

Esterification of Gondorukem with Glycerol and Malic Anhydride Acid Using Hypophosphorous Acid Catalyzer

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Abstract: Gondorukem as a non-wood product is widely used as an auxiliary material in the paper industry, as a plaster softener, as a mixture for eyeshadow, batik ink, soap, varnish, electrical equipment insulation and printing ink. Gondorukem is also used as an adhesive which functions as a tackifier, adhesion promoter or viscosity promoter to improve the properties of the final product. Gondorukem has unsaturated alkyl tricyclic organic acids derived from natural derivatives that can dissolve in organic solvents, consisting of 80-90% resin acids and around 10% neutral components. To overcome the influence of the tricyclic framework structure, the phenanthrene of the rosin and the high viscosity of the reaction mixture, the esterification of gondorukem carried out for a reaction time of 6 h at 270°C with an acid catalyst. The esterification reaction was carried out in a three neck flask. The reaction temperatures used were 260°C, 270°C, and 280°C, and the use of 1%, 3%, and 5% catalyst. Data obtained from the research results in the form of acid numbers based on temperature and catalyst percentage resulted in conversions of 86%, 92% and 94%.

Keywords: rosin; maleat; esterification.

Introduction

The forestry sector has forest products in the form of wood products and also has a very diverse range of non-timber forest products (NTFPs). The Indonesian government is reducing wood forest products, with this policy the government is maximizing non-timber forest products (Daryono, 2015).

Gondorukem as a non-wood product is widely used as an auxiliary material in the paper industry, as a plaster softener, as a mixture for eyeshadow, batik, soap, varnish, electrical equipment insulation and printing ink. Gondorukem is also used as an adhesive which functions as a tackifier, adhesion promoter or viscosity promoter to improve the properties of the final product (Coppen et al., 1995). Gondorukem can be obtained from tapping pine trees (gum rosin), pine wood extraction (wood rosin) and by-products from pulp

mills that use pine wood as raw material (tall oil) which is referred to as non-modified gondorukem (Kirk and Othmer 2007).

Rosin or gondorukem has unsaturated alkyl tricyclic organic acids derived from natural derivatives that can dissolve in organic solvents, consisting of 80-90% resin acids and around 10% neutral components. The main compound components of rosin are abietic acid and pimaric acid which have amphipathic properties, namely having a carboxyl group which is hydrophilic and a tricyclic molecule which is hydrophobic (Wiyono, 2009). The types of resin acids included in abietic acid are abietic acid, neoabietic acid, levopimaric acid, dehydroabietic acid, palustric acid, tetraabietic acid. Abietic acid is easily isomerized by heat and is also easily oxidized by oxygen in the air, levopimaric acid, which is less in quantity, is easily isomerized into other acids by the influence of heat and is also very reactive. Types of resin

acids included in pimaric acid include pimaric acid, isopimaric acid. This type is more stable than other acids found in gum rosin. The resin acid contained in gum rosin has the same empirical formula, namely $C_{20}H_{30}O_2$ (Kirk, 2007). To overcome the influence of the tricyclic, phenanthrene framework structure of the rosin and the high viscosity of the reaction mixture, the esterification of gondorukem should usually be carried out for a long reaction time (10–48 h) at 260–300 °C with an acid catalyst, such as: H_2SO_4 or ZnO (Zhou, et. al., 2020).

This research aims to determine the results of esterification of gondorukem with glycerol and maleic acid anhydride with the help of hypophosphorus acid as catalyst. Gondorukem which is commonly used in industry has a relatively high acid number, this is due to the large amount of acid in gondorukem which can be used to improve the chemical and physical properties of gondorukem products by modify acid using various methods by reacting the acid contained in gondorukem with catalyst using esterification process is expected to improve the properties of gondorukem (Kugler et al., 2019). It is hoped that the results of this research can produce better rosin esters and can determine the characteristics results of gondorukem. The parameters to be tested include the acid number, quality and physical and chemical properties of the resulting product in order to obtain a rosin ester product that meets market demand specifications and can be applied in a wider field.

Material and Methodes

Material

Gondorukem (at a softening point of 82°C, acid number of 190), Glycerol, Anhydride Maleic Acid, and Hypophosphorous Acid was kindly supplied by PT. Perhutani Pine Chemical Industry Pematang, Central Java, Indonesia. The tools used in this reaserch are a simple distillation tool using a 3 neck flask, a mechanical stirrer, and a simple titration using a burette.

Esterification

Esterification of gondorukem is carried out by making Gum Rosin products from gondorukem with WW quality, namely by carrying out an esterification process assisted by maleic acid anhydride and hypophosphorus acid catalyst at temperatures up to 280°C. Add 30 grams of glycerol and add hypophosphorus acid. Then stir until homogeneous. After the temperature reaches 280°C, maintain this temperature for 2 hours. The processing of gondorukem glycerol ester take 6 hours. The results of separating gondorukem with water are distilled to produce gondorukem. After producing gondorukem glycerol ester or gum rosin, the product is poured into containers that have been prepared for quality testing based on its physical and chemical properties.

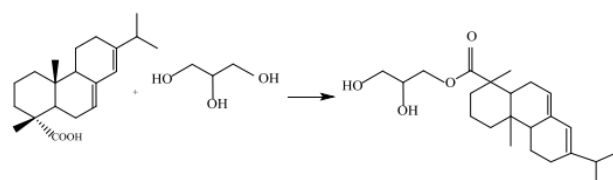


Figure 1. Esterification reaction of carboxylic acid and glycerol (Kalberg and Hagvall, 2018).

Analysis Methods

The analysis in this research was carried out at the PT. Perhutani Pine Chemical Industry Pematang and Gadjah Mada University, Yogyakarta, Central Java. The synthesis was carried out within 6 hours by maintaining the reaction temperature at 260°C, 270°C, and 280°C. The reaction time is calculated after the godorukem is completely liquid, where the godorukem will liquid at temperatures above 100°C. Gondorukem in liquid form is reacted with glycerol and acid as a catalyst which will be used in the esterification process, then the temperature is raised to a specified limit and sampling is carried out every 30 minutes to determine changes in the acid number and find out whether the desired product can react according to initial expectations.

The acid number test based on RSNI3 7636: 2010 is carried out by weighing gondorukem which has been made into a fine powder of 2 grams in a 300 ml Erlenmeyer flask. In the Erlenmeyer flask, 2,5 ml of toluene and 7.5 ml of propanol were added which were used to dissolve the sample before adding the indicator so that the color change could be seen during the titration to determine the acid

number of the sample. After the sample has dissolved, titration is carried out with KOH to determine the acid number and conversion. The same analysis was conducted for the blank solution. The acid number was calculated with Equation (1):

$$AN = \frac{V \times N \times 56,1}{ms} \quad (1)$$

Where AN is the acid number of the sample. V is the volume of potassium hydroxide solution to reach the equivalent point in the sample test (mL), N is the potassium hydroxide solution normality (N), and ms is the mass of the sample (g). After titrating the sample variations that already obtained, calculations are carried out to find the conversion of the acid that reacts during the esterification process. The conversion was calculated with Equation (2):

$$C = \frac{Ga - AN}{Ga} \times 100\% \quad (2)$$

Where C is conversion by percent, Ga is the acid number of the raw gondorukem sample obtained through the same calculation as equation 1 which is then used in the calculation to determine the conversion of the product obtained. Esterification in this research is a reversible reaction, so in this research the water vapor produced from the reaction is removed by a distillation process. So this reaction can be considered a non-reversible reaction. Rosin esterification at temperatures of 260°C, 270°C, and 280°C can cause rosin decarboxylation as a side reaction. The reaction of the resin acid carboxylic group in rosin and the hydroxyl group produces rosin esters, namely mono-, di-, tri-, and tetra-esters.

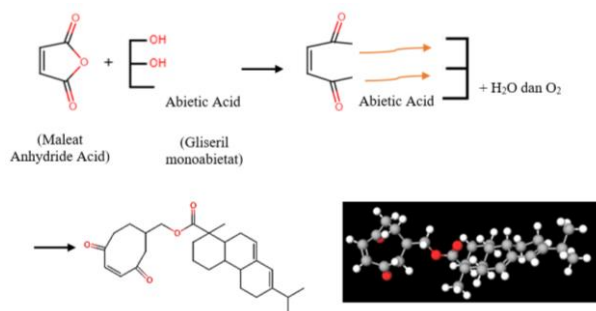


Figure 1. Reaction of maleic anhydride acid with groups carboxyl glycerol gondorukem

For color analysis will be carried out later at PT. Perhutani Pine Chemical Industry Pemalang Central Java.

Results and Discussion

Esterification of gondorukem is carried out by making Gum Rosin products from gondorukem with WW quality. Esterification process assisted by maleic acid anhydride and hypophosphorus acid catalyst at temperatures 260°C to 280°C. Glycerol used in the esterification process is 30 grams to the initial weight of gondorukem used and add hypophosphorus acid. After the temperature reaches 260°C, 270°C, and 280°C maintain this temperature for 6 hours. The processing of gondorukem glycerol ester take about 6 hours with a distillation process under vacuum conditions. carried out under vacuum conditions due to the nature of gondorukem which is easily oxidized during the esterification process, so to reduce the oxidation process and the appearance of excess by-products it is treated in the esterification process for 6 hours under vacuum conditions to get bright color results. The esterification reaction is used to make the abietic acid chain longer so it is expected to be more flexible. One of the substances that can react with the carboxylate group of rosin is glycerol. Esterification reaction, where interaction occurs between the hydroxyl group of glycerol and the carboxylic group of abietic acid. The product of this reaction is glycerolabietate with the hydroxyl position of glycerol. The reaction product consists of primary glycerolabietate and secondary glycerolabietate. The ratio of primary and secondary hydroxyl groups in glycerol is determined by the number of -OH groups in glycerol.

The acid number is obtained to determine how influential the use of maleic anhydride and hypophosphorous acid is in the esterification process. The results show a decrease in the acid number before and after esterification. The results of esterification are analyzed by titration using KOH to determine the acid number. Samples were taken consistently at certain times to determine the characterization produced by analyzing the

hydroxyl group in glycerol and the carboxylate group in gondorukem which reacts with the ester group.

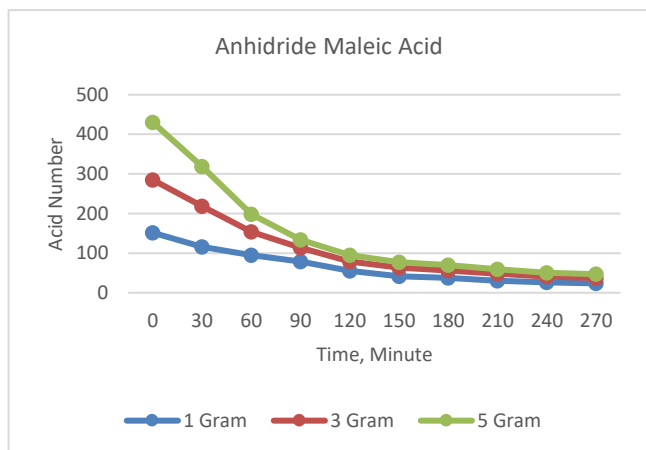


Figure 2. Acid number by Maleic variable.

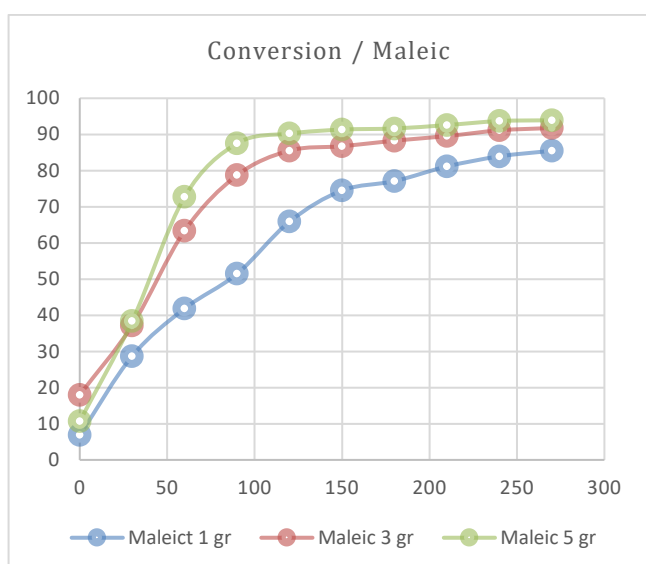


Figure 3. Conversion after esterification.

The glycerol used in esterification is 30% of the weight of the gondorukem sample used, variations in the research used are maleic anhydride of 1%, 3% and 5% of the weight of the sample used. and the temperatures used are 260°C, 270°C, and 280°C, using temperatures that are too high can cause side reactions and failure of the esterification process because at temperatures above 280°C, the catalyst in the form of hypophosphorus acid will react to produce black soot which results in an increase in acid groups in gondorukem which results in The resulting product cannot solidify so it cannot be analyzed and used as a by-product. The optimum

point for the results obtained is when using acid of 5% of the sample weight and using a temperature of 270°C. The graph obtained shows that the higher the reaction temperature, the lower the abietic acid number. This results in the higher the reaction temperature used, the greater the number of carboxylic groups consumed. Increasing the temperature of the reaction causes the carboxylic group in abietic acid and the increased reaction rate of the hydroxyl group in glycerol to be activated—intermolecular interactions.

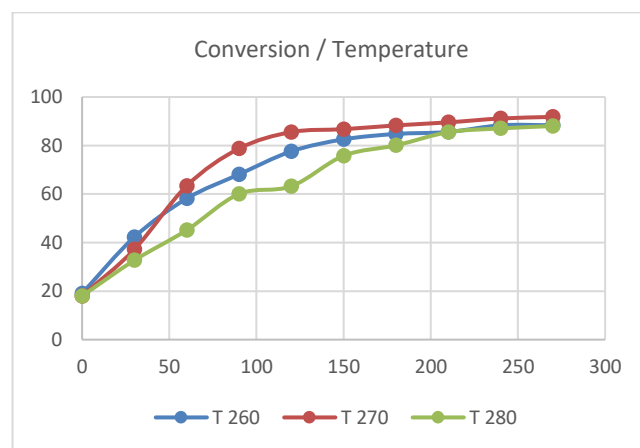


Figure 4. Conversion by temperature.

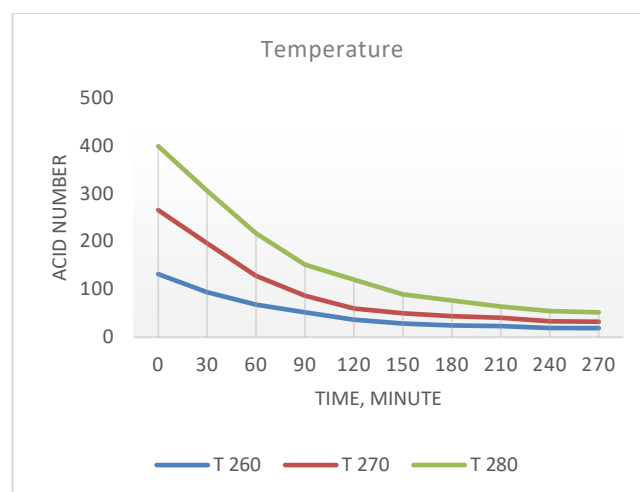


Figure 5. Acid number by temperature.

Determination of the acid number aims to determine the amount of free fatty acids contained in the material and is used to determine the level of damage to the material caused by the hydrolysis process. It is known that gondorukem is an acidic material, the gondorukem industry is very dependent on its acid function, a high acid number is an indication of the quality of gondorukem.

Modified gondorukem has varying soft points and acid numbers, so it can improve its function in the quality of gondorukem. Each variation in the gondorukem modification process aims to obtain the desired product properties generated depends on the goals to be achieved.

By using variations in the percentage of maleic acid, the acid number increases. This is thought to be because the greater the amount of acidic material added during the esterification process, the more acid groups produced in the acid reaction in gondorukem and maleate react, resulting in a lower acid number of the gondorukem derivative product. In gondorukem, maleic acid anhydride will react with glycerol which binds abietic acid in gondorukem. The modification of gondorukem into maleic gondorukem is carried out after the pine sap distillation process, namely processing the sap from pine trees into gondorukem. The resulting gondorukem is further processed into maleic gondorukem by the process of making gondorukem with glycerol ester and maleic acid, the -OH bond in Abietic acid in the sap is released and reacts with the carboxylate group in glycerol, binding maleic acid anhydride and abietic acid. This reaction continues until all the abietic acid has reacted with glycerol and this acid reacts with maleic acid anhydride to form the final product in the form of glycerol maleic rosin ester which can be used for polymer synthesis.

Conclusion

In this study, the optimum time used was 6 hours while maintaining a constant temperature of 270°C. The results of the research show that the use of Maleic Anhydride has an optimal point at 3% of the weight of the Gondorukem material, and temperature greatly influences the results of the esterification product. Using a temperature that is too low causes the Gondorukem esterification process to not be optimal so that using temperatures up to 270°C can increase the conversion of abietic acid. However, using too high a temperature will damage the product yield and esterification reaction. This results in the higher the reaction temperature used, the greater the number

of carboxylic groups consumed. Increasing the temperature of the reaction causes the carboxylic group in abietic acid and the increased reaction rate of the hydroxyl group in glycerol to be activated—intermolecular interactions.

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

References

- Coppen JJW, Hone GA. 1995. Non Wood Forest Products 2. <http://www.fao.org>. [August 15, 2008]
- Daryono, E. D., 2015. Sintesis α -Pinene menjadi α -Terpineol menggunakan Katalis H₂SO₄ dengan Variasi Suhu Reaksi dan Volume Etanol. *Jurnal Teknik Kimia USU*.4(2).
- Wiyono, B., (2009). Chemical Treatment on Indonesian Pine Oleoresin and Rosin in Making Fortified Rosin used for Sizing Agent in Paper Making Process. Ehime University, Japan, in press.
- Zhou, D., Wang, L., Chen, X., Wei, X., Liang, J., Tang, R., Xu, Y. (2020). *Reaction mechanism investigation on the esterification of rosin with glycerol over annealed Fe₃O₄/MOF-5 via kinetics and TGA-FTIR analysis*. *Chemical Engineering Journal*, 126024. doi:10.1016/j.cej.2020.126024
- Fachrodji, A. 2010. "Model Daya Saing Produk Gondorukem di Pasar Internasional dan Implikasinya terhadap Pengembangan Industri Gondorukem di Indonesia", Tesis. Fakultas kehutanan. Institut Pertanian Bogor.
- Felthouse, T. R., Burnett, J. C., Horrell, B., Mummey, M. J., & Kuo, Y.-J. (2001). *Maleic Anhydride, Maleic Acid, and Fumaric Acid*. *Kirk-Othmer Encyclopedia of Chemical Technology*.
- James, M.N.G. & Williams, G.J.B. 1974. A Refinement of the Crystal Structure of Maleic Acid. *Acta Crystallographica*. B30 (5) : 1249-1275
- Karlberg, A. T. dan Hagvall, L. 2018. *Colophony: Rosin in Unmodified and Modified Form*. Sweden: University of Gothenburg
- Khadafi, M., (2014). *PENGOLAHAN GONDORUKEM MENJADI BAHAN PENDARIHAN SEBAGAI ADITIF PADA PEMBUATAN KERTAS*. Balai Besar Pulp dan Kertas
- Kirk, R. E. dan Othmer, D. F. 2007. *Rosin dan Rosin Derivate*. *Encyclopedia of Chemical Technology*. Volume ke21. New York: The Interscience Encyclopedia. Inc.
- Kugler, S., Ossowicz, P., Malarczyk-Matusiak, K. and Wierzbicka, E., 2019, *Advances in rosin-based*

- chemicals: The latest recipes, applications and future trends, *Molecules*, 24 (9), available at: <https://doi.org/10.3390/molecules24091651>.
- Kusumadiya, P. 2009. PEMBUATAN DARIH ROSIN MALEAT SECARA LANGSUNG DARI GETAH PINUS DAN APLIKASINYA PADA KERTAS. Institut Pertanian Bogor
- Kolio D. Troev. 2018. Chapter 4 - Reactivity of P-H Group of Hypophosphorous Acid and Its Derivatives. Academic press Reactivity of PH Group of Phosphorus Based Compounds. Pages 199-244.
- Ladero, M. Gracia, M., Tamayo, J. J., Ahumada, I. L., Trujillo, F., Ochoa, F. G., (2011). Kinetic modelling of the esterification of rosin and glycerol: Application to industrial operation. *Chemical Engineering Journal*, 169(1-3), 319-328. <https://doi.org/10.1016/j.cej.2011.03.012>
- Melnyk, I.V., *et. al.* 2012. Sorption properties of porous spray-dried microspheres functionalized by phosphonic acid groups. *Microporous Mesoporous Mater.* 153, 171-177.
- M. N. G James, G. J. B Williams (1974). "A Refinement of the Crystal Structure of Maleic Acid". *Acta Crystallographica*. B30 (5): 1249-1275. [doi:10.1107/S0567740874004626](https://doi.org/10.1107/S0567740874004626)
- O'Neil, J.M, Smith, A, and Heckleman, E. P. 2001. The Mark Index an Encyclopedia of Chemical, Drug, and Biological. New York: Merk Research Laboratories
- Purnavita, S. (2017). FORMULASI VERNIS POLIESTER BERBASIS GONDORUKEM - ASAM LAKTAT DAN GLISEROL DENGAN KATALIS SnCl₂. Fakultas Teknik Universitas Wahid Hasyim Semarang.
- Rachmawati, M. A. 2011. ESTERIFIKASI GONDORUKEM MALEAT DENGAN GLISEROL. Bogor: Institut Pertanian Bogor
- Silitonga, Toga. 1988. The Influence of Maleic Unhydride Acid on Rosin Soap Properties. *Forest Product Research Journal*. Vol 5, No 4: 173-176
- Solomons, T. W. G dan Fryhle C. B. 2011. *Organic Chemistry*, 10th ed. New Jersey: John Wiley & Sons, Inc.
- Sun, Z. 2016. Design og a Highly Efficient Indium-Exchanged Heteropolytungtic Acid for Glycerol Esterification with Acetic Acid. *Catalysis Surveys from Asia*. 20:82-90
- Wang, L. 2016. A Suported Nano ZnO Catalyst Based on a Spent Fluid Cracking Catalyst (FC3R) for The Heterogeneous Esterification of Rosin. *Reaction Kinetics, Mechanisms and Catalysis*. 119:219-233
- Wang, X. 2019. An effective flame retardant containing hypophosphorous acid for poly (lactic acid): Fire performance, thermal stability and mechanical properties. *Polymer testing*, 78, 105940
- Wardani, C. 2007. Pemanfaatan Gliserol sebagai Bahan Baku Sintesa Gliserol Karbonat. Bogor: Fakultas Teknologi Pertanian.
- Wiyono, B., 2007. *Effect of Maleic Anhydride Concentration on Properties of Maleopimaric Rosin directly made from Merkus Pine Resin*. *Jurnal Penelitian Hasil Hutan* Vol. 25 No. 1, 28-40
- Wiyono, B., (2009). Chemical Treatment on Indonesian Pine Oleoresin and Rosin in Making Fortified Rosin used for Sizing Agent in Paper Making Process. Ehime University, Japan, in press.
- Zhou, D., Wang, L., Chen, X., Wei, X., Liang, J., Tang, R., Xu, Y. (2020). *Reaction mechanism investigation on the esterification of rosin with glycerol over annealed Fe₃O₄/MOF-5 via kinetics and TGA-FTIR analysis*. *Chemical Engineering Journal*, 126024. [doi:10.1016/j.cej.2020.126024](https://doi.org/10.1016/j.cej.2020.126024)