

Potassium Alum

by Nanik Wijayati

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Research article

Potassium Alum [KAl(SO₄)₂·12H₂O] solid catalyst for effective and selective methoxylation production of alpha-pinene ether productsNanik 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).<https://doi.org/10.1016/j.heliyon.2021.e06058>

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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 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 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 10 minutes under argon flow to generate conductive layers. The catalyst was characterized on an X-Ray diffractometer (D-Max III (Rigaku) with a $\text{Cu K}\alpha$ 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].

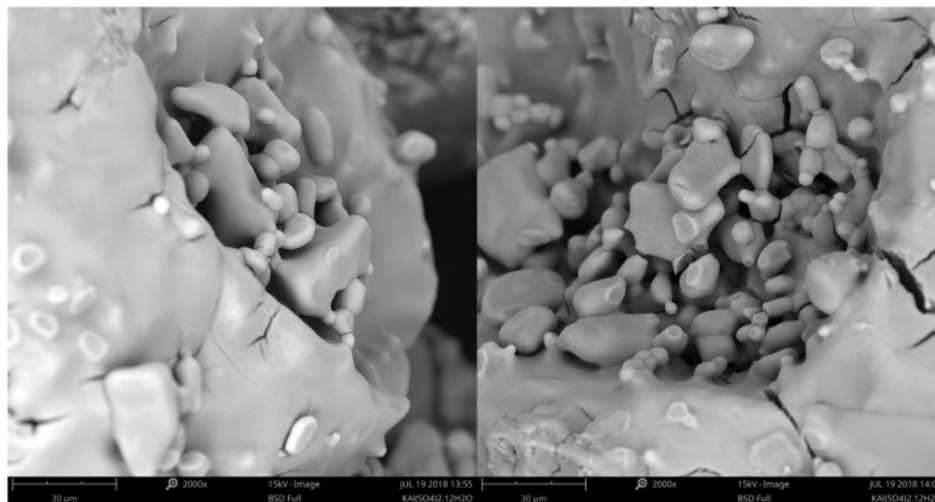


Figure 1. Scanning Electron Microscope (SEM) micrograph of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ magnified 2000 x.

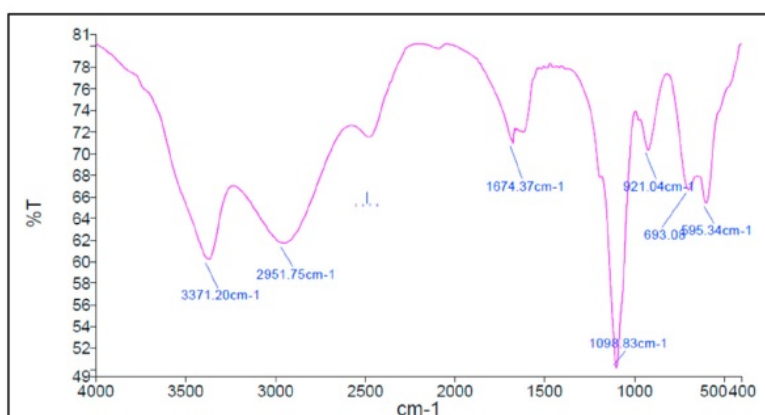


Figure 2. Fourier Transform-Infrared (FT-IR) spectrum of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

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

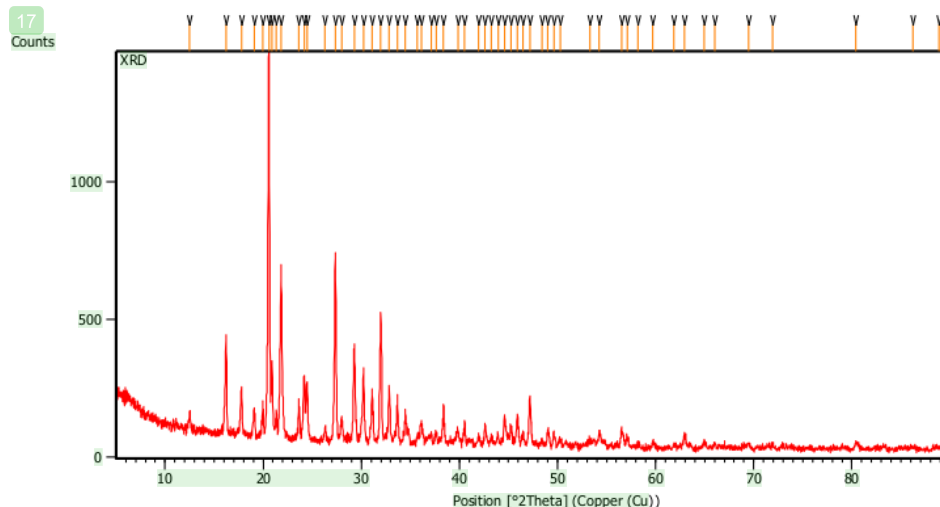


Figure 3. X-ray diffractogram of $KAl(SO_4)_2 \cdot 12H_2O$.

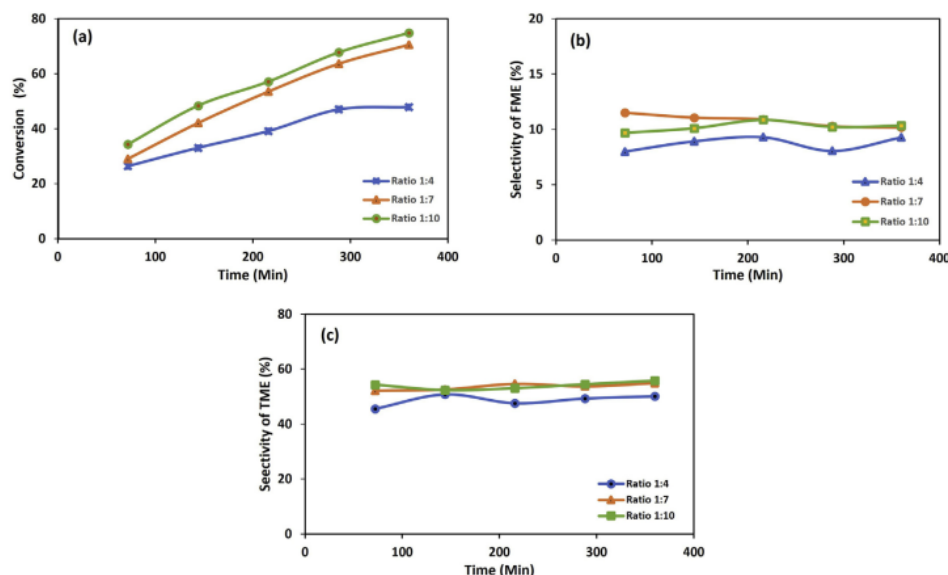


Figure 4. Influence of volume ratio of reactants on the methoxylation of α -pinene: (a) conversion of α -pinene (b) selectivity of Fencl methyl Ether (FME) (c) selectivity of Terpinyl Methyl Ether (TME).

α -pinene to produce ether. Figure 4b and c show the most prominent products to be terpinyl methyl ether (TME) (55.8%) and fencl 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 $KAl(SO_4)_2 \cdot 12H_2O$ 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 $KAl(SO_4)_2 \cdot 12H_2O$ 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].

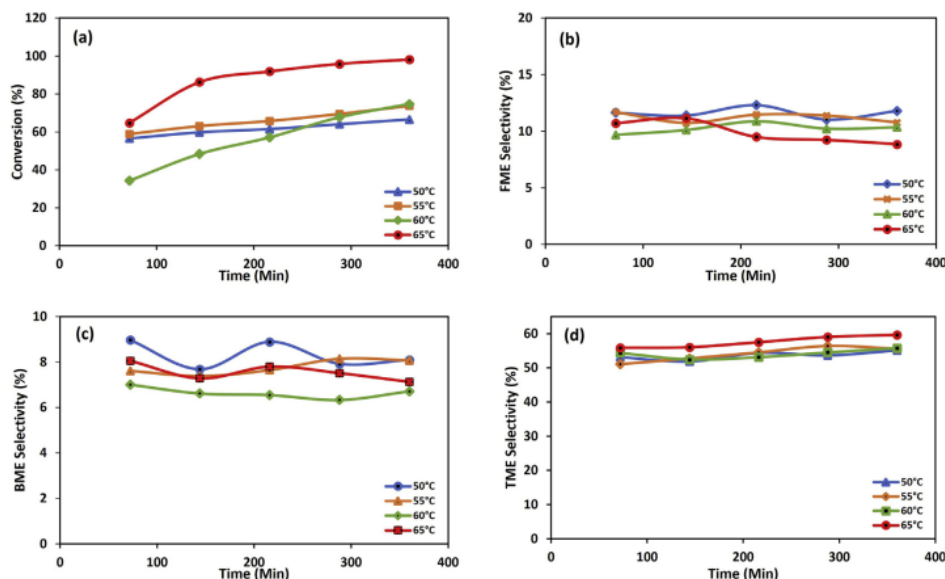


Figure 5. Effect of temperature on α -pinene methoxylation: (a) α -pinene conversion vs time (b) Fenchyl Methyl Ether (FME) selectivity vs time (c) Bornyl Methyl Ether (BME) selectivity vs time (d) Terpinyl Methyl Ether (TME) selectivity vs time.

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-SO3H-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.

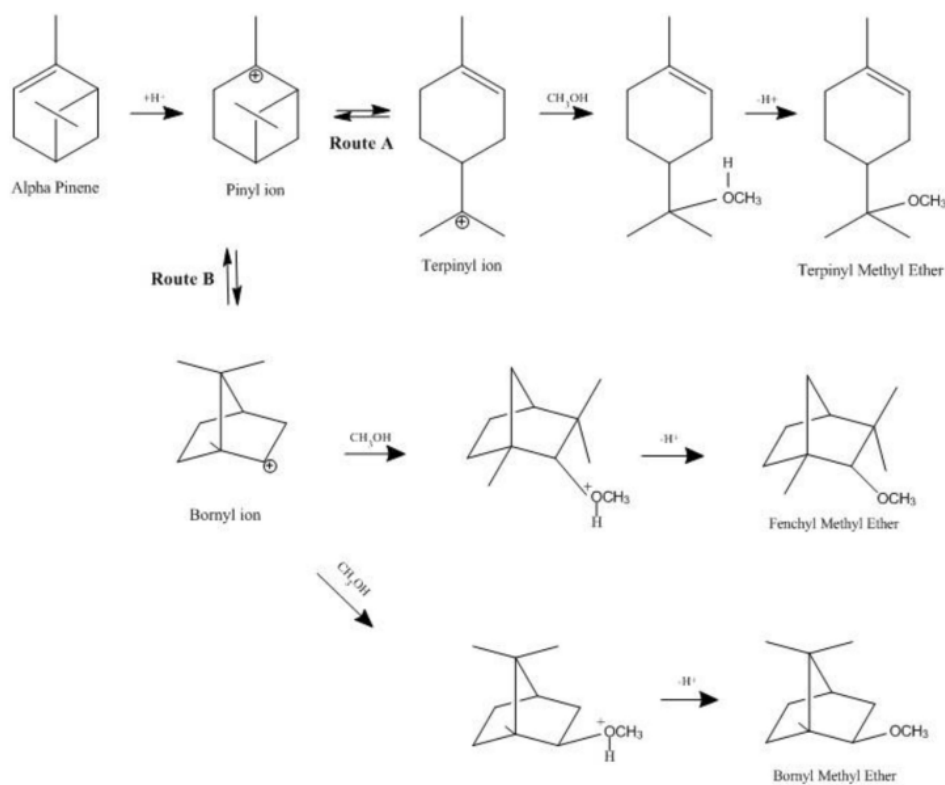
Alum (g)	t (min)	Conversion (% C)	Selectivity of reaction products (%S)		
			TME	BME	FME
0.5	72	18.3	54.9	7.8	11.6
	144	28.7	54.9	7.4	11.2
	216	36.4	54.8	6.9	11.1
	288	44.2	53.8	8.4	10.9
	360	50.1	54.1	7.2	10.9
1.0	72	25.3	53.2	7.6	9.8
	144	37.2	55.2	7.5	10.4
	216	45.1	54.4	7.3	10.3
	288	53.4	54.2	7.7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

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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.

15 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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