# Microwave irradiation assisted methoxylation of α-pineneusing potassium alum [KAl(SO4)2] catalyst

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# Microwave irradiation assisted methoxylation of α-pinene using potassium alum [$KAl(SO_4)_2$] catalyst

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**Abstract.** Methoxylation is a reaction to produce of ether compounds using methoxy ions. The α-pinene methoxylation using potassium alum catalyst was carried out using a microwave with power variations of 320, 480 and 640 W, mass of the catalyst 0.3; 0.6 and 0; 9 g, and mole ratio of reactants 1:15, 1:30 and 1:45 mole. Identification of the reaction results was performed using GC, GC-MS and FT-IR. The product obtained in α-pinene methoxylation is mirtenyl methyl ether (MME) and terpinyl methyl ether (TME). The conversion of α-pinene with the variation of 480 W microwave power, mass of catalyst 0.3 g and mole ratio of reactants 1:15 at 120 seconds was 99.82% with the selectivity of MME and TME were obtained 32.0 % and 1.4%, respectively.

## 1. Introduction

Turpentine oil is an essential oil that contains monoterpenes. Monoterpenes and their derivatives are used as basic ingredients in the flavor and fragrance industry. The development of turpentine oil in the industrial world is carried out through the transformation of acid-catalyzed α-pinene compounds to produce monocyclic and bicyclic compounds which have higher economic value [1-3]. Transformation of α-pinene terpenes have been carried out using various acid catalysts, such as carbon-based catalysts [4-5]; $Al^{3+}$ ion exchanger clays [6]; acid oxides [7], zeolites [8-15]; HPW / SBA-15 [16]; TCA / $ZrO_2$.n $H_2O$ [17] and Nanoparticles (SLN) [18].

One of the transformation of pinene compounds is through a methoxylation using a heterogeneous acid catalyst. The methoxylation of α-pinene to ether compounds has been carried out by several researchers with various catalysts such as mesoporous and micropore carbon [4], $Al^{3+}$ ion exchanger clay [5], NiO/Y-Zeolite [19], polyvinyl alcohol which contains acid groups [20] and H-Beta [21]. So far, the production of ether compounds from pinene with various catalysts has not been efficient, low quality, and not environmentally friendly. The compound α-terpinyl methyl ether can be used as flavors and aromas for perfumes and cosmetic products, as an additive to pharmaceuticals and agricultural chemicals, and is also used in the food industry [1-5].

The use of heterogeneous catalysis in the methoxylation is a Green Chemistry process. The heterogeneous acid catalyst that can be used is potassium alum. Potassium alum / alum is an aluminum sulfate compound with the chemical formula [$KAl(SO_4)_2.12H_2O$]. Potassium alum [$KAl(SO_4)_2.12H_2O$] is a colorless compound that has an octahedral or cubic crystal form. Alum is soluble in water but not soluble in alcohol, and it is stable in air [22-23].

One method that applies Green Chemistry is the Microwave Assisted Organic Synthesis (MAOS) method. The MAOS method is a chemical process that uses microwaves in the reaction. Microwaves uses microwave radiation, which is in the electromagnetic spectrum between infrared radiation and radio waves. The short reaction time and various reaction extensions are the advantages of Microwave Assisted Organic Synthesis (MAOS) which are very helpful, especially in product improvement in an industry [24-27].

The objective of this work is to study the methoxylation of turpentine, via heterogeneous catalysis using potassium alum catalyst [$KAl(SO_4)_2.12H_2O$]. Methoxylation was carried out under microwave irradiation as an alternative energy source of energy.

## 2. Method

All chemicals without further purification were acquired commercially from Aldrich or Merck Company. Crude turpentine oil, was donated by KBM Perhutani Pine Chemical Company. Turpentine oil compositions is: α-pinene at 54–55%, β-pinene at 44–45% and camphene 1–2%. α-pinene, E-Merck was used as internal standard for conversios calculations. Microwave was performed in the ultrasonic probe is a Q-Sonica (Q700W) in frequency of 20 kHz. The GCMS analyzes were performed in a Shimadzu model GCMS-QP2010 ULTRA.

The material needed in this study is α-pinene obtained from the KBM Perhutani Pine Chemical Industry Pemalang, Methanol for analysis (Merck, Mr = 32.04 g/mol), alum potassium [$KAl(SO_4)_2.12H_2O$] (Merck, Mr = 474.39 g / mol). The catalyst preparation was performed by weighing 20 g sample of potassium alum [$KAl(SO_4)_2.12H_2O$], then sifted using 100 mesh, and dried in an oven at 105$^{o}$C.

All samples collected were analyzed using a Gas Chromatograph (GC Agilent 6890 Series), comparing the retention times of the compounds in the reaction mixture with those of standard compounds. The analysis were performed in a Shimadzu model GCMS-QP2010 ultra gas chromatograph. The separation was performed using Restek Rtx-5MS capillary column and Flame Ionization Detector with helium as a carrier gas. The GC oven temperature was set at initial temperature of 50$^{o}$C, held for 5 min, increased at a rate of 4$^{o}$C/min to 150$^{o}$C and then increased to 240$^{o}$C at a rate of 15$^{o}$C/min. The injector and detector temperatures were set at 240$^{o}$C.

The methoxylation of α-pinene was carried out in a microwave beaker glass at 320, 480 and 640 watt. The reaction was carried out by inserting 1 mL of α-pinene, added with 4 mL of methanol and 0.3 g of potassium alum [$KAl(SO_4)_2.12H_2O$] catalyst into the beaker glass. Sampling was carried out at 1 minute, 1 minute 30 seconds, and 2 minutes. Furthermore, centrifugation for 15 minutes to separate the mixture into sediment and supernatant liquid. The reaction results were analyzed using GC. Furthermore, it is done by using variations in the amount of catalyst (0.3; 0.6 and 0.9 g) and variations in the mole ratio of reactant (1:15, 1:30 and 1:45).

## 3. Result and Discussion

Synthesis of α terpinyl methyl ether from alkene compounds in the world of organic synthesis is now widely carried out. The synthesis of α-terpinyl methyl ether from α-pinene by methoxylation using acid catalyst is a very important method used in the flavor and fragrance industry. The methoxylation of α-pinene is a reaction to produce ether compounds using methoxy ions. The result of α-pinene methoxylation is terpinyl methyl ether. In this study, the variations in microwave power, mass of catalyst, and ratio of reactants was used. Each of the results of the α-pinene methoxylation was analyzed using GC.

### 3.1. *Effect of microwave power*

Microwave power plays a role in the methoxylation of α-pinene which causes the reaction to produce mirtenyl methyl ether (MME) and terpinyl methyl ether (TME). Figure 1 shows that the highest conversion (99.8%) obtained with the reaction time of 120 seconds, mass of catalyst of 0.3 g, and at 480 watts of power, with the selectivity of MME and TME 32.0% and 1.4%, respectively. The highest selectivity of MME and TME was obtained at microwave power of 320 watt and 60 s was 60.4% and 40.5%, respectively, and conversion of 4%.

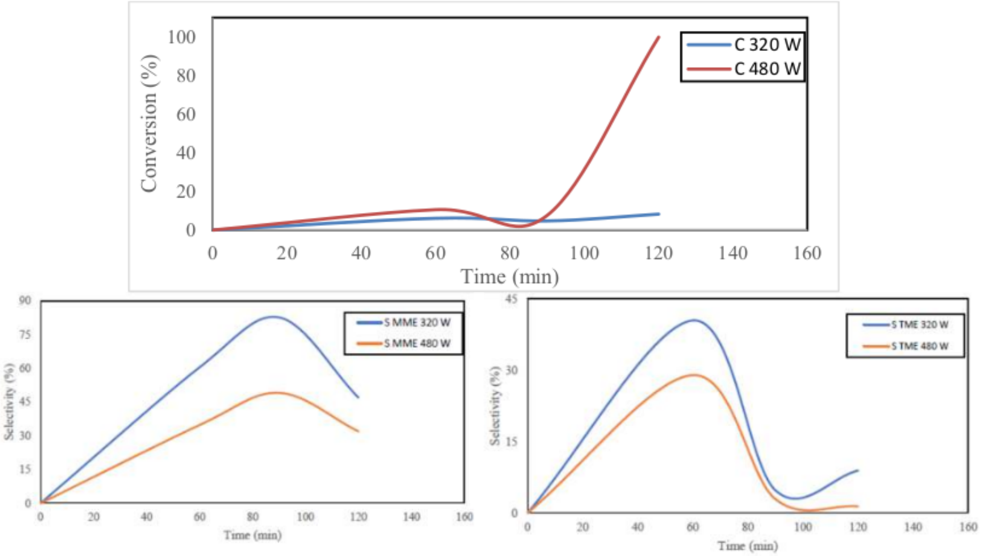

**Figure 1.** Effects of microwave power on α-pinene conversion and MME and TME selectivity

### 3.2. *Effect of mass of catalyst*

The mass of the catalyst plays a role in the methoxylation of α-pinene which causes many molecules to collide with each other in a faster rate. Figure 2 shows that the highest conversion (99.82%) was obtained at reaction time of 120 seconds and mass of catalyst 0.3 g, with the selectivity of MME and TME 32.0% and 1.4%, respectively. The highest MME and TME selectivity obtained at reaction time of 60 seconds and mass of catalyst 0.9 g.was 96.7% and 47.5%, respectively, and conversion of 2.3%.

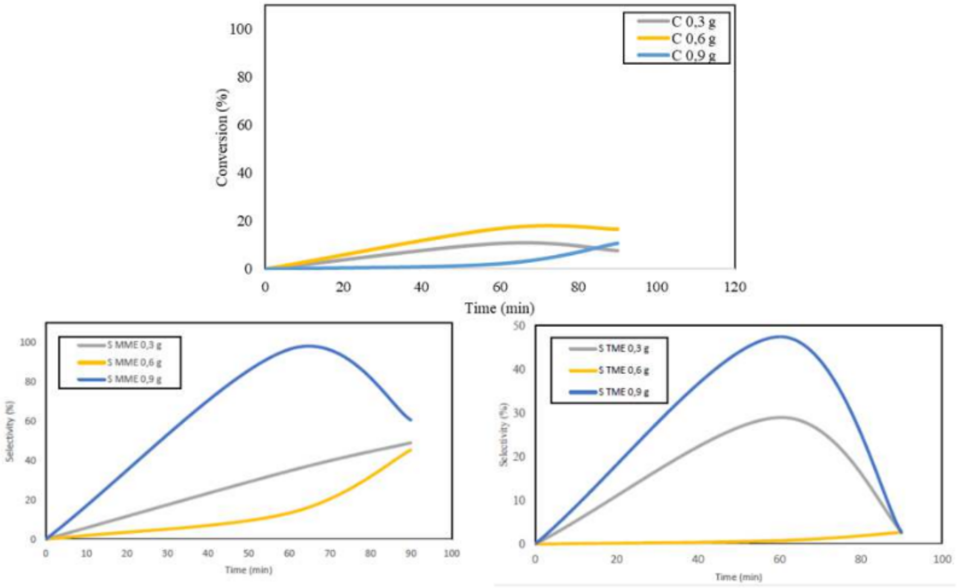

**Figure 2.** The effect of catalyst mass on α-pinene conversion and the selectivity of MME and TME

### *3.3. Effect of Ratio of Reactants*

The mole ratio of the reactants plays a role in the methoxylation of α-pinene. Figure 7 shows that the highest conversion is obtained when the reaction time is 120 seconds, mass of catalyst pf 0.3 g, and the mole ratio of the reactants used is 1:15 moles, which is 99.8%. The highest MME and TME selectivity obtained with the mole ratio of the reactants of 1:45 at 90 seconds, was 81.3% and 78.8%, respectively, and conversion of 4%.

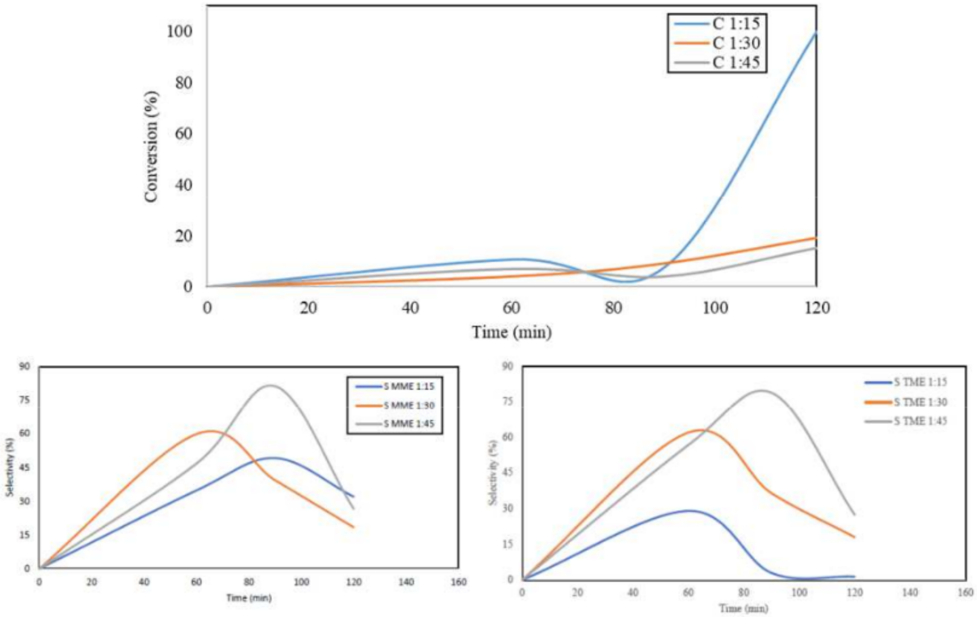

**Figure 3.** Effect of mole ratio of reactants on α-pinene selectivity and the selectivity of dan TME

A schematic of the methoxylation reaction mechanism is presented in Figure 4.

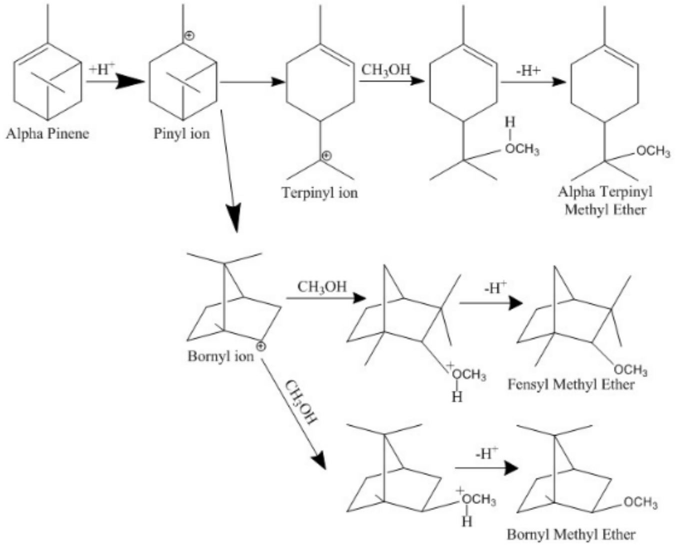

**Figure 4.** Scheme of reaction mechanism of α-pinene methoxylation with potassium alum catalyst assisted with microwave power

## 4. Conclusion

Potasium Alum [$KAl(SO_4)_2.12H_2O$] has been proposed as active and selective catalysts for the methoxylation of α-pinene with methanol. The GC–MS analysis of the reaction mixtures showed that terpinyl methyl ether (TME) and mirtenyl methyl ether (MME) were obtained with good selectivity over the potasium alum catalysts. Reaction parameters, such as the microwave power, ratio of mole reactants and mass of catalyst could be utilized to optimize the catalytic activity.

## References

[1] Salvador VT, Silva ES, Gonçalves PGC, and Cella R 2020 *Sustain. Chem. Pharm.* **15** 100214.
[2] Wijayati N, Widiyastuti A, Mursiti S, Rakainsa SK 2020 *IOP Conf Ser Mater Sci Eng*. **846**(1) 012069
[3] Prakoso T, Putra IA, Handojo L, Soerawidjaja TH, Winoto HP, Indarto A *Heliyon* **6**(10) e04984
[4] Wei Z, Xiong D, Duan P, Ding S, Li Y, Li L, Niu P, and Chen X *Catalysts* **10**(2) 213.
[5] Matos I, Silva MF, Rosas RR, Vital J, Mirasol JR, Cordero T, Castanheiro JE, Fonseca IM 2014 *Microporous Mesoporous Mater.* **199** 66-73.
[6] Catrinescu C, Fernandes C, Castilho P, Breen C 2015 *Appl. Catal. A: Gen.* **489** 171-179.
[7] Grzona L, Comelli N, Masini O, Ponzi E, Ponzi M 2000 *React. Kinet. Catal. Lett*. **69**(2) 271-276.
[8] Wijayati N, Handayani T, Supartono 2017 *Asian J. Chem*. **29**(8) 1705-1708.
[9] Wijayati N, Supartono, Kusumastuti, E 2018 *Mater. Sci. Eng.* **349** 1–5.
[10] Yadav MK, Patil M V and Jasra RV 2009 *J. Mol. Catal. A: Chem*. **297**(2) 101-109.
[11] Mochida T, Ryuichiro O, Naoto H, Yuichi K, Toshio O 2007 *Microporous Mesoporous Mater.* **101** 176-183.
[12] Su H, Kim HS, Seo SM, Ko SO, Suh JM, Kim GH, and Lim WT 2012 *Bull. Korean Chem. Soc.* **33**(8) 2785.
[13] Telalovic´ S, Ramanathan A, Ng JF, Maheswari R, Kwakernaak C, Soulimani F, Brouwer H C, Chuah G K, Weckhuysen BM, and Hanefeld U 2011 *Chem. Eur. J.* **17** 2077 – 2088.
[14] Gackowski M, Kuterasiński Ł, Podobiński J, Korzeniowska A, Sulikowski B, Datka J 2019 *Appl. Catal. A: Gen.* **578** 53–62
[15] Rachwalik R, Góra-marek K, Olejniczak Z, Hunger M, and Sulikowski B 2019 *Catal. Today* **10** 1–10.
[16] Frattini L, Isaacs MA, Parlett CMA, Wilson K, Kyriakou G, Lee AF 2017 *Appl. Catal. B: Environ.* **200** 10–18
[17] Avila M C, Nora A C, Castellon E R, Lopez A J 2010 *J.Mol. Catal. A: Chemical* **322**(1-2) 106-112.
[18] Zielińska A, Ferreira N R, Durazzo A, Lucarini M, Cicero N, Mamouni SE, Silva AM, Nowak I, Santini A, Souto E B 2019 *Molecules* **24**(15) 2683.
[19] Wijayati N, Solikhah, Widiarti N, Mahatmanti W, Rakainsa SK 2020 *J. Phys.: Conf. Ser.* **1567** (2) 022032.
[20] Pito DS, Fonseca IM, Ramos AM, Vital J, Castanheiro JE 2009 *Chem. Eng. J.* **147** 302-306
[21] Jensen K, Mahaim C, Holderich WF 1997 *Appl. Catal. A: Gen.* **149** 311-329
[22] Souza R, Navarro R, Grillo A V, Brocchi E 2019 *J. Mater. Res. Technol.* **8**(1) 745–751.
[23] Abdulwahab A M, Al-magdashi YAA, Meftah A, Al-Eryani D A, Qaid AA 2019 *Growth. Chin. J. Phys.* **60** 510–521.
[24] He W, Fang Z, Zhang K, Tu T, Lu N, Qiu C, Guo K 2018 *Chem. Eng. J* **331** 161–168.
[25] Kappe C O 2004 *Angewandte Chemie* **35** 6250–6284
[26] Liu Y, Zheng D, Li B, Lyu Y, Wang X, Liu X, Li L, Yu S, Liu X, and Yan Z 2020 *Microporous Mesoporous Mater.***299** 1–9
[27] Wijayati N, Lestari LR, Wulandari LA, Mahatmanti FW, Rakainsa SK, Cahyono E, and Wahab RA 2021 *Heliyon* **7**(1) e06058

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