was performed under reduced pressure to prepare and concentrate α -pinene as the starting material for the methoxylation process. The isolated α -pinene was then analyzed by GC-MS where the column and injection temperature of 70 °C and 200 °C, respectively with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min, ion source and interface temperature of 200 °C and 240 °C, correspondingly.

2.3.3 Catalytic experiments

The catalytic experiments were performed in a stirred batch reactor under reflux at different temperatures (50–65 °C) and ambient pressure. A known amount of the ~~The activated~~ $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was thermally activated in an oven at 110 °C and then left to cool in a desiccator at room temperature (15 min) to prevent rehydration. The catalyst was quickly transferred into the reaction vessel containing 20 mL dry methanol and was preheated (50–65 °C) before the addition of α -pinene (5 mL), followed by continuous stirring for 360 min. The samples were then collected periodically, and the catalyst was removed using a syringe filter with no impact on the products. It is worth mentioning here that no reaction was observed during storage. The α -pinene methoxylation reaction yields were identified by a GC-MS (Shimadzu QP-2010 Plus) and then quantified on an HP-5 column with helium as carrier gas using the GC Agilent 6820 with a FID detector (T = 300 °C). All samples collected were analyzed using a Gas Chromatograph (GC), comparing the retention times of the compounds in the reaction mixture with those of standard compounds.

The reaction conditions were optimized by evaluating the effects of parameters, reaction temperature (50, 55, 60 and 65 °C), catalyst loading (0.5; 1; and 1.5 g), and volume ratio of reactants (α -pinene:methanol of 1:4, 1:7, 1:10) during the methoxylation process. In this study, external standard was used to estimate the α -terpinyl methyl ether selectivity, and the percentage conversion of α -pinene by preparing the corresponding standard curves. The conversion of α -pinene (X) and the selectivity (S) for the desired products were defined as follows [5]:

$$X = \frac{\text{converted } \alpha \text{ pinene } \%}{\text{initial } \alpha \text{ pinene } \%}, S = \frac{\text{desired product } \%}{\text{conversion of } \alpha \text{ pinene } \%}$$

3 Results and discussions

3.1 Characterization of catalyst

Potassium Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) is an inexpensive, non-toxic, water-soluble, and commercially available compound frequently used in the laboratory with no special precautions [24, 25, 26, 27, 28, 29, 30, 31]. Data on the characterization of the produced $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ by scanning electron microscopy (SEM), FT-IR, and XRD, are illustrated in Figure 1, Figure 2, and Figure 3, respectively. The micrographs of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ showed reasonable similarities with the microstructure of ammonium aluminum sulfate dodecahydrate [$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$]. However,

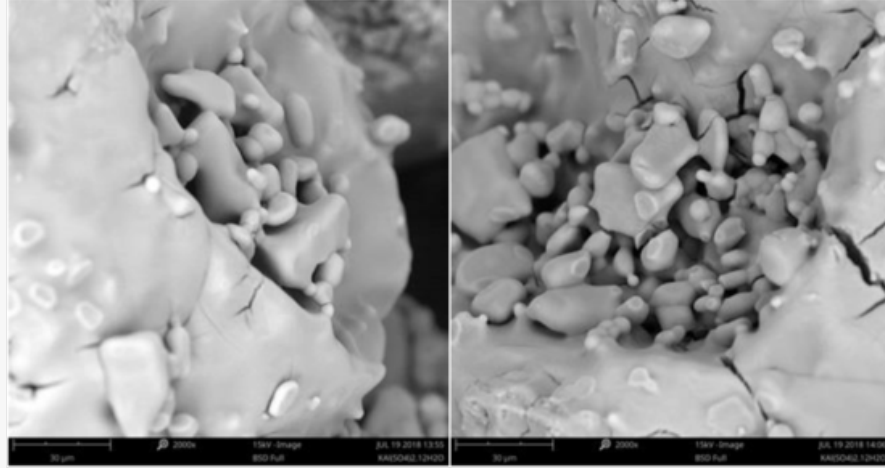
the latter are reportedly to be of a more rounded shape, with a size range of between 100–200 μm at higher temperatures of 1100–1200 $^{\circ}\text{C}$ (Figure 1). However, the overall construct of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is altered, and adopts an overall more elongated oval shape, thus corroborated the findings of an earlier study [33].

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alt-text: Figure 1

Figure 1

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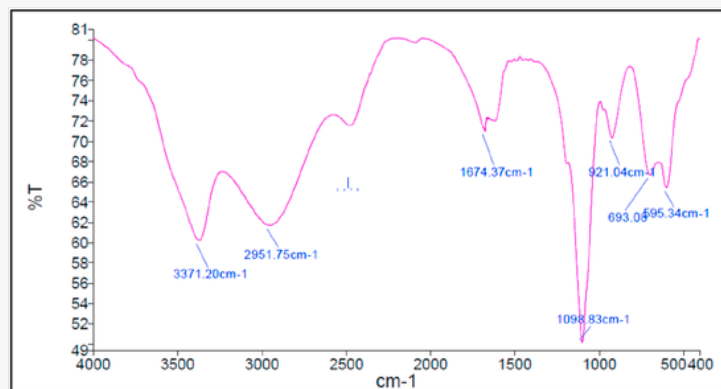
Scanning Electron Microscope (SEM) micrograph of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ magnified 2000 x.

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alt-text: Figure 2

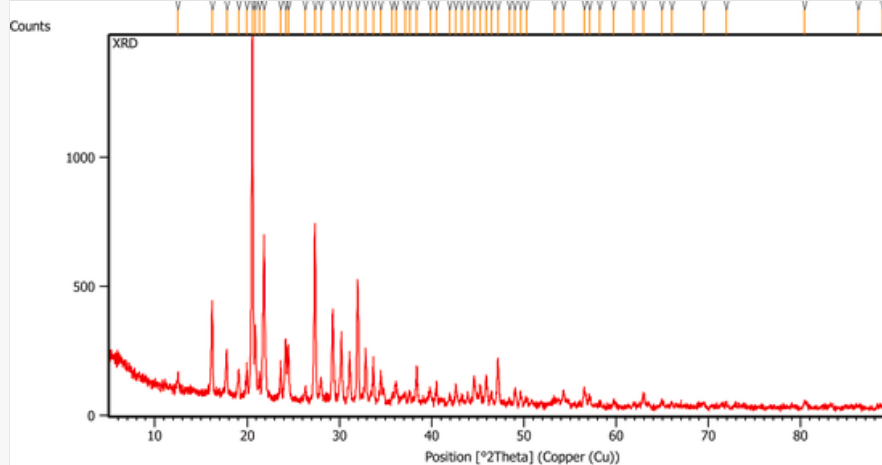
Figure 2



Fourier Transform-Infrared (FT-IR) spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

alt-text: Figure 3

Figure 3



X-ray diffractogram of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Infrared spectroscopy is often used to characterize solid-state catalysts to identify both the organic and inorganic surface functional groups. Figure 2 shows the spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, with the peaks at 1195 cm^{-1} and 1077 cm^{-1} ascribed to the stretching vibration of a S=O group, while peaks at 933 cm^{-1} and 737 cm^{-1} were the result of the stretching vibrations of S—O and Al—O bonds, respectively. Peaks that emerged in the region of $750\text{--}400\text{ cm}^{-1}$ indicated the vibration of Al—O [34]. Figure 2 illustrates characteristic sharp sulfate (SO_4^{2-}) peaks at $468\text{--}471\text{ cm}^{-1}$, $603\text{--}608\text{ cm}^{-1}$, $657\text{--}686\text{ cm}^{-1}$, $1104\text{--}1115\text{ cm}^{-1}$ and $1237\text{--}1247\text{ cm}^{-1}$ that corresponded to the symmetrical bending mode of SO_4^{2-} degeneration of asymmetric bending, symmetrical bending, degenerate symmetric stretching and degenerate asymmetric stretching [24].

Figure 3 depicts the crystallinity and crystal lattice of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, evaluated by XRD. It is important to indicate here, a high crystallinity insinuates appreciable catalytic properties, and better stability at high temperatures, alongside extensive porosity and purity of the sample [35]. The main composition of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was affirmed to be aluminum potassium sulfate, based on the characteristic peaks and it at $2\theta = 21^\circ$, 28° , and 32° . Based on the diffractogram in Figure-3, Al_2O_3 was represented by peaks at 36° , 46° and 58° , while the 68.54% of $\text{K}_2(\text{SO}_4)$ corresponded to 22° , 32° , and 45° . The results seen here corroborate previous investigation for a similar compound [36], and the 2θ peaks observed at 21° , 22° , and 28° were consistent with the JPDF JCPDF File 07-0017 for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Thus, the diffractogram affirmed the prepared catalyst show high crystallinity, matching a recent report from another analogous compound [37].

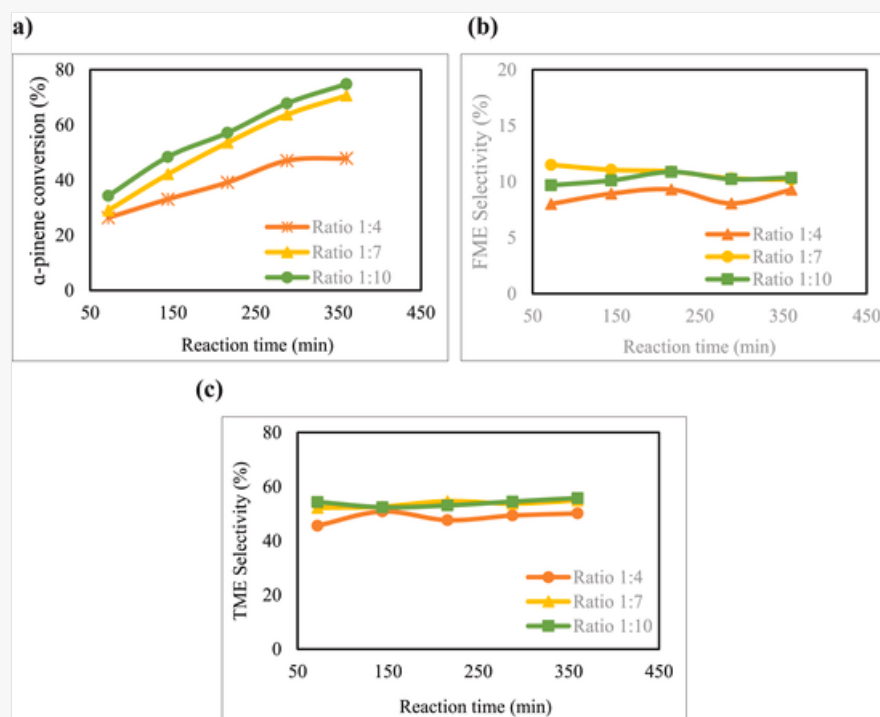
3.2 Catalytic test

In order to optimise the reaction conditions, the effect of different parameters (volume ratio of α -pinene and methanol, temperature, and catalyst loading) on the methoxylation of α -pinene over $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was studied.

3.2.1 Effect of volume ratio of α -pinene and methanol

The effect of the volume ratio of α -pinene to methanol (α -pinene:methanol; 1:4, 1:7, 1:10) on the selectivity of α -terpinyl methyl ether by over $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was also evaluated. In this investigation, the reactions were done at $60\text{ }^\circ\text{C}$ using a 0.1 g of potassium alum catalyst. The study noted that the catalysts yielded good selectivity values ($\sim 56\%$ with a 75% conversion of α -pinene) of the methoxylation. Results of the α -pinene conversion and relative product selectivity are shown in Figure 4.

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Influence of volume ratio of reactants on the methoxylation of α -pinene: (a) conversion of α -pinene (b) selectivity of Fenchyl Methyl Ether (FME) (c) selectivity of Terpinyl Methyl Ether (TME).

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The volume ratio of the reactant was found to influence the outcome of the methoxylation reaction, as higher concentrations of methanol in the mixture led to a higher ether yield (Figure 4a). Also, the percentage of the produced ether products increased with longer reaction time. The highest α -pinene conversion (74.8%) was attained with the use of 1:10 ratio of α -pinene:methanol and a reaction time of 360 min. The outcome seen here possibly resulted from the surplus presence of methanol molecules to simultaneously act as a reactant and solvent. This augmented the integration of the reactants and accelerated the conversion of α -pinene into the main ether product, α -terpinyl methyl ether and other ether by-products. In this study, the by-products were formed were from the isomerization of α -pinene under the methoxylation process, including camphene, limonene, and terpinolene, as similarly described by an earlier study [17, 18, 19, 20, 21, 22].

Similarly, the highest selectivity of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation was observed at 1:10 ratio of α -pinene:methanol, with stirring for 360 min at 60 °C. This also goes to show that the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was capable of carrying out selective methoxylation of the α -pinene to produce ether. Figure 4b and c show the most prominent products to be terpinyl methyl ether (TME) (55.8%) and fenchyl methyl ether (FME) (10.3%).

3.2.2 Effect of reaction temperature

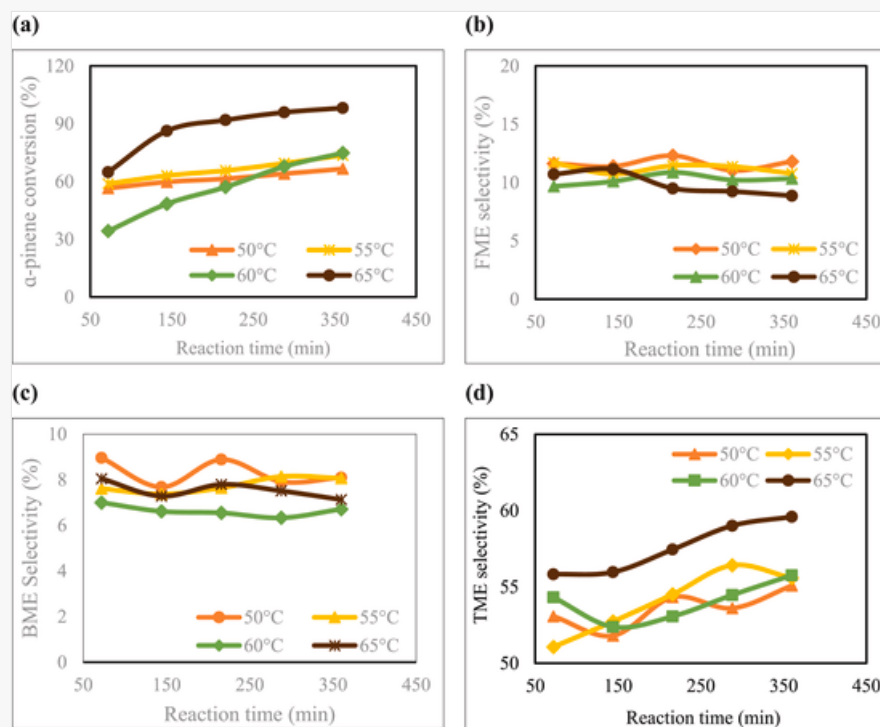
The effect of temperature (50, 55, 60 and 65 °C) on the selective production of α -terpinyl methyl ether by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was also investigated, under a constant catalyst loading, and volume ratio of α -pinene:methanol. As anticipated, the percentage conversion increased with the rise in temperature, which resulted in the concomitant increase in methoxylation selectivity towards mono-ether products (Figure 5a-d). Figure 5a revealed that the conversion of α -pinene steadily increased at 60 °C. It is worth to indicate here, since the boiling point of methanol was 65 °C; hence a lower temperature of 60 °C was the suitable reaction temperature for the methoxylation process [21]. However, a notable elevation in reaction time from 72 to 144 min was observed at 65 °C, wherein the best methoxylation temperature on α -pinene by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ occurred at 65 °C for a 98.2% conversion. The outcome seen here

also signified that the temperatures assessed in this study promoted good selectivity of the methoxylation reaction to yield ~60% of the ether products.

alt-text: Figure 5

Figure 5

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Effect of temperature on α -pinene methoxylation: (a) α -pinene conversion vs time (b) Fenchyl Methyl Ether (FME) selectivity vs time (c) Bornyl Methyl Ether (BME) selectivity vs time (d) Terpinyl Methyl Ether (TME) selectivity vs time.

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The highest selectivity was at 65 °C over a reaction time of 360 min, to produce 8.7% of FME (Figure 5b), 7.1% BME (Figure 5c), and 59.6% TME (Figure 5d). Likewise, another study documented a similar trend for the methoxylation of limonene through acid-activated ions and clay exchangers, whereby a higher reaction temperature prevented the decline in catalyst selectivity [38]. Another work saw the alkoxylation of pinene yielded the maximum conversion of the reactant when the reaction temperature and duration were set to 60 °C and $t = 120$ min, respectively [21].

Nonetheless, higher temperatures approaching 80 °C or higher were found to be counterproductive and promoted the reverse reaction that reformed the pinene isomers in the methanol solvent. The same outcome was also corroborated by an earlier study that investigated a similar reaction using 100 mg of Al-SA_z-1 as the catalyst [23]. Also, a decline in selectivity was not observed during the methoxylation of limonene [38], where the reaction selectivity for mono-ether was largely unaffected when the reaction temperature was increased up to 65 °C. Table 1 shows the comparative study of α -pinene methoxylation process in the presence of various catalysts. The highest percentage conversion was obtained using the catalysts, AlSA_z-1.

alt-text: Table 1

Table 1

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Catalysts	Temp (°C)	Reaction Time (h)	Conversion (%)	Selectivity (%)	Literature
Beta Zeolite	40	5	92	54	[17]
PMO-SO ₃ H-g	100	-	90	45	[19]
PVSSA-20	60	24	40	60	[20]
PW2-S	60	27	40	60	[21]
CB, CMN, CNorit	60	250	55–75	50–55	[22]
AISAz-1	60	1	65	65	[23]
AISAz-1	40	20	71	91	[38]
KAl(SO ₄) ₂ ·12H ₂ O	65	6	98	60	-

3.2.3 Effect of the catalyst loading

The selectivity of KAl(SO₄)₂·12H₂O to produce α -terpinyl methyl ether was also studied, using three catalyst loadings of 0.5, 1, and 1.5 g, while other reaction conditions were held constant at 60 °C, and α -pinene:methanol volume ratio at 1:10. Table 2 shows the conversion and product selectivity, where the different treatments yielded reasonably good amount of TME (~54%, 75% α -pinene conversion). The KAl(SO₄)₂·12H₂O solid catalyst prepared in this study successfully converted the α -pinene into the expected ether products. Also, there was an upsurge in the yields of the reaction products following an increase catalyst quantity in the reaction mixture. Interestingly, 0.5 g of the catalyst gave the highest methoxylation α -pinene selectivity for FME and BME, while 1 g prompted higher production of TME. The improved percentage conversion seen here was the likelihood of the higher availability of catalyst active centers to carry out the conversion reaction [22]. The yields of TME in the methoxylation reaction appeared comparable for KAl(SO₄)₂·12H₂O loadings between 0.5–1.5 g, thus evidently indicating the futile use of the catalyst at higher loadings. A lower KAl(SO₄)₂·12H₂O is more economical to produce the ethers in this study.

alt-text: Table 2

Table 2

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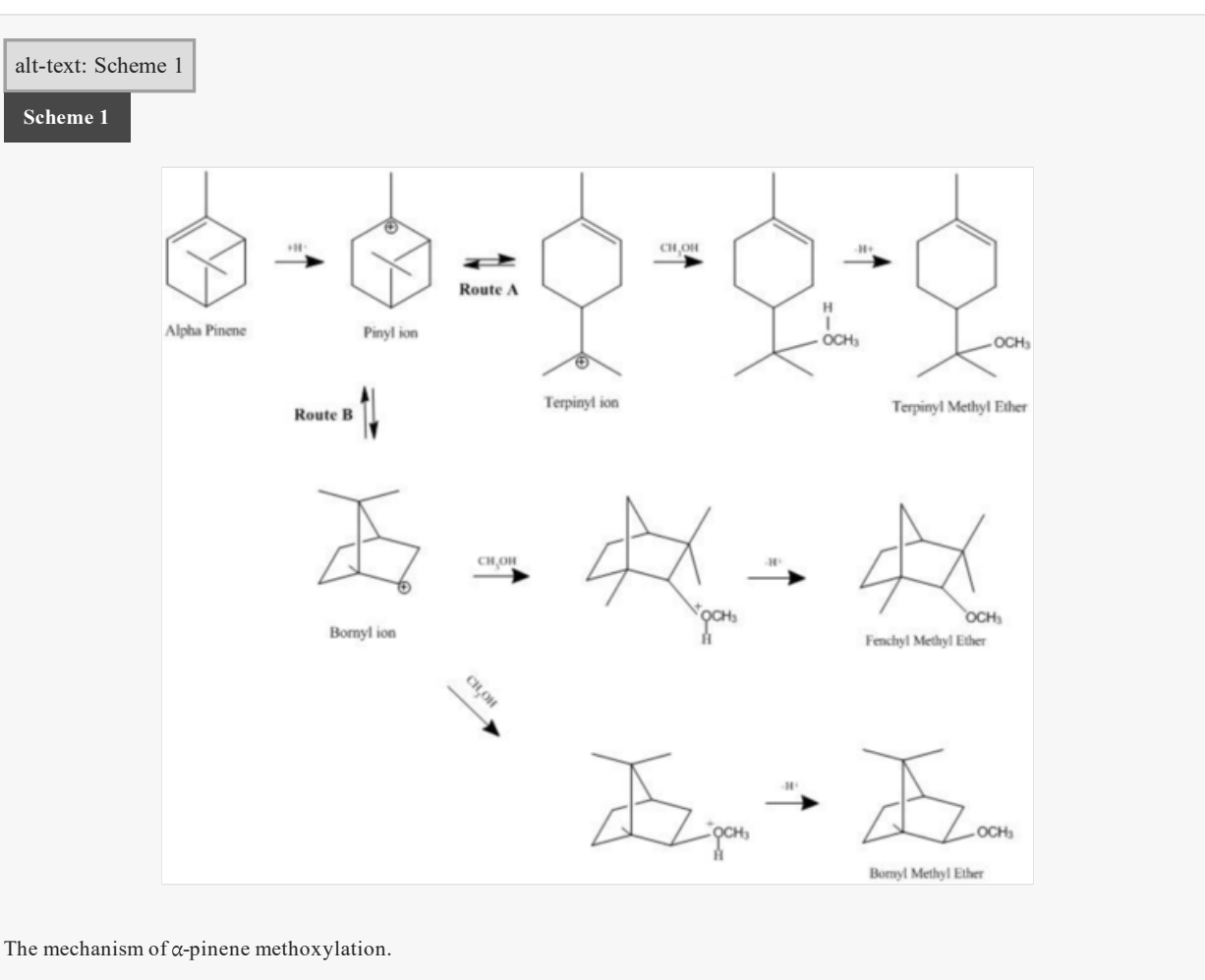
Data on the conversion (% C) and selectivity of methoxylation of α -pinene with a variable of the KAl(SO₄)₂·12H₂O catalyst loading.

Alum (g)	t (min)	Conversion (% C)	Selectivity of reaction products (%S)		
			TME	BME	FME
0.5	72	18.3	54.9	7.8	11.6
	144	28.7	54.9	7.4	11.2
	216	36.4	54.8	6.9	11.1
	288	44.2	53.8	8.4	10.9
	360	50.1	54.1	7.2	10.9
1.0	72	25.3	53.2	7.6	9.8
	144	37.2	55.2	7.5	10.4
	216	45.1	54.4	7.3	10.3
	288	53.4	54.2	7.7	10.0
	360	60.5	54.5	6.8	10.0

1.5	72	41.9	53.5	7.7	10.5
	144	52.7	53.8	7.2	10.4
	216	61.1	53.3	6.8	10.2
	288	68.5	53.5	6.9	9.8
	360	74.5	53.7	7.0	9.6

Note: %C (% Conversion), %S (% Selectivity), TME (Terpinyl Methyl Ether), BME (Bornyl Methyl Ether), and FME (α -Fenchyl Methyl Ether).

Scheme 1 shows the reaction mechanism of α -pinene methoxylation with potassium alum $KAl(SO_4)_2 \cdot 12H_2O$ catalyst. According to literary review, acid catalysis by potassium alum ensues via two routes, including A and B, obtained by terpinyl and bornyl ion, respectively [21, 22]. The alkoxylation process was initiated by protonation of the α -pinene double bond to create the pinyll ion. This reaction proceeded through two parallel pathways, dependent on the product rearrangement which include bicyclic and monocyclic type. The bornyl and terpinyl ions present in the reaction mixture then react with methanol, and consequently deprotonate to yield the ethers *viz.* TME, BME, and FME. Previous investigation also reported on the reaction of pinene with methanol over the acid sites available on the clay surface, to form terpinyl methyl ether, TME, as the main product [23].



Meanwhile, other compounds identified in the complex include bicyclic ethers, encompassing the fenchyl and bornyl methyl varieties [23]. Formation of several reaction products in the $KAl(SO_4)_2 \cdot 12H_2O$ catalyzed methoxylation process was associated with the irreversible rearrangements of pinyll ion [20], resulting from the intrinsic ability to rearrange into the bornyl ion. This leads to the formation of bornyl methyl ether, and fenchyl methyl ether, following the addition of methanol. Therefore, pinyll ion is further rearranged into the terpinyl ion after the generation of terpinyl methyl ether, using methanol as a solvent. In all, the collective results seen in this study advocated the feasibility of $KAl(SO_4)_2 \cdot 12H_2O$ for a reasonably satisfactory methoxylation of α -pinene into α -terpinyl methyl ether (TME) as the main product, with relatively good selectivity.

4 Conclusion

In this study, we have successfully demonstrated that the potassium alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] is a potentially effective acid catalyst in the methoxylation of α -pinene, to give α -terpinyl methyl ether (TME) as the main product with fenchyl methyl ether (FME), bornyl methyl ether (BME), limonene, and terpinolene as the by-products. Results revealed that the highest selectivity of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to catalyze the methoxylation of α -pinene was achieved under an optimal condition of 1 g of catalyst, volume ratio of 1:10, as well as the reaction temperature and reaction time of 65 °C and 6 h, respectively. This gave the final yield of the ether products as 59.6%, 8.9%, and 7.1% for TME, FME, BME, respectively, following a 98.2% conversion of α -pinene. Further research into the use of nanocatalysts for improving processes using α -pinene chemical as the starting material may prove useful in improving the product yields and selectivity of the methoxylation process. In a nutshell, the results obtained in this study affirmed the suitability of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to selectively catalyze the methoxylation of α -pinene to produce TME.

Declarations

Author contribution statement

N. Wijayati^a: Conceived and designed the experiments.

L. R. Lestari^a: Performed the experiments and wrote the paper.


L. A. Wulandari^a: Performed the experiments.

F. W. Mahatmanti^a and S. K. Rakainsa^a: Analyzed and interpreted the data.

E. Cahyono^b: Contributed reagents, materials, analysis tools or data.

R. A. Wahab: Analyzed and interpreted the data, Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.


Additional information

No additional information is available for this paper.

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 The corrections made in this section will be reviewed and approved by a journal production editor. The newly added/removed references and its citations will be reordered and rearranged by the production team.

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α -pinene; methoxylation; potassium alum; catalyst.

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Research article

Potassium Alum [KAl(SO₄)₂·12H₂O] solid catalyst for effective and selective methoxylation production of alpha-pinene ether products

Nanik Wijayati^{a,*}, Lulua Romjanah Lestari^a, Lisa Ayuningtyas Wulandari^a,
F. Widhi Mahatmanti^a, Senda Kartika Rakainsa^a, Edi Cahyono^b, Roswanira Abdul Wahab^{c,d}

^a Department of Chemistry, Universitas Negeri Semarang, Semarang 50229, Central Java, Indonesia

^b Perhutani Pine Chemical Industry, Pemalang 52319, Central Java, Indonesia

^c Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Malaysia

^d Enzyme Technology and Green Synthesis Group, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

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ABSTRACT

Methoxylation is a relevant technological process applied in the production of high-value α-pinene derivatives. This report investigates the use of potassium alum [KAl(SO₄)₂·12H₂O] as a catalyst in the methoxylation of α-pinene. In this study, the methoxylation reaction was optimized for the highest conversion of α-pinene and selectivity, assessed for the factors, catalyst loading (0.5; 1.0; and 1.5 g), volume ratio of α-pinene: methanol (1:4, 1:7, 1:10), reaction temperature (50, 55, 60 and 65 °C), and reaction time (72, 144, 216, 288, 360 min). The highest selectivity of KAl(SO₄)₂·12H₂O in the methoxylation of α-pinene was achieved under an optimal condition of 1 g of catalyst loading, volume ratio of 1:10, as well as the reaction temperature and incubation time of 65 °C and 6 h, respectively. GC-MS results revealed the yields of the methoxylated products from the 98.2% conversion of α-pinene, to be 59.6%, 8.9%, and 7.1% for α-terpinyl methyl ether (TME), fenchyl methyl ether (FME), bornyl methyl ether (BME), respectively. It was apparent that a lower KAl(SO₄)₂·12H₂O loading (0.5–1.5 g) was more economical for the methoxylation reaction. The findings seen here indicated the suitability of the KAl(SO₄)₂·12H₂O to catalyze the methoxylation of α-pinene to produce an commercially important ethers.

1. Introduction

α-Pinene is the main constituent of turpentine, the essential oil obtained from pine gum, in Pine trees, making cuts in the trunk openings of the wood (similar to the extraction of latex for rubber in *Hevea brasiliensis*) so the resin present in the resinous channels exudes under pressure [1, 2]. Turpentine is a valuable and renewable natural resource widely used in the medical industry, for the synthesis of new important chemicals for use as cosmetic, flavours, fragrances, and pharmaceuticals sectors as well as in the synthesis of chemical intermediates [3]. Thus, α-Pinene is considered a versatile building block for the synthesis of high-value added chemicals, mainly through catalytic processes, such as hydration [4, 5, 6, 7, 8, 9], isomerization [10, 11], epoxidation and pinene oxide isomerization [12, 13, 14], esterification [15, 16], and etherification [17, 18, 19, 20, 21, 22], among others can be applied to obtain a wide variety of added value products.

The main product of the acid-catalysed methoxylation of α-pinene is α-terpinyl methyl ether, which smells grape fruit-like and might be used

as flavour and fragrance and as additive for pharmaceuticals and food industry [23]. Traditionally, sulfuric acid has been used in this reaction, as catalyst [17]. However, solid catalysts have many advantages over liquid acids, such as they do less harm to the environment, can be easily separated from liquid phase and can be reusable. The α-pinene methoxylation has been carried out over beta zeolite [18], sulfonic-modified mesoporous silica/MCM-41, PMO [19], poly(vinyl alcohol) containing sulfonic acid groups [20], heteropolyacids immobilized in silica [21] and microporous and mesoporous carbons [22] and clays mineral [23] reported good selectivities, of ca. 60%, at almost complete conversion.

Potassium Alum (KAl(SO₄)₂·12H₂O), which cost significantly less than the catalysts listed above, is versatile and environmentally friendly catalysts to promote a wide variety of organic reactions. This study introduces the term "dreamland catalyst" to denote a heterogeneous catalyst which is a cheap, water-soluble, mild, efficient, safe, stable, non-toxic, reliable, incorruptible, recyclable and commercially available compound that can be used in the laboratory without special precautions (easy to use). Moreover, the catalyst has been commonly applied in

* Corresponding author.

E-mail address: nanikanang@gmail.com (N. Wijayati).

several other synthetic reactions with good success, for example, including in the transesterification of palm oil [24], acylals [25], Azlactone [26]; coumarins [27], amides [28], β -acetamido ketones [29], novel bis[spiro(quinazoline-oxindole)] derivatives [30], and bispyrazole derivatives [31]. It was therefore decided to investigate alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in catalyzing certain synthetic reactions, this study assumed that this catalyst may be effective to catalyze the methoxylation of α -pinene to produce α -terpinyl methyl ether.

In this work we report the synthesis of α -terpinyl methyl ether via the methoxylation of α -pinene over Potassium Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) catalysts. The influence of various reaction parameters, such as, reaction times, α -pinene to methanol volume ratio, temperature, and catalyst loading on catalyst activity of the active catalyst, is also studied. The parameters were chosen in this study as the are also commonly assessed in similar organic reactions involving polar reagents. It is worth to mention here that the optimal condition for the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation must be found.

2. Materials and methods

2.1. Materials

α -Pinene standard (98%) was obtained from Sigma Aldrich, while turpentine oil was acquired from KBM Perhutani Pine Chemical Industry, Pemalang, Indonesia. Methanol and potassium alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] for analysis were procured from Merck (Germany).

2.2. Instrumentations

Quantitative and qualitative analyses of the isolated α -pinene and the corresponding methoxylation products were conducted using the GC 23 Agilent 6820 (Version A. 01. 03, South Korea), HP-5 column and FID detector (detector temperature of 300 °C), with helium as the carrier gas. The injection temperature was set to 280 °C, while the column was maintained at an initial temperature of 70 °C for 10 min and was increased gradually to 280 °C (5°C/min), and ramped up to 300 °C at 20°C/min. Analysis of the methoxylation products was done on a GC-MS (Shimadzu QP-2010 Plus, Japan) equipped with an AOC-20i + s auto-sampler that was operated under the following conditions: column and injection temperature of 70 °C and 200 °C, respectively with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min, ion source and interface temperature of 200 °C and 240 °C, correspondingly. Here, helium (He) gas was used as the carrier at a constant flow rate of 0.1 $\mu\text{L}/\text{min}$. The percentage of the methoxylation process was estimated from the area beneath each peak. Furthermore, the percentage of each ether product was achieved by dividing the respective peak area with the isolated α -pinene and multiplied by 100. The qualitative analysis on the produced ether products were done on a Fourier-Transform Infrared Spectrophotometer (PerkinElmer Spectrum Version 10.4.00, US). Each sample was prepared on KBr pellets and the analysis was done in the wavenumber region of 4000–400 cm^{-1} .

2.3. Procedures

2.3.1. Preparation of the catalysts

The $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was thermally activated in the oven at 110 °C and then left to cool in a desiccator at room temperature (15 min) to prevent rehydration before used. The morphology of alum was determined by scanning electron microscopy (SEM) performed on a JEOL JFC-1600 and JSM-6701F equipment. Alum catalyst was spray-coated over AuPd plates for 10 minutes under argon flow to generate conductive layers. The catalyst was characterized on an X-Ray diffractometer (D-Max III (Rigaku) with a Cu $\text{K}\alpha$ radiation source ($\alpha = 1.5378 \text{ \AA}$, 40kV, 30mA). The crystallinity index was estimated using previously described method [32]. FT-IR analysis that was performed within the spectral region of 4000 to 400 cm^{-1} under room temperature.

2.3.2. Isolation of α -pinene

Fractional distillation of turpentine oil was performed under reduced pressure to prepare and concentrate α -pinene as the starting material for the methoxylation process. The isolated α -pinene was then analyzed by GC-MS where the column and injection temperature of 70 °C and 200 °C, respectively with split injection mode, pressure 13.7 kPa, flow column 0.50 mL/min, ion source and interface temperature of 200 °C and 240 °C, correspondingly.

2.3.3. Catalytic experiments

The catalytic experiments were performed in a stirred batch reactor under reflux at different temperatures (50–65 °C) and ambient pressure. The activated $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was quickly transferred into the reaction vessel containing 20 mL dry methanol and was preheated (50–65 °C) before the addition of α -pinene (5 mL), followed by continuous stirring for 360 min. The samples were then collected periodically, and the catalyst was removed using a syringe filter with no impact on the products. It is worth mentioning here that no reaction was observed during storage. The α -pinene methoxylation reaction yields were identified by a GC-MS (Shimadzu QP-2010 Plus) and then quantified on an HP-5 column with helium as carrier gas using the GC Agilent 6820 with a FID detector ($T = 300 \text{ }^\circ\text{C}$). All samples collected were analyzed using a Gas Chromatograph (GC), comparing the retention times of the compounds in the reaction mixture with those of standard compounds.

The reaction conditions were optimized by evaluating the effects of parameters, reaction temperature (50, 55, 60 and 65 °C), catalyst loading (0.5; 1; and 1.5 g), and volume ratio of reactants (α -pinene:methanol of 1:4, 1:7, 1:10) during the methoxylation process. In this study, external standard was used to estimate the α -terpinyl methyl ether selectivity, and the percentage conversion of α -pinene by preparing the corresponding standard curves. The conversion of α -pinene (X) and the selectivity (S) for the desired products were defined as follows [5]:

$$X = \frac{\text{converted alpha pinene \%}}{\text{initial alpha pinene \%}}, S = \frac{\text{desired product \%}}{\text{conversion of alpha pinene \%}}$$

3. Results and discussions

3.1. Characterization of catalyst

Potassium Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) is an inexpensive, non-toxic, water-soluble, and commercially available compound frequently used in the laboratory with no special precautions [24, 25, 26, 27, 28, 29, 30, 31]. Data on the characterization of the produced $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ by scanning electron microscopy (SEM), FT-IR, and XRD, are illustrated in Figure 1, Figure 2, and Figure 3, respectively. The micrographs of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ showed reasonable similarities with the microstructure of ammonium aluminum sulfate dodecahydrate [$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$]. However, the latter are reportedly to be of a more rounded shape, with a size range of between 100–200 μm at higher temperatures of 1100–1200 °C (Figure 1). The overall construct of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is altered, and adopts an overall more elongated oval shape, thus corroborated the findings of an earlier study [33].

Infrared spectroscopy is often used to characterize solid-state catalysts to identify both the organic and inorganic surface functional groups. Figure 2 shows the spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, with the peaks at 1195 cm^{-1} and 1077 cm^{-1} ascribed to the stretching vibration of a S=O group, while peaks at 933 cm^{-1} and 737 cm^{-1} were the result of the stretching vibrations of S–O and Al–O bonds, respectively. Peaks that emerged in the region of 750–400 cm^{-1} indicated the vibration of Al–O [34]. Figure 2 illustrates characteristic sharp sulfate (SO_4^{2-}) peaks at 468–471 cm^{-1} , 603–608 cm^{-1} , 657–686 cm^{-1} , 1104–1115 cm^{-1} and 1237–1247 cm^{-1} that corresponded to the symmetrical bending mode of SO_4^{2-} degeneration of asymmetric bending, symmetrical bending, degenerate symmetric stretching and degenerate asymmetric stretching [24].

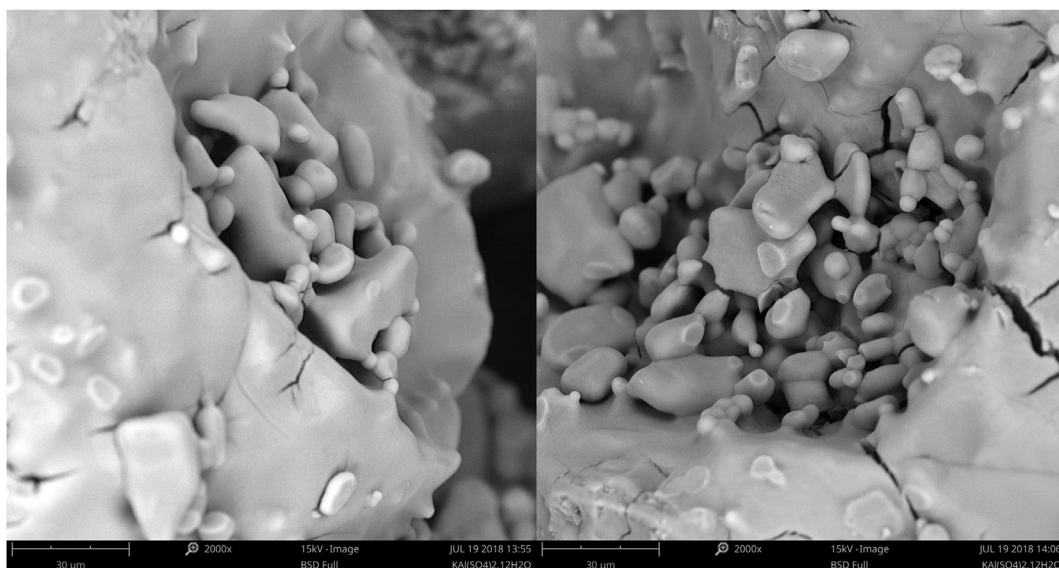


Figure 1. Scanning Electron Microscope (SEM) micrograph of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ magnified 2000 x.

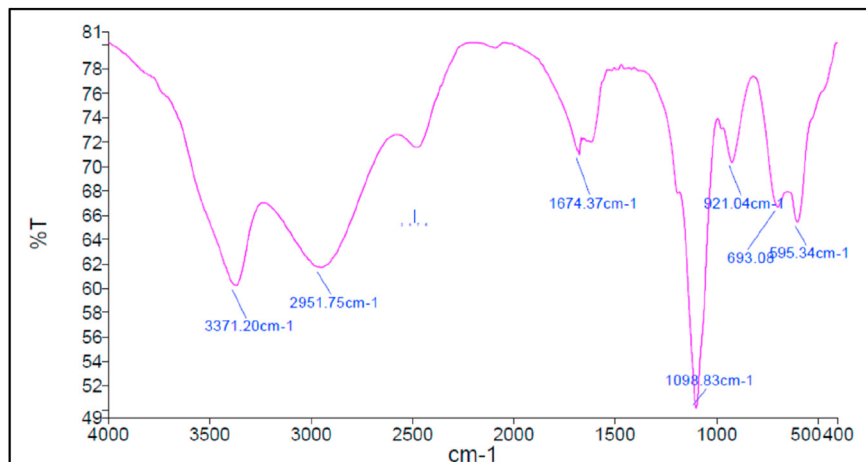


Figure 2. Fourier Transform-Infrared (FT-IR) spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Figure 3 depicts the crystallinity and crystal lattice of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, evaluated by XRD. It is important to indicate here, a high crystallinity insinuates appreciable catalytic properties, and better stability at high temperatures, alongside extensive porosity and purity of the sample [35]. The main composition of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was affirmed to be aluminum potassium sulfate, based on the characteristic peaks and it were consistent with the JCPDF 07-0017 for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Thus, the diffractogram affirmed the prepared catalyst show high crystallinity, matching a recent report from another analogous compound [36].

3.2. Catalytic test

In order to optimise the reaction conditions, the effect of different parameters (volume ratio of α -pinene and methanol, temperature, and catalyst loading) on the methoxylation of α -pinene over $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst was studied.

3.2.1. Effect of volume ratio of α -pinene and methanol

The effect of the volume ratio of α -pinene to methanol (α -pinene:methanol; 1:4, 1:7, 1:10) on the selectivity of α -terpinyl methyl ether over $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was also evaluated. In this investigation, the reactions were done at 60 °C using a 0.1 g of potassium alum catalyst. The

study noted that the catalysts yielded good selectivity values (56% with a 75% conversion of α -pinene) of the methoxylation. Results of the α -pinene conversion and relative product selectivity are shown in Figure 4.

The volume ratio of the reactant was found to influence the outcome of the methoxylation reaction, as higher concentrations of methanol in the mixture led to a higher ether yield (Figure 4a). Also, the percentage of the produced ether products increased with longer reaction time. The highest α -pinene conversion (74.8%) was attained with the use of 1:10 ratio of α -pinene:methanol and a reaction time of 360 min. The outcome seen here possibly resulted from the surplus presence of methanol molecules to simultaneously act as a reactant and solvent. This augmented the integration of the reactants and accelerated the conversion of α -pinene into the main ether product, α -terpinyl methyl ether and other ether by-products. In this study, the by-products were formed were from the isomerization of α -pinene under the methoxylation process, including camphene, limonene, and terpinolene, as similarly described by an earlier study [17, 18, 19, 20, 21, 22].

Similarly, the highest selectivity of the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation was observed at 1:10 ratio of α -pinene:methanol, with stirring for 360 min at 60 °C. This also goes to show that the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was capable of carrying out selective methoxylation of the

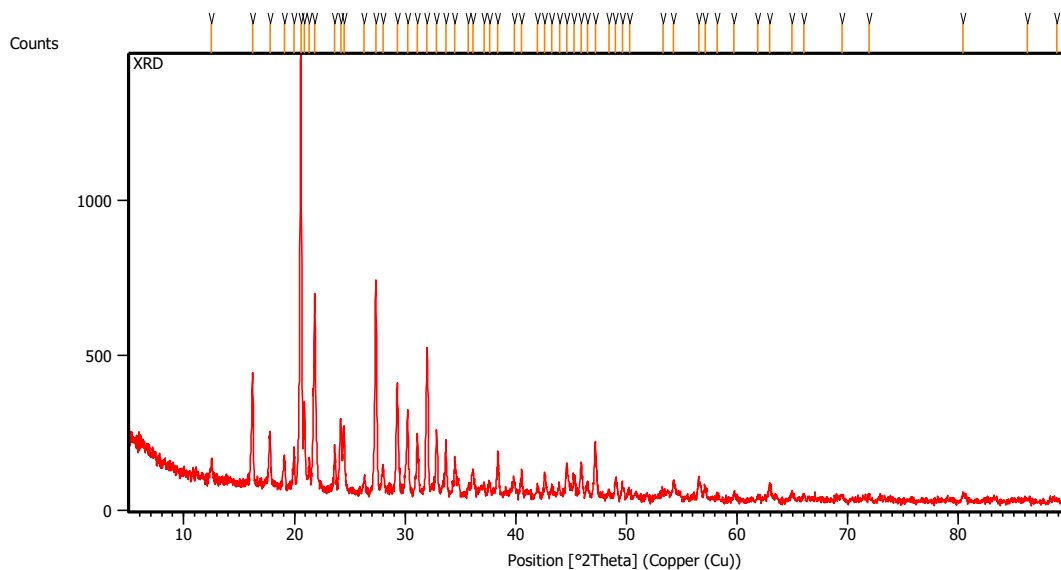


Figure 3. X-ray diffractogram of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

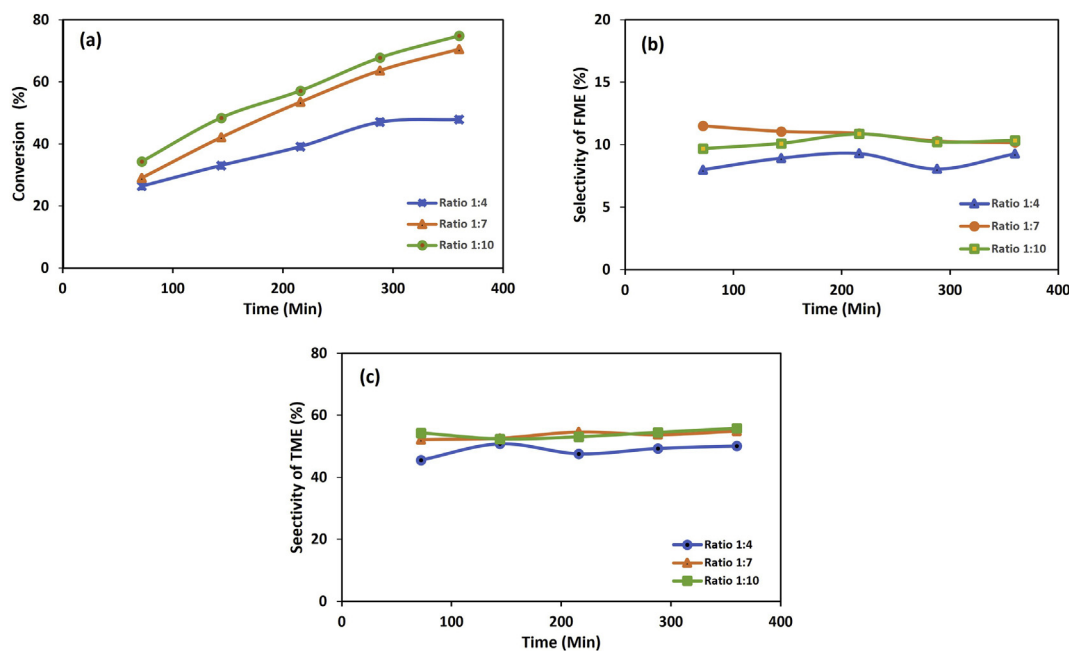


Figure 4. Influence of volume ratio of reactants on the methoxylation of α -pinene: (a) conversion of α -pinene (b) selectivity of Fenchyl Methyl Ether (FME) (c) selectivity of Terpinyl Methyl Ether (TME).

α -pinene to produce ether. Figure 4b and c show the most prominent products to be terpinyl methyl ether (TME) (55.8%) and fenchyl methyl ether (FME) (10.3%).

3.2.2. Effect of reaction temperature

The effect of temperature (50, 55, 60 and 65 °C) on the selective production of α -terpinyl methyl ether by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was also investigated, under a constant catalyst loading, and volume ratio of α -pinene:methanol. As anticipated, the percentage conversion increased with the rise in temperature, which resulted in the concomitant increase in methoxylation selectivity towards mono-ether products (Figure 5a-d). Figure 5a revealed that the conversion of α -pinene steadily increased at 60 °C. It is worth to indicate here, since the boiling point of methanol was 65 °C; hence a lower temperature of 60 °C was the suitable reaction temperature for the methoxylation process [21]. However, a notable

elevation in reaction time from 72 to 144 min was observed at 65 °C, wherein the best methoxylation temperature on α -pinene by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ occurred at 65 °C for a 98.2% conversion. The outcome seen here also signified that the temperatures assessed in this study promoted good selectivity of the methoxylation reaction to yield 60% of the ether products.

The highest selectivity was at 65 °C over a reaction time of 360 min, to produce 8.7% of FME (Figure 5b), 7.1% BME (Figure 5c), and 59.6% TME (Figure 5d). Likewise, another study documented a similar trend for the methoxylation of limonene through acid-activated ions and clay exchangers, whereby a higher reaction temperature prevented the decline in catalyst selectivity [37]. Another work saw the alkoxylation of pinene yielded the maximum conversion of the reactant when the reaction temperature and duration were set to 60 °C and $t = 120$ min, respectively [21].

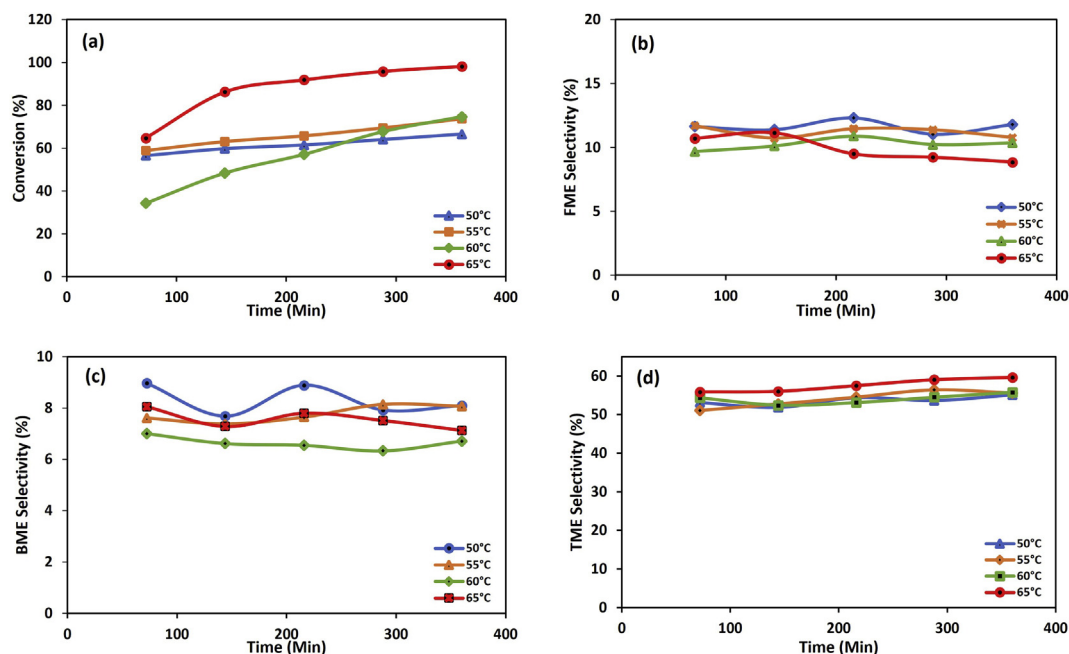


Figure 5. Effect of temperature on α -pinene methoxylation: (a) α -pinene conversion vs time (b) Fenchyl Methyl Ether (FME) selectivity vs time (c) Bornyl Methyl Ether (BME) selectivity vs time (d) Terpinyl Methyl Ether (TME) selectivity vs time.

Nonetheless, higher temperatures approaching 80 °C or higher were found to be counterproductive and promoted the reverse reaction that reformed the pinene isomers in the methanol solvent. The same outcome was also corroborated by an earlier study that investigated a similar reaction using 100 mg of Al-SAz-1 as the catalyst [23]. Also, a decline in selectivity was not observed during the methoxylation of limonene [37], where the reaction selectivity for mono-ether was largely unaffected when the reaction temperature was increased up to 65 °C. Table 1 shows the comparative study of α -pinene methoxylation process in the presence of various catalysts. The highest percentage conversion was obtained using the catalysts, AlSAz-1.

3.2.3. Effect of the catalyst loading

The selectivity of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to produce α -terpinyl methyl ether was also studied, using three catalyst loadings of 0.5, 1, and 1.5 g, while other reaction conditions were held constant at 60 °C, and α -pinene:methanol volume ratio at 1:10. Table 2 shows the conversion and product selectivity, where the different treatments yielded reasonably good amount of TME (54%, 75% α -pinene conversion). The $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ solid catalyst prepared in this study successfully converted the α -pinene into the expected ether products. Also, there was an upsurge in the yields of the reaction products following an increase catalyst quantity in the reaction mixture. Interestingly, 0.5 g of the catalyst gave the highest methoxylation α -pinene selectivity for FME and BME, while 1 g prompted higher production of TME. The

improved percentage conversion seen here was the likelihood of the higher availability of catalyst active centers to carry out the conversion reaction [22]. The yields of TME in the methoxylation reaction appeared comparable for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ loadings between 0.5–1.5 g, thus evidently indicating the futile use of the catalyst at higher loadings. A lower $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is more economical to produce the ethers in this study.

Scheme 1 shows the reaction mechanism of α -pinene methoxylation with potassium alum $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyst. According to literary review, acid catalysis by potassium alum ensues via two routes, including A and B, obtained by terpinyl and bornyl ion, respectively [21, 22]. The alkoxylation process was initiated by protonation of the α -pinene double bond to create the pinyl ion. This reaction proceeded through two parallel pathways, dependent on the product rearrangement which include bicyclic and monocyclic type. The bornyl and terpinyl ions present in the reaction mixture then react with methanol, and consequently deprotonate to yield the ethers *viz.* TME, BME, and FME. Previous investigation also reported on the reaction of pinene with methanol over the acid sites available on the clay surface, to form terpinyl methyl ether, TME, as the main product [23].

Meanwhile, other compounds identified in the complex include bicyclic ethers, encompassing the fenchyl and bornyl methyl varieties [23]. Formation of several reaction products in the $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ catalyzed methoxylation process was associated with the irreversible rearrangements of pinyl ion [20], resulting from the intrinsic ability to

Table 1. Comparative summary of α -pinene methoxylation in the presence of various catalysts in a batch reactor.

Catalysts	Temp (°C)	Reaction Time (h)	Conversion (%)	Selectivity (%)	Literature
Beta Zeolite	40	5	92	54	[17]
PMO-SO ₃ H-g	100	-	90	45	[19]
PVSSA-20	60	24	40	60	[20]
PW2-S	60	27	40	60	[21]
CB, CMN, CNorit	60	250	55–75	50–55	[22]
AlSAz-1	60	1	65	65	[23]
AlSAz-1	40	20	71	91	[37]
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	65	6	98	60	-

Table 2. Data on the conversion (% C) and selectivity of methoxylation of α -pinene with a variable of the $KAl(SO_4)_2 \cdot 12H_2O$ catalyst loading.

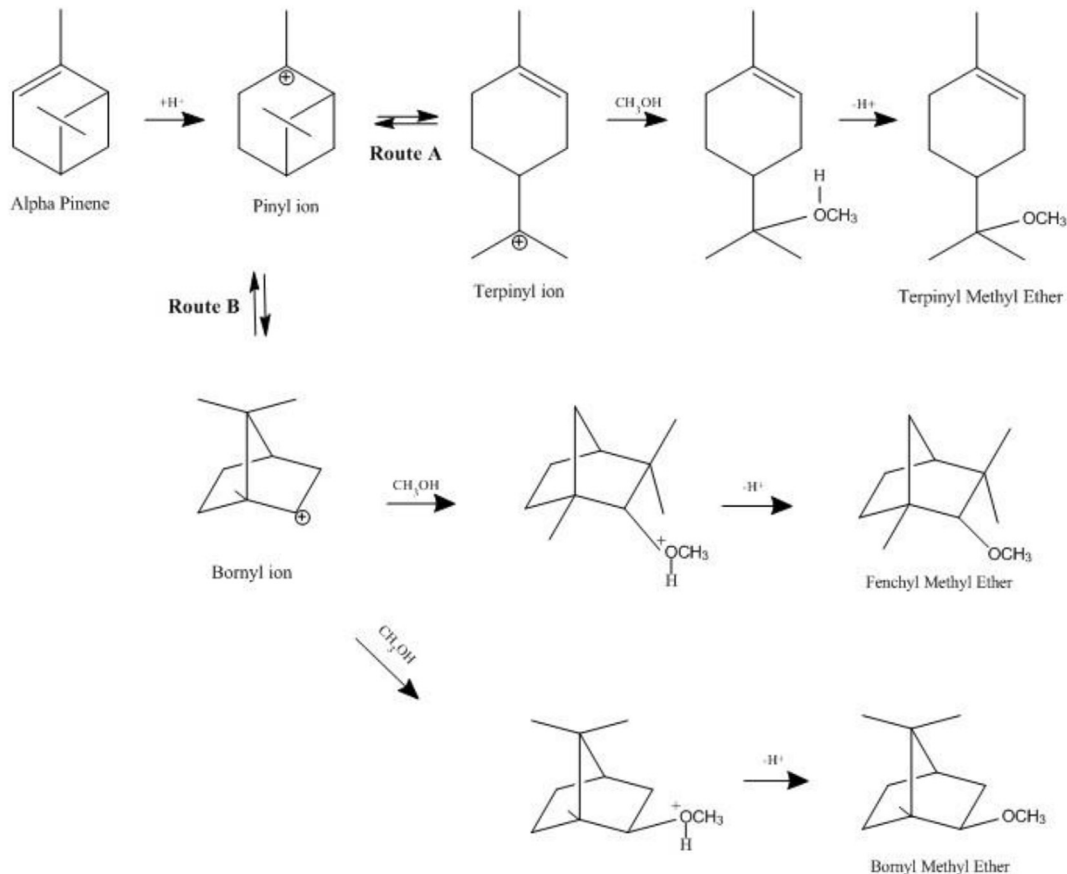
Alum (g)	t (min)	Conversion (% C)	Selectivity of reaction products (%S)		
			TME	BME	FME
0.5	72	18.3	54.9	7.8	11.6
	144	28.7	54.9	7.4	11.2
	216	36.4	54.8	6.9	11.1
	288	44.2	53.8	8.4	10.9
	360	50.1	54.1	7.2	10.9
1.0	72	25.3	53.2	7.6	9.8
	144	37.2	55.2	7.5	10.4
	216	45.1	54.4	7.3	10.3
	288	53.4	54.2	7.7	10.0
	360	60.5	54.5	6.8	10.0
1.5	72	41.9	53.5	7.7	10.5
	144	52.7	53.8	7.2	10.4
	216	61.1	53.3	6.8	10.2
	288	68.5	53.5	6.9	9.8
	360	74.5	53.7	7.0	9.6

Note: %C (% Conversion), %S (% Selectivity), TME (Terpinyl Methyl Ether), BME (Bornyl Methyl Ether), and FME (α -Fenchyl Methyl Ether).

rearrange into the bornyl ion. This leads to the formation of bornyl methyl ether, and fenchyl methyl ether, following the addition of methanol. Therefore, pinyl ion is further rearranged into the terpinyl ion after the generation of terpinyl methyl ether, using methanol as a solvent. In all, the collective results seen in this study advocated the feasibility of $KAl(SO_4)_2 \cdot 12H_2O$ for a reasonably satisfactory methoxylation of α -pinene into α -terpinyl methyl ether (TME) as the main product, with relatively good selectivity.

4. Conclusion

In this study, we have successfully demonstrated that the potassium alum $[KAl(SO_4)_2 \cdot 12H_2O]$ is a potentially effective acid catalyst in the methoxylation of α -pinene, to give α -terpinyl methyl ether (TME) as the main product with fenchyl methyl ether (FME), bornyl methyl ether (BME), limonene, and terpinolene as the by-products. Results revealed that the highest selectivity of $KAl(SO_4)_2 \cdot 12H_2O$ to catalyze the



Scheme 1. The mechanism of α -pinene methoxylation.

methoxylation of α -pinene was achieved under an optimal condition of 1 g of catalyst, volume ratio of 1:10, as well as the reaction temperature and reaction time of 65 °C and 6 h, respectively. This gave the final yield of the ether products as 59.6%, 8.9%, and 7.1% for TME, FME, BME, respectively, following a 98.2% conversion of α -pinene. Further research into the use of nanocatalysts for improving processes using α -pinene chemical as the starting material may prove useful in improving the product yields and selectivity of the methoxylation process. In a nutshell, the results obtained in this study affirmed the suitability of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to selectively catalyze the methoxylation of α -pinene to produce TME.

Declarations

Author contribution statement

N. Wijayati: Conceived and designed the experiments.
 L. R. Lestari: Performed the experiments and wrote the paper.
 L. A. Wulandari: Performed the experiments.
 F. W. Mahatmanti and S. K. Rakainsa: Analyzed and interpreted the data.
 E. Cahyono: Contributed reagents, materials, analysis tools or data.
 R. A. Wahab: Analyzed and interpreted the data, Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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