Synthesis of Maleic-Modified Rosin Ester from Pine Rosin

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Abstract. Rosin is the major component of Pine sap that has a composition of up to 90%. Rosin is an organic compound that consists of diterpene tricyclic compounds with carboxyl functional group. The presence of this functional group makes rosin becoming acidic and corrosive. Furthermore, rosin also has double bonds that are prone to oxidation when exposed to air. To improve the weaknesses, modifications shall be done. Esterification reaction can be done through transforming into a more stable functional group, i.e. ester, while Diels-Alder reaction will saturate the double bonds into more stable cyclic compounds. The results indicate that synthesizing maleic modified rosin ester could improve the properties of pine rosin. Esterification was done using a ratio of glycerol to rosin of 1:3 mol. Esterification was done for 6 hours at 250°C at room and vacuum pressure. The Diels-Alder reaction was done using maleic anhydride at 1:1 stoichiometric ratio to rosin, reacted at 150°C for 1 hour at vacuum condition.

Keywords: Rosin modification, Esterification, Glycerol, Diels-Alder, Maleic

1. Introduction
Pine rosin is one of the most abundant natural resources in Indonesia. From global market data, Indonesia was ranked third in production with a total of 8% global production, after China and Brazil. Indonesia produces around 60 kilotonnes annually where 80% of it was exported while the rest supplies the domestic needs [1].

Pine rosin is commonly used as antibacterial agent [2], paints, ink toners, and also coatings [3]. It is an organic compound that consists of two major groups of rosin acids, i.e. abietic acid (consists of abietic, livomiric, polustoric, neoabietic, dehydroabietic, and tetrahydroabietic acid) and pimamic acid (pimamic and isopimamic). These rosin acids are diterpene tricyclic (C\textsubscript{20}H\textsubscript{30}O\textsubscript{2}) compound that has double bonds in their molecular structure [4]. The double bonds are easy to be oxidized, making rosin unstable and prone to oxidation such as oxygen [5]. The carboxyl group that is also present in rosin increases the acidity of rosin. By modifying rosin by chemical reactions, these weaknesses will be eliminated and the process produces rosin that is more commercially desirable. Several chemical reactions can be used; for example, hydrogenation, esterification, disproportionation, and polymerization [5,6]. In this study, a preliminary reaction to improve the property of pine rosin was done by esterification using glycerol and Diels-Alder reaction using maleic anhydride.
2. Experimental Setup

The experimental work was divided into three major steps. First, evaluation of optimum parameters to react rosin with maleic anhydride in an esterification reaction. The second is determining the parameters to optimally react rosin with maleic anhydride in a Diels-Alder reaction. The last is to examine the resistance of the product against oxidation at open-air conditions. The parameters include the reaction time, temperature, stoichiometric ratio of reactants, and also the use of vacuum conditions to improve the conversion of the reaction. The use of vacuum condition could be deduced from the previous results [7,8]. To quantify the conversion of both esterification and Diels-alder reaction, acid and iodine values were done for each reaction respectively while percent clarity was measured directly to determine the oxidation resistance of the product [9].

Reagents used in this study include raw pine rosin, glycerol, and maleic anhydride. Pine rosin was the distilled pine resin obtained from Perhutani Pine Chemical Industry (PPCI) located in Pemalang, Indonesia with quality of X on the Gardner scale. Glycerol used was in technical grade while maleic anhydride was in analytical grade.

The reactor consists of a three-headed round-bottomed flask that is connected to a vacuum pump to adjust the reaction pressure and a thermometer to measure the temperature of the reaction during the experiment. Nitrogen injection was done to purge all possible oxygen in the overhead of the flask before and during the experiment. The condenser that was connected further to a vacuum pump was used to condense all vaporized rosin.

Solid pine rosin was first broken apart into smaller chunks however the size was maintained just enough to fit into the opening of the three-headed flask. The small size of rosin will have more risk of being oxidized and will turn solid rosin into brown color. At first, 80 grams of rosin was introduced into the flask. Nitrogen was then injected to purge the reactor of any oxygen that remains inside the flask; this was done to further protect rosin from early oxidation [10,11]. Then the heating mantle was turned on to melt the solid rosin. Once the rosin was perfectly melted, maleic anhydride was added to the reactor and the vacuum pump was turned on. In case of room pressure condition was used, the vacuum adaptor was left unconnected to the vacuum pump system. The final step was to melt of product into an appropriate aluminum cast (preferably from metal due to the high temperature of rosin). The procedure for the esterification reaction was identical to the one previously done in the Diels-Alder reaction with maleic anhydride. The difference is maleic anhydride was used instead of glycerol. Furthermore, due to the commercial demand for rosin triesters; the stoichiometric ratio used was 1:3 moles of rosin esters.

For the oxidation resistance test, the product was exposed to conditions that promote oxidation. Modified rosin will be put inside an oven at 150°C for 24 hours. Afterward, the color of the rosin was measured using a light source and a lux meter, mentioned in the previous method [9]. Unmodified rosin will also be subjected to an identical treatment and measurements to be used as a comparison.

3. Result and Discussions

3.1. Diels-Alder reaction with Maleic Anhydride

Based on the Iodine value comparison between feed and products, the reaction time required to react maleic anhydride was roughly 1 hour as seen in Figure 1. The reaction conversion of rosin at above 1 hour did not improve or change significantly. This indicates that longer reaction times (more than 1 h) would not yield any better results. Furthermore, the optimal stoichiometric ratio of pine rosin to maleic anhydride was 1:1. The conversion of rosin was very low for a stoichiometric ratio of 1:0.5 that gave ca. 26.6% of conversion. Meanwhile, ratios of 1:1 and 1:2 have a better conversion at 84.7% and 85.65%, respectively. However, the use of 1:2 ratio causes a problem that is the darkening of the rosin product, making 1:1 ratio a more desired option especially since a lesser amount of maleic was used.
3.2. Esterification with Glycerol

In the case of the esterification reaction, glycerol was used as the reactant. The selection of glycerol was done to result in ester group product with improved properties compared to the properties of the original rosin. The reaction will result in water as a by-product and the use of vacuum condition will be an advantage. The purpose of using vacuum condition was mainly to draw out water vapor that is produced by esterification. Water left in rosin can react with maleic anhydride later on to produce maleic acid that will cause rosin color darkening.
As shown in Figure 3, the esterification conversion percentage is higher when vacuum condition was applied (black color bar = vacuum condition while grey color bar = room pressure condition). This is following the theoretical evaluation that the presence of a vacuum will help to remove water from the reactor. This will drive the reaction to the product side and increase the conversion of the reaction. Moreover, vacuum conditions will help to melt the rosin at lower temperatures. The reaction will be more reactive and result higher in terms of reaction conversion. Rosin boiling point at atmospheric condition was around 250°C. However, the vacuum condition should be adjusted, as a strong vacuum condition could lead the rosin into vapor condition and reduce the yield of the product. In very low vacuum conditions, vapor rosin will be sucked into the vacuum pump together with vapor water (steam). This condition should be avoided.

In terms of reaction time, the conversion of reaction will increase at a longer reaction time. As shown in Figure 4, the acid value of the product was lower at a longer reaction time. Using a reaction temperature of 250°C, the acid value of the product reached 22 mg KOH/gr sample and reduced to 15 mg KOH/gr sample at 8 hours of reaction time. The possibility of reducing the reaction temperature was also conducted. However, Figure 5 shows clearly that the optimum reaction occurred at 250°C. Some literature has pointed out the optimal reaction for esterification occurred at 250°C. For rosin that is reacted at 200°C, the conversion only reached 40% while the rosin that is reacted at 150°C, the
conversion is even lower at less than 10%. From this evaluation, it is proven that the optimal temperature was 250°C.

![Graph showing esterification conversion at different temperatures](image)

**Figure 5.** Influence of reaction temperature on the esterification conversion at 6 h of reaction time.

3.3. **Effect of Different Additives Thickness on the Evaporation of Crude Oil**

A direct comparison between the tested rosin is shown in Figure 6. It is visually clear that modified rosin (see red arrow in Figure 6b) using esterification and Diels-Alder resists oxidation better than the others. No significant change occurs before and after being oxidized.

![Image of pine rosin samples before and after oxidation](image)

**(a)** Pine rosin samples before being oxidized

**(b)** Pine rosin samples after the oxidation process

*Note for Fig. 6b:* red arrow: maleic modified rosin ester; blue arrow: unmodified rosin

**Figure 6.** Pine rosin samples (a) before being oxidized and (b) after the oxidation process.
As a comparison, the unmodified rosin has the highest value of color change. It means that the product color is the darkest among other products (see blue arrow in Figure 6b). The other samples were obtained from products of esterification with variation in reaction temperature and time. From Figure 7, it can be observed that it is indeed true that the maleic modified rosin ester produces the least amount of change in color as it only changes by 0.5% while the unmodified rosin reaches up to 8%.

4. Conclusions
In order to obtain oxidized resistance maleic modified rosin ester, esterification is done first then followed by Diels-Alder reaction. Esterification was done at 250°C for 6 hours and glycerol to rosin ratio used was 1:3. For the Diels-Alder reaction, it was done at 150°C for an hour and rosin to maleic ratio used was 1:1. The modified rosin product was proven to be resistant to oxidation with a color change of approximately only 0.5%.

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