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Effect of Acid Activation and Al Impregnation in Preparation of Bleaching Earth Catalyst for Glyerol Ketalization

Fadhil Muhammad Tarmidzi[1*], Desly Angeline Sa'pangan[1], Winda Robiatul Adawiyah[1], Adrian Gunawan[1]

[1]*Study Program of Chemical Engineering, Department of Industrial Technology and Process, Institut Teknologi Kalimantan, Balikpapan 76127, Indonesia*

*Corresponding author email: fadhil.tarmidzi@lecturer.itk.ac.id

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ABSTRACT

Indonesia's increased biodiesel production represents the government's support for implementing replacement strategy of diesel to biodiesel (B30). The consequence's includes a higher production of glycerol as a byproduct. Currently, glycerol's use in Indonesia has remained limited to the pharmaceutical, polymer, and agricultural industries. On the other side, another application for glycerol as a biodiesel additive is being explored. Therefore, glycerol must be valorized in order to promote the development of clean bioenergy in Indonesia. Solketal as biodiesel additive can be produced by ketalizing glycerol with acetone in the presence of catalyst under acidic condition. In this research, a bleaching earth catalyst, one of the components utilized as a bleaching agent in the biodiesel industries, was developed. Bleaching earth is a form of clay with acidic characteristics that makes it an excellent catalyst in the ketalization process. To increase its surface area and active side, it was activated with sulfuric acid and impregnated with aluminum. The XRD and SEM analyses revealed no significant changes in the catalyst, however the IR spectra revealed a drop in the intensity of the Al-O group. The ketalization process was carried out at 60oC for 2 hours with a catalyst load of 1.5% and a glycerol:acetone:ethanol ratio of 1:1:1. The activation process with 15 M sulfuric acid and 1:1 impregnation was able to convert 15.22% glycerol while 1:5 impregnation is 23.73%. In this study, the catalyst load variation was also carried out which also increased the conversion to 60.53% with 5% catalyst load. Based on these results, it shows that the activation process has more effect on glycerol conversion compared to the impregnation process. In addition, the catalyst load in ketalization is also able to increase the conversion of glycerol.

Keywords: Aluminum, Clay, Ketalization, Solketal, Sulphuric Acid.

Introduction

Biodiesel development is currently expanding in Indonesia. In 2016, Indonesia produced 3.6 million kL, with a target of up to 8.7 million kL by 2025. This is a form of support for the use of renewable energy which has been regulated in several regulations including the implementation of B30 in Indonesia [1].

The transesterification of palm oil with ethanol produces biodiesel. It produces by-products such as glycerol in amounts as high as 12% with a purity of 50% [2]. Nowadays, glycerol is a commodity that is widely used in the plastic, pharmaceutical, and agricultural sectors. On the other side, there is a possibility to convert glycerol into solketal, which can be utilized as a biodiesel additive [4,5]. Furthermore, in the polymer industries,

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solketal can be turned into a green solvent and plasticizer [6].

Solketal can be obtained from the ketalization process of glycerol with acetone under acidic conditions. A catalyst is required to deliver H^+ ions in the process in order to establish acidic conditions [7], [8]. The use of homogeneous catalysts currently produces the highest conversion; however, issues arise when the acid separation process needs high temperatures. Meanwhile, the components involved in the ketalization process are particularly sensitive to high temperatures and have the potential to deteriorate. As a result, current research is focused on developing heterogeneous catalysts for a more efficient separation process, one of which is the use of clay.

Clay offers various advantages that can aid in the ketalization process, including its acidic nature and the ability to adjust crystal and pore sizes by further processing. Clay consists primarily of silica and alumina. In comparison to other metals, the alumina content has been shown to provide good conversion results in the ketalization process. The swelling properties of clay, on the other hand, can be used to shift the reaction equilibrium towards solketal compounds due to the reversible nature of the reaction (Equation 2) and the formation of water as a by-product [9], [10].

According to Che et al., metals play a part in the ketalization process through a Brønsted acid catalytic mechanism [11]. However, Da Silva et al. also claimed that the Lewis acid catalyst mechanism may be important during the process of breaking water molecules into H^+ ions [7]. Based on this potential, bleaching earth's ability to absorb water can be employed to generate H^+ ions. The presence of alumina in the bleaching earth also aids in the synthesis of H^+ ions, maximizing the formation of solketal.

One form of clay that can be used is bleaching earth, which is commonly used in the palm oil industry's oil bleaching process [12]. However, various processes are required to improve the ability of bleaching earth to be utilized as a catalyst in the glycerol ketalization process. Bleaching earth can be improved by increasing the pores and the acidic functional groups to provide a shorter diffusion distance. Because of the existence of sulfonate groups, acidic functional groups can be boosted by utilizing H_2SO_4, which has been shown to achieve conversions of up to 97% [13]. However, the use of acid has the unintended consequence of removing alumina from the clay structure, limiting its efficacy as a catalyst [14]. Thus, alumina impregnation is required to enhance the amount of active metal groups in the catalyst.

This study aims to see the effect of sulfuric acid activation and alumina impregnation on the preparation of bleaching earth catalyst for the ketalization process of glycerol with acetone.

Methods

The materials used for this research are Bleaching Earth (Tianyu, China), Glycerol (Merck), Sulfuric Acid – H_2SO_4 (Smartlab), and Aluminum Nitrate Nonahydrate – $Al(NO_3)_3.9H_2O$ (Merck). For glycerol analysis according to the SNI 06-1564-1989 method, the materials used are sodium periodate - $NaIO_4$ (Merck), Ethylene glycol – $C_2H_6O_2$ (Merck), bromthymol blue (Merck), Potassium hydroxide – NaOH (Merck), and Oxalic Acid – $C_2H_2O_4$ (Merck).

Preparation of Bleaching Earth Catalyst

A total of 10 grams of bleaching earth (VBE) was activated using H_2SO_4 with varied concentrations of 5, 10, and 5 M. The activated BE (ABE) was impregnated using $Al(NO_3)_3.9H_2O$ with BE/Al ratio of 1:1, 1:3, and 1:5. The catalyst preparation was drying at 110^{o}C and calcination at 850^{o}C for 6 hours. The resulting catalyst was then stored in a dry container.

Bleaching Earth Catalyst Characterization

FTIR is used to identify bleaching eart functional groups and XRD is used to analyze crystallinity and crystal size. The constituent crystals that dominate the bleaching earth were identified via FTIR and XRD analysis, which were quartz (SiO_2), calcite ($CaCO_3$), and kyanite (Al_2SIO_5).

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Ketalization of Glycerol with Acetone

The ketalization process was carried out by adopting the method by Da Silva with some modifications [7]. The reaction took place in a three-neck flask reactor equipped with a stirrer and reflux system. Acetone:glycerol:ethanol with mole ratio of 1:1:1 and catalyst loading of 1.5%w/w was reacted at 60^{o}C for 2 hours. Liquid samples were taken and cooled rapidly to stop the reaction. The liquid will then be analyzed. The best activation and impregnation variable was continued to determine the effect of catalyst loading on the ketalization process. The catalyst loading varied in this experiment is 1.5%, 3%, and 5%w/v.

Product Analysis

Analyzing solketal products is performed indirectly by measuring the converted glycerol content. To determine the glycerol conversion, the SNI 06-1564-1989 method was utilized to evaluate the crude glycerol content. A 0.5 gram sample in 50 mL of distilled water was placed in an Erlenmeyer flask and the indicator bromthymol blue was added. H_2SO_4 0.2 N was added until the mixture turned greenish yellow. The solution was neutralized with 0.05 N NaOH until it turned blue. The procedure was also carried out on the blank solution.

50 mL of $NaIO_4$ solution was added to the sample and blank solutions and stored in a dark room for 30 minutes. Then ethylene glycol solution (1:1) was added and stored again in a dark room for 20 minutes. The solution was diluted with 300 mL of water and bromthymol blue indicator was added. Finally, 0.5 N NaOH solution was used to titrate both the sample and blank until a blue color was formed. The glycerol content (%gly) in the sample solution and blank was calculated using equation 1.

$$\%gly = \frac{(T_1 - T_2)\ x\ N\ x\ 9.209}{W} \qquad (1)$$

Where, T_1 and T_2 are NaOH used for titration of sample and blank respectively. N is NaOH normality, W is sample weight.

Analysis was carried out before ($\%gly_{initial}$) and after ($\%gly_{final}$) the reaction. The conversion (conv) of the reaction was calculated using equation 2.

$$Conv, \% = \frac{\%gly_{initial} - \%gly_{final}}{\%gly_{initial}} \qquad (2)$$

Results and Discussions

Effect of Alumina Impregnation on the Crystallinity of Bleaching Earth Catalysts

The crystallinity values were measured at a wavelength of 0.15406 nm and a constant (K) of 0.89. Table 1 shows that the impregnation followed by calcination processes can reduce crystal size, particularly in quartz and kyanite [15]. Furthermore, the resulting crystallinity rose as a result of the alumina impregnation process.

Table 1. Crystal Size and Its Crystallinity of Various Al Ratio in the Impregnated Bleaching Earth of Majority Constituent Minerals

Sample	Mineral	Crystal Size (nm)	Crystallinity (%)
IBE 1:1	Quartz	2.25	20.15%
	Calcite	0.12	1.13%
	Kyanite	2.93	10.31%
IBE 1:3	Quartz	2.09	28.65%
	Calcite	0.12	1.62%
	Kyanite	2.66	11.14%
IBE 1:5	Quartz	1.92	38.26%
	Calcite	0.12	4.72%
	Kyanite	2.23	11.11%

According to the Table 1, the impregnation process after calcination can reduce crystal size and increase crystallinity. The reduction in acid group activity will depend on how the zeolite crystallinity changes. The tiny amount of alumina can increase the hydrophobicity of the catalyst, preventing hydrolysis of the product [16].

Effect of Alumina Impregnation on the Functional Group of Bleaching Earth Catalysts

According to the FTIR analysis (Figure 1), the most significant functional groups can be detected at wavenumber 1055 cm^{-1}, which defines Si–O and Al–O vibration, and the peak at wavenumber 800 cm^{-1}, which describes Si–O–Si symmetric stretching vibration [17], [18]. The impregnation process has an effect on the

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Al–O peak, as displayed by the increased intensity of the group, but has no effect on the 800 cm^{-1} peak.

Morphologies of Bleaching Earth Catalyst

The activation process aims to increase the contact area of the catalyst to provide more space for ketalization. Followed by the activation process to add active site of alumina to the catalyst. The XRD study results can be viewed in greater detail in the SEM image (Figure 3). Calcite appears in large aggregates, whereas quartz appears as small grains [19], [20]. Kyanite also appears in small fraction is prismatic, elongated, tabular crystal [21].

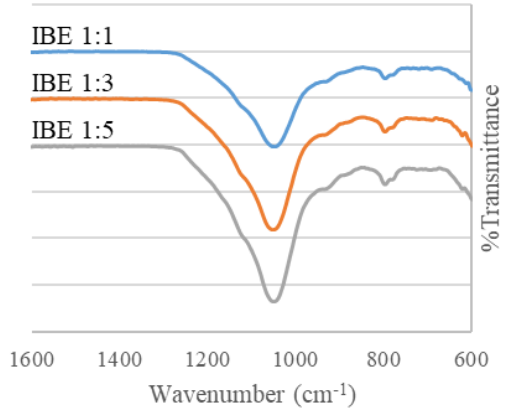

Figure 1. IR Spectra of Various Al Ratio in the Impregnated Bleaching Earth at Segmented Wavenumber 600 – 1600 cm^{-1}

Figure 2 shows little distinction between the activation and impregnation phases. However, it is clear that the activation process roughens the surface morphology of bleaching earth, particularly quartz, increasing its contact area.

Ketalization of Glycerol with Acetone

The formation of solketal produces a by-product in the form of water following the reaction equation below [22].

$$C_3H_8O_3 + C_3H_6O \leftrightarrow C_6H_{12}O_3 + H_2O \qquad (3)$$

Because the ketalization reaction is reversible, the initial reaction conditioned in line with stoichiometry will generate products with the same ratio. The use of clay has three possible reaction pathways: (1) providing acidic conditions for the reaction process that follows the Lewis acid catalyst reaction mechanism, (2) providing a place to support Al to ensure that the ketalization process follows the Bronsted acid catalyst reaction mechanism, or (3) the bleaching earth used is able to absorb the resulting water molecules and continue to shift the reaction equilibrium towards the product [7], [11], [18]. Impregnated bleaching earth catalyst and mixture of glycerol, acetone, and solketal from this research is shown in Figure 2.

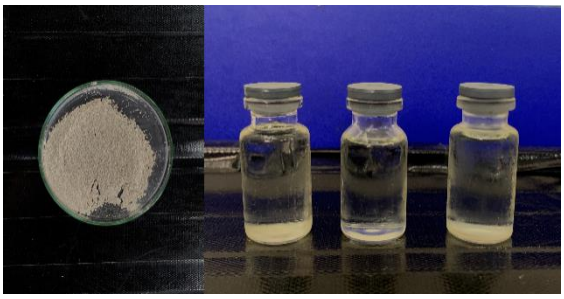

Figure 2. Impregnated Bleaching Earth (left) and Solketal Mixture Before Purification (right)

In the ketalization process of glycerol with acetone. The activation process on the catalyst has a greater influence than the activation process (Table 2). It demonstrates that acid activation has a greater influence than Al impregnation. Acid activation increased conversion by more than twice, whereas impregnation just raised it by 1.5 times. However, both processes have a favorable effect on enhancing the conversion of glycerol to solketal.

Table 2. Effect of Activation and Impregnation to Glycerol Conversion

Parameter		Conversion, %
H_2SO_4 Activation (with 1:1 Al impregnation)	5 M	6.82
	10 M	8.16
	15 M	15.22
Al Impregnation (with 15 M activation)	1:1	15.22
	1:3	20.00
	1:5	23.73

To maximize conversion, increasing the amount of catalyst in the ketalization process (Figure 4) has a considerable impact. A 5% increase in catalyst loading can produce a conversion of up to 60.53%.

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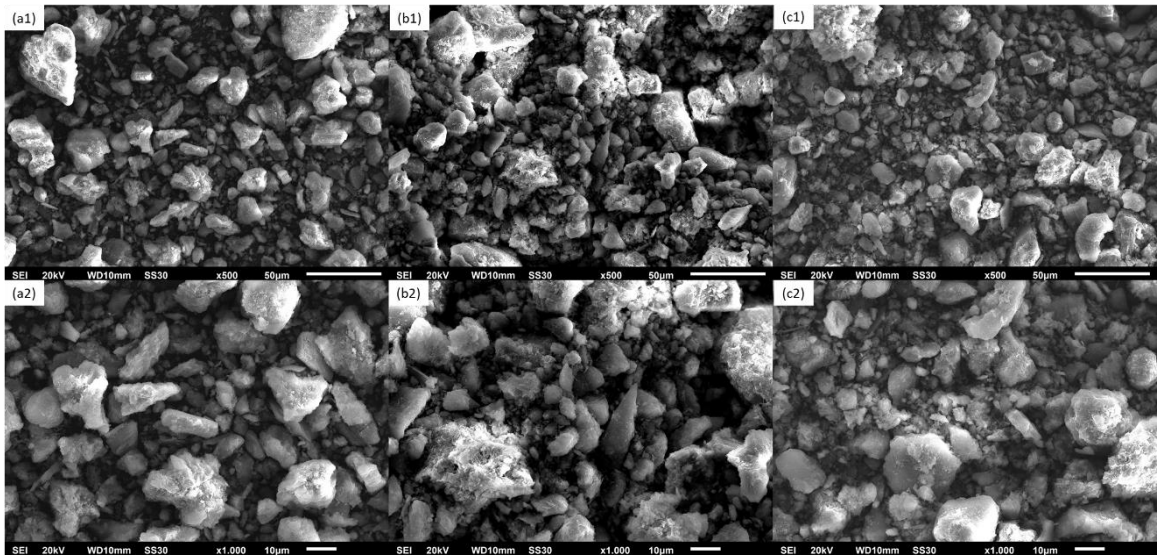

Figure 3. SEM Surface Image of Bleaching Earth Catalysts: (a) Untreated BE, (b) Activated BE, and (c) Impregnated BE with magnification: (1) 500x and (2) 1000x

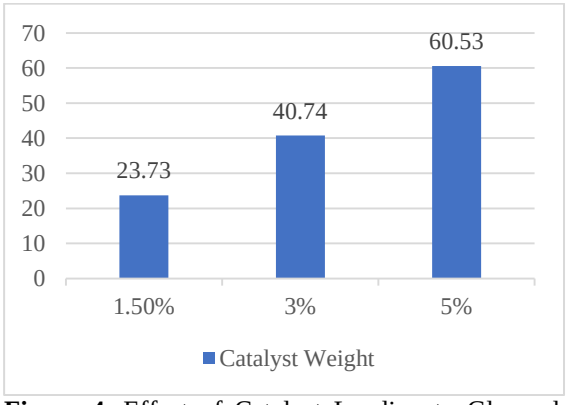

Figure 4. Effect of Catalyst Loading to Glycerol Conversion Using 15 M Activation and 1:5 Al Impregnation Bleaching Earth

Results are the main part of scientific articles, containing: net results without data analysis process, results of hypothesis testing. The results can be presented with a table or graph, to clarify the results verbally.

Discussion is the most important part of the entire content of a scientific article. The purpose of the discussion is: Answering the research problem, interpreting the findings, integrating the findings from the research into the existing body of knowledge and compiling a new theory or modifying the existing theory.

Conclusions

The results of the investigation demonstrated that the Al impregnation into the bleaching earth catalyst was successful. The XRD study results, on the other hand, did not reveal an increase in kyanite crystallinity, which is directly related to the Al component elements. SEM image shows the different morphology of quartz, calcite, and kyanite clearly. There is no significant effect of activation and impregnation in bleaching earth, but activation process changes the roughness of quartz. Effect of activation also clearly shows by the IR spectrum of Al-O which lowering its peak. The highest conversion achieved is 60.53% from bleaching earth catalyst treatment with 15 M acid activation and 1:5 aluminum impregnation, with catalyst loading 5%.

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Author Contributions

F. M. Tarmidzi and A. Gunawan presented the idea, developed the theory and methodologies. F.M. Tarmidzi supervise the project, carried out the analysis of ketalization, and wrote the manuscript with input from all authors. A. Gunawan helped supervise the project anad carried out catalyst characterization. D.A. Sa'pangan and W.R. Adawiyah conceived, planned, and carried out the experiment, performed the analytic calculation. D.A. Sa'pangan contributed to catalyst preparation. W.R. Adawiyah contributed to ketalization of glycerol. All authors provided feedback to the final manuscript.

Conflicts of Interest

All authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

[1] D. A.H. *et al.*, *Pengembangan bioenergi di Indonesia: Peluang dan tantangan kebijakan industri biodiesel*. Center for International Forestry Research (CIFOR), 2018. doi: doi.org/10.17528/cifor/006975

[2] S. Brahma *et al.*, "Biodiesel production from mixed oils: A sustainable approach towards industrial biofuel production," *Chemical Engineering Journal Advances*, vol. 10, p. 100284, 2022, doi: doi.org/10.1016/j.ceja.2022.100284

[3] I. Zahid, M. Ayoub, B. B. Abdullah, and M. Hamza Nazir, "Glycerol Derivatives as Fuel Additive: Synthesis of Solketal From Glycerol and Acetone With Various Acid Clay Catalysts," in *Advances in Engineering Research*, 2020, pp. 292–296. doi: doi.org/10.2991/aer.k.201229.038

[4] A. R. Trifoi, P. Ş. Agachi, and T. Pap, "Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols," *Renewable and Sustainable Energy Reviews*, vol. 62, pp. 804–814, 2016, doi: doi.org/10.1016/j.rser.2016.05.013

[5] D. Gielen, F. Boshell, D. Saygin, M. D. Bazilian, N. Wagner, and R. Gorini, "The role of renewable energy in the global energy transformation," *Energy Strategy Reviews*, vol. 24, pp. 38–50, 2019, doi: doi.org/10.1016/j.esr.2019.01.006

[6] R. Zhou, Y. Jiang, H. Zhao, B. Ye, L. Wang, and Z. Hou, "Synthesis of solketal from glycerol over modified SiO2 supported p-phenolsulfonic acid catalyst," *Fuel*, vol. 291, p. 120207, 2021, doi: doi.org/10.1016/j.fuel.2021.120207

[7] M. J. da Silva, A. A. Rodrigues, and P. F. Pinheiro, "Solketal synthesis from glycerol and acetone in the presence of metal salts: A Lewis or Brønsted acid catalyzed reaction?," *Fuel*, vol. 276, p. 118164, 2020, doi: doi.org/10.1016/j.fuel.2020.118164

[8] J. A. Vannucci, N. N. Nichio, and F. Pompeo, "Solketal synthesis from ketalization of glycerol with acetone: A kinetic study over a sulfated zirconia catalyst," *Catal Today*, vol. 372, pp. 238–245, 2021, doi: doi.org/10.1016/j.cattod.2020.10.005

[9] S. Amri *et al.*, "Green production of glycerol ketals with a clay-based heterogeneous acid catalyst," *Applied Sciences (Switzerland)*, vol. 9, no. 21, Nov. 2019, doi: doi.org/10.3390/app9214488

[10] F. M. Perez, M. N. Gatti, G. F. Santori, and F. Pompeo, "Transformations of

Glycerol into High-Value-Added Chemical Products: Ketalization and Esterification Reactions," *Reactions*, vol. 4, no. 4, pp. 569–634, 2023, doi: doi.org/10.3390/reactions4040034

[11] P. Che, F. Lu, X. Si, H. Ma, X. Nie, and J. Xu, "A strategy of ketalization for the catalytic selective dehydration of biomass-based polyols over H-beta zeolite," *Green Chemistry*, vol. 20, no. 3, pp. 634–640, 2018, doi: doi.org/10.1039/c7gc03248j

[12] M. Rossi, M. Gianazza, C. Alamprese, and F. Stanga, "The role of bleaching clays and synthetic silica in palm oil physical refining," *Food Chem*, vol. 82, no. 2, pp. 291–296, 2003, doi: doi.org/10.1016/S0308-8146(02)00551-4

[13] M. S. Khayoon and B. H. Hameed, "Acetylation of glycerol to biofuel additives over sulfated activated carbon catalyst," *Bioresour Technol*, vol. 102, no. 19, pp. 9229–9235, Oct. 2011, doi: doi.org/10.1016/j.biortech.2011.07.035

[14] A. Al-Nayili, M. Albdiry, and N. Salman, "Dealumination of Zeolite Frameworks and Lewis Acid Catalyst Activation for Transfer Hydrogenation," *Arab J Sci Eng*, vol. 46, no. 6, pp. 5709–5716, Jun. 2021, doi: doi.org/10.1007/s13369-020-05312-w

[15] S. Mukherjee, "Classification and Composition of Clay Constituents," in *The Science of Clays: Applications in Industry, Engineering and Environment*, Dordrecht: Springer Netherlands, 2013, pp. 23–32. doi: doi.org/10.1007/978-94-007-6683-9_2

[16] V. Rossa, Y. da S. P. Pessanha, G. Ch. Díaz, L. D. T. Câmara, S. B. C. Pergher, and D. A. G. Aranda, "Reaction Kinetic Study of Solketal Production from Glycerol Ketalization with Acetone," *Ind Eng Chem Res*, vol. 56, no. 2, pp. 479–488, 2017, doi: doi.org/10.1021/acs.iecr.6b03581

[17] N. Sedira and J. Castro-Gomes, "Low Liquid-to-solid Ratio of Mining Waste and Slag Binary Alkali-activated Material," *KnE Engineering*, May 2020, doi: doi.org/10.18502/keg.v5i5.6941

[18] I. Zahid, M. Ayoub, B. Bin Abdullah, M. Hamza Nazir, M. Ameen Kaimkhani, and F. Sher, "Activation of nano kaolin clay for bio-glycerol conversion to a valuable fuel additive," 2021, doi: doi.org/10.3390/su1307389

[19] Z. Namazifar, F. Saadati, and A. A. Miranbeigi, "Synthesis and Characterization of Novel Phenolic Derivatives with The Glycerol Ketal Group as an Efficient Antioxidant for Gasoline Stabilization," *New J. Chem.*, vol. 43, no. 25, pp. 10038–10044, 2019, doi: doi.org/10.1039/C8NJ05923C

[20] P. C. Nobre *et al.*, "Synthesis of enantiomerically pure glycerol derivatives containing an organochalcogen unit: In vitro and in vivo antioxidant activity," *Arabian Journal of Chemistry*, vol. 13, no. 1, pp. 883–899, 2020, doi: doi.org/10.1016/j.arabjc.2017.08.007

[21] F. R. Barrientos-Hernández *et al.*, "Effect of Particle Size and Sintering Temperature on the Formation of Mullite from Kyanite and Aluminum Mixtures," *Advances in Materials Science and Engineering*, vol. 2021, 2021, doi: doi.org/10.1155/2021/6678297

[22] M. Alsawalha, "Catalytic Activity and Kinetic Modeling of Various Modules

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HZMS-5 and Treated MCM-41 Catalysts, for the Liquid-Phase Ketalization of Glycerol With Acetone," *Front Chem*, vol. 7, Nov. 2019, doi: doi.org/10.3389/fchem.2019.00799