processes

Article

Kinetic Studies of Esterification of Rosin and Pentaerythritol

Meiga Putri Wahyu Hardhianti, Rochmadi and Muhammad Mufti Azis *

Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jl. Grafika No. 2, Yogyakarta 55281, Indonesia; meiga.p.w@mail.ugm.ac.id (M.P.W.H.); rochmadi@ugm.ac.id (R.)
* Correspondence: muhammad.azis@ugm.ac.id

Abstract: Esterification of rosin with pentaerythritol produces rosin pentaerythritol ester (RPE) which is widely used in paint, coating, and pressure-sensitive and hot-melt adhesive industries. Although RPE has excellent valuable applications and has been industrially produced, studies on the reaction kinetics have not been widely reported in the present literature. This work proposed a kinetic study of RPE synthesis by including a series of consecutive reactions forming mono-, di-, tri-, and tetra-ester with decarboxylation of rosin as a side reaction in the kinetics model. For esterification, the reaction rates were determined by the second-order kinetic model. The first-order kinetic order was proposed for decarboxylation. Kinetic experiments were performed at a temperature range of 260 °C to 290 °C. The initial molar ratio of pentaerythritol to rosin (in the mole of OH/COOH) used was between 0.8 and 1.2. A small amount of samples were withdrawn in certain time interval. The sample was analyzed to evaluate their acid and saponification number. Afterward, those experimental data were used to simulate and validate the proposed kinetic model. In general, the proposed model could capture the experimental data well. The resulting activation energies ranged from 65.81 to 129.13 kJ mol^{-1} for esterification and 233.00 kJ mol^{-1} for decarboxylation. This model also offers a new insight that correlates well with tetra-ester formation and the softening point.

Keywords: rosin; pentaerythritol; esterification; kinetic model

check for updates

Citation: Hardhianti, M.P.W.; Rochmadi; Azis, M.M. Kinetic Studies of Esterification of Rosin and Pentaerythritol. *Processes* **2022**, *10*, 39. https://doi.org/10.3390/pr10010039

Academic Editor: Tamás Varga

Received: 19 November 2021
Accepted: 22 December 2021
Published: 25 December 2021

1. Introduction

Rosin, or colophony, is a semi-transparent brittle, non-volatile part of pine tree resin or other conifer tree resin. It is generally composed of diterpenic monocarboxylic acids (90–95%), commonly known as resin acids. The remaining components are neutral compounds [1–3]. There are three types of rosin depending on their origin, i.e., gum rosin, tall oil rosin, and wood rosin. Gum rosin is the heavier fraction of the distillation of pine resin obtained by tapping the living tree, while rosin obtained from the solvent extraction of harvested wood is called wood rosin. Tall oil rosin is a by-product of wood pulping from the kraft process. The highest resin acid concentration in gum rosin are abietane-type acids (64–87%) having a conjugated double bond with the general formula of $C_{19}H_{29}COOH$ [1].

The reactivity of rosin is largely influenced by the carboxyl group and the conjugated double bond in its structure. Therefore, a chemical modification of rosin is performed to improve its stability and valuable properties. Rosin can be modified by various methods to enhance its oxidative stability, including dimerization [4], isomerization, and disproportionation [5,6]. Esterification with alcohol or polyol produces rosin esters. Commonly used alcohols are methanol, ethylene glycol, glycerol, and pentaerythritol. By using the appropriate alcohol, rosin products can be varied from liquids, through balsamic resins, to hard resins [7]. This results in greater possibilities of using this raw material for varying applications based on its properties.

Rosin pentaerythritol ester (RPE) is obtained from the esterification of rosin with pentaerythritol. The reaction is industrially performed at a high temperature and leads to a side reaction. Decarboxylation in the non-catalyzed esterification of rosin with glycerol at 285 °C to 290 °C was observed and produces carbon dioxide [8]. RPE has better water resistance, alkali resistance, oxidation resistance [9,10], and a higher softening point than rosin glycerol ester [11]. As a result, it is widely used in paints, varnishes, as an additive in oil lubricant [12], a tackifier in pressure-sensitive and hot-melt adhesive [13], and as a coating material for drug controlled release [10].

Although RPE from pine rosin is very well known and industrially produced, there have been only a few studies that reported the kinetics of the reactions needed to design and operate the manufacturing process. Previous work of kinetic studies on similar esterification was investigated by using a second-order kinetic model to describe the esterification of a simple acid and alcohol [14]. For the esterification of free fatty acids with alcohol or polyol, the second-order kinetic model was also proposed [15–17]. Moreover, a pseudo-first-order reaction was also used as a simplification model when using an excess of alcohol [18,19]. A consecutive parallel scheme was proposed for the esterification of pentaerythritol with caproic acid [20]. Additionally, the esterification of hydrogenated rosin and glycerol has also been reported previously. Here, a series of reaction schemes incorporating mono-, di-, and triglyceride formation was proposed. The reaction rates were the second-order reaction, except for the formation of monoglyceride which was proposed as a pseudo-first-order reaction due to the excess use of glycerol [21].

The kinetic model for the esterification of wood rosin with pentaerythritol at 260 °C to 300 °C was also reported. The kinetic model is heavily dependent on the temperature; the second-order reaction occurs at low temperatures and the third-order at higher temperatures [22]. Ladero et al. [11] proposed a simple second-order model for pentaerythritol and rosin esterification. However, those models neglected the forming of mono-, di-, and tri-ester.

Thus, this work aims to obtain a kinetic model of the esterification of pine rosin and pentaerythritol that includes the formation of mono-, di-, and tri-ester as a series combined with the decarboxylation of rosin as a side reaction. In addition, this research also investigates the effect of temperature and the initial molar ratio of pentaerythritol to rosin (in the mole of OH/COOH) on the softening point.

2. Materials and Methods

2.1. Materials

Rosin (at a softening point of 82 °C, acid number of 190 mgKOH g^{-1}) was kindly supplied by PT. Perhutani Anugerah Kimia (PAK) Trenggalek, East Java, Indonesia. Pentaerythritol for synthesis was purchased from Sigma Aldrich (Saint Louis, MO, USA). The materials used for analysis were potassium hydroxide pellets obtained from Merck KGaA (Darmstadt, Germany), 96% ethanol purchased from CV. Progo Mulyo (Yogyakarta, Indonesia), amyl acetate obtained from BDH Chemicals Ltd. (Poole, England), hydrochloride acid (approx. 37%) for analytical reagent obtained from Mallinckrodt Baker Inc. (Paris, KY, USA), and isoamyl alcohol for pro analysis obtained from Merck KGaA (Darmstadt, Germany).

2.2. Esterification Runs

Esterification was performed at temperatures from 260 °C to 290 °C. The initial molar ratio of pentaerythritol to rosin (in the mole of OH/COOH) used was between 0.8 and 1.2. For each trial, 100 g of rosin was added to a 500 mL three-necked round-bottom flask with a propeller agitator and a distillation system to condensate the water obtained from the reaction. The agitator speed was set at 600 rpm. When the reaction temperature reached the targeted value, a zero-time sample was withdrawn with a glass pipe and pentaerythritol was added to the flask. During the 4 h reactions, initial samples were taken every 15 min in the first 30 min and then taken every 30 min. Those samples were then analyzed by acid-base titration to determine the acid number. The saponification test was performed only on the samples at the end of the reaction.

2.3. Analyses Methods

The acid number was determined by acid-base titration using a pH meter. In this method, the sample was prepared by dissolving 0.6 g of sample in 3 mL of amyl acetate, followed by the addition of 30 mL of distilled water. The samples were titrated with 0.1 N potassium hydroxide in ethanol (standardized). The same analysis was conducted for the blank solution. The acid number was calculated with Equation (1):

$$AV = \frac{(V_s - V_b) \times N_{KOH}}{m_s} \tag{1}$$

where AV is the acid number of the sample (meq g^{-1}), V_s is the volume of potassium hydroxide solution to reach the equivalent point in the sample test (mL), V_b is the volume of potassium hydroxide solution to reach the equivalent point in the blank solution test (mL), N_{KOH} is the potassium hydroxide solution normality (N), and m_s is the mass of the sample (g).

The ester number (EV) was calculated by the difference between the saponification and acid number. The samples were saponified by 0.5 N potassium hydroxide in isoamyl alcohol for 4 h and titrated with 0.5 N hydrochloride acid (standardized) [8]. The saponification number was calculated with Equation (2),

$$SV = \frac{(V_b - V_s) \times N_{HCl}}{m_s} \tag{2}$$

where SV is the saponification number of the sample (meq g^{-1}), V_b is the volume of hydrochloride acid solution to reach the equivalent point in the blank solution test (mL), V_s is the volume of hydrochloride acid solution to reach the equivalent point in the sample test (mL), N_{HCl} is the hydrochloride acid solution normality (N), and m_s is the mass of the sample (g).

Conversion of rosin was calculated by Equation (3),

$$X_R = \frac{AV_0 - AV_t}{AV_0} \times 100\% \tag{3}$$

where AV_t is the acid number at a certain reaction time (meq g^{-1}) and AV_0 is the acid number at a time zero after adding pentaerythritol (meq g^{-1}) which is calculated with Equation (4),

$$AV_0 = \frac{AV \times m_R}{m_R + m_P} \tag{4}$$

where AV is the acid number at a time zero before adding pentaerythritol (meq g^{-1}), m_R is the mass of rosin (g), and m_P is the mass of pentaerythritol (g).

2.4. Characterization Methods

FT-IR analysis was conducted using Shimadzu FT1R-8201PC Infrared Spectrophotometer. FT-IR spectra were collected in the range of 400 and 4000 cm^{-1}. This analysis was used for characterizing rosin, pentaerythritol, and RPE produced from the reaction.

Softening point is one of the basic parameters to assess the quality of rosin and its derivatives. In this work, it was determined according to the ASTM D36 standard. This test method determines softening points in the range from 30 °C to 157 °C using a ring-and-ball apparatus immersed in USP glycerin.

2.5. Kinetic Modelling

The reaction between the carboxylic group of resin acids in rosin and the hydroxyl groups of pentaerythritol produces rosin esters, i.e., mono-, di-, tri-, and tetra-ester. Considering that esterification is a reversible reaction, in this work, the water vapor obtained from the reaction was removed by a distillation system. Thus, the reaction can be assumed to be an irreversible reaction. Esterification of rosin with pentaerythritol at 260 °C to 290 °C can lead to decarboxylation of rosin as a side reaction. The proposed model was an irreversible series reaction, forming mono-, di-, tri-, and tetra-ester with the decarboxylation rosin as a side reaction. The reaction scheme is shown in Figure 1.

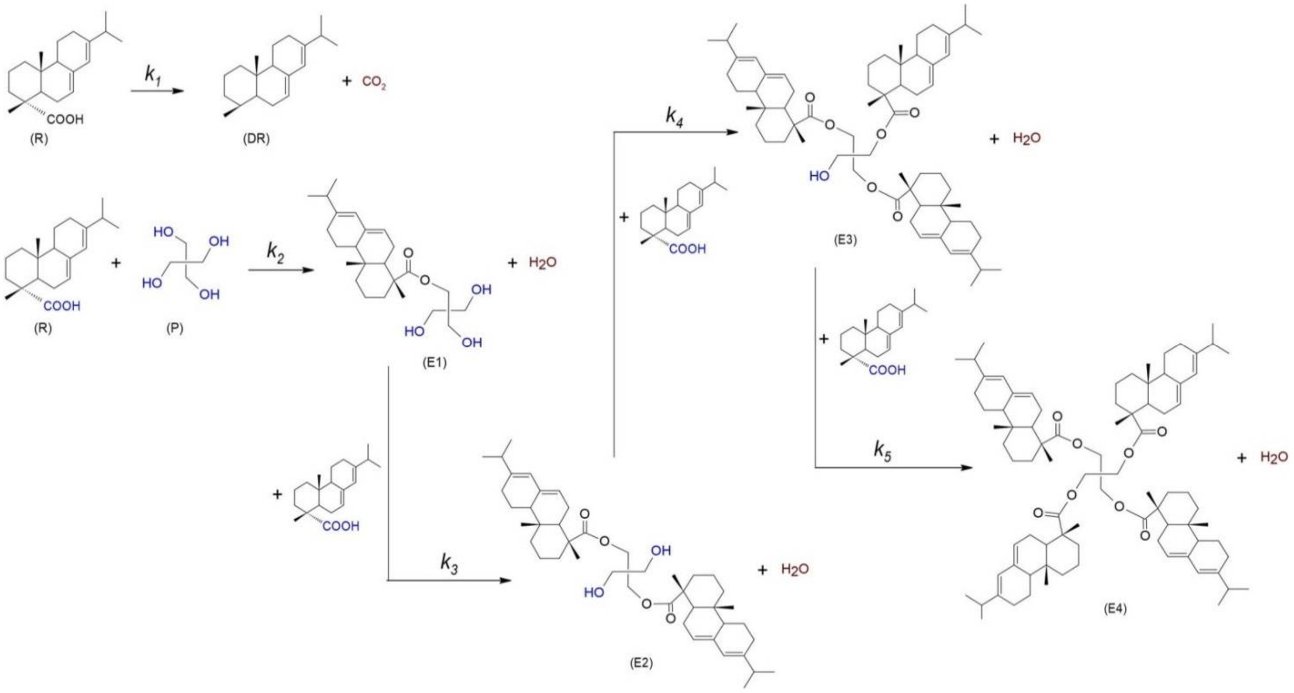


Figure 1. The reaction scheme of esterification of rosin and pentaerythritol.

The second-order reactions for esterification and first-order reaction for decarboxylation were proposed. The esterification of carboxyl acids (C_5–C_9) and pentaerythritol at the temperature range of 150 °C to 170 °C produced water. It caused a minor (not greater than 6%) decrease in the reaction volume and mass, which can be neglected in the calculation [20]. The mass of carbon dioxide from the decarboxylation of rosin also caused a minor change in the reaction mass [8]. Therefore, the mass of water and carbon dioxide were neglected in this work. The external mass transfer resistance can also be neglected at vigorous stirring speeds higher than 200 rpm [11]. Thus, in this work, the chemical reaction is assumed to be the rate-controlling step (kinetic regime). The concentration of each component was determined from the mass balance, written as follows:

$$\frac{dC_P}{dt} = -k_2 C_R C_P \tag{5}$$

$$\frac{dC_R}{dt} = -k_1 C_R - k_2 C_R C_P - k_3 C_R C_{E1} - k_4 C_R C_{E2} - k_5 C_R C_{E3} \tag{6}$$

$$\frac{dC_{E1}}{dt} = k_2 C_R C_P - k_3 C_R C_{E1} \tag{7}$$

$$\frac{dC_{E2}}{dt} = k_3 C_R C_{E1} - k_4 C_R C_{E2} \tag{8}$$

$$\frac{dC_{E3}}{dt} = k_4 C_R C_{E2} - k_5 C_R C_{E3} \tag{9}$$

$$\frac{dC_{E4}}{dt} = k_5 C_R C_{E3} \tag{10}$$

with the initial condition of

$$t = 0; C_P = C_{P0}; C_R = C_{R0}; C_{E1} = C_{E2} = C_{E3} = C_{E4} = 0 \tag{11}$$

where k_1, k_2, k_3, k_4, and k_5 respectively denote the reaction rate constants for the first, second, third, fourth, and fifth reactions; C_P, C_R, C_{E1}, C_{E2}, C_{E3}, and C_{E4} represent the concentration of pentaerythritol, rosin, mono-, di-, tri-, and tetra-ester (mol kg^{-1}); and C_{P0} and C_{R0} are the initial concentration of pentaerythritol and rosin, respectively.

The reaction rate constants were calculated according to the Arrhenius equation,

$$k_i = A_i \cdot \exp\left(-\frac{E_i}{RT}\right) \tag{12}$$

where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, T is temperature, and i = 1, 2, 3, 4, and 5.

Equations (5)–(11) are the simultaneous ordinary differential equations that can be numerically solved, e.g., using the Runge-Kutta method. The pre-exponential factor and activation energy values were estimated by minimizing the Sum of the Square of Errors (SSE) with constraints of $0 \leq k_i \leq 1$; $A_i \geq 0$; and $E_i \geq 0$. All computations were performed using Microsoft Excel.

$$SSE = \sum_{t=0}^{t=n} (AV_{cal,t} - AV_{data,t})^2 + (EV_{cal} - EV_{data})^2 \tag{13}$$

$$AV_{cal,t} = C_{R,t} \tag{14}$$

$$EV_{cal} = C_{E1} + 2C_{E2} + 3C_{E3} + 4C_{E4} \tag{15}$$

with $AV_{cal,t}$ and $AV_{data,t}$ as the acid numbers from the calculation and the experimental data at various time points, respectively, $C_{R,t}$ is the concentration of rosin at various time points, EV_{cal} and EV_{data} are the ester numbers from the calculation, and the experimental data at the end of reaction time, respectively.

The model accuracy was determined by regression analysis and the mean absolute percentage error (MAPE), which is calculated by the following equation:

$$MAPE = \frac{1}{n} \sum_{t=1}^{n} \frac{|\hat{y}_t - y_t|}{y_t} \times 100 \tag{16}$$

where n is the sample size, $\hat{y}_t$ is the value predicted by the model for time point t, and y_t is the value observed at time point t [23].

3. Results and Discussion

3.1. Characterization of the RPE

The result from Fourier-transform infrared (FT-IR) spectral analysis confirmed that the esterification of rosin and pentaerythritol occurred in this study. The peak at 3325 cm^{-1} in Figure 2 (a) is the stretching vibration mode of the OH bonds of pentaerythritol. The peak at 1134 cm^{-1} (b) is the C–O–C stretch. The peak at 1700 cm^{-1} (c) is the stretching vibration mode of COOH bonds of rosin, which shifts to 1728 cm^{-1} (C=O ester) after esterification with pentaerythritol (b). These values indicate that rosin has reacted with pentaerythritol to produce rosin ester.

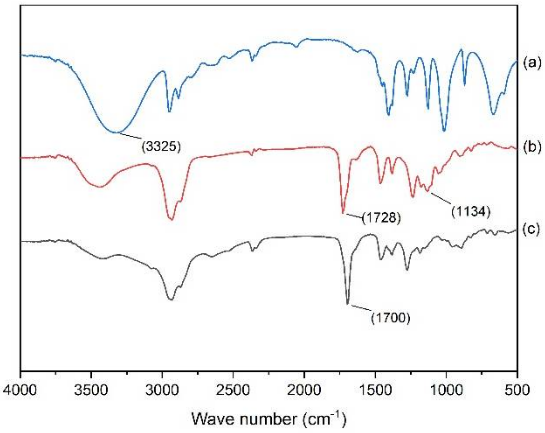
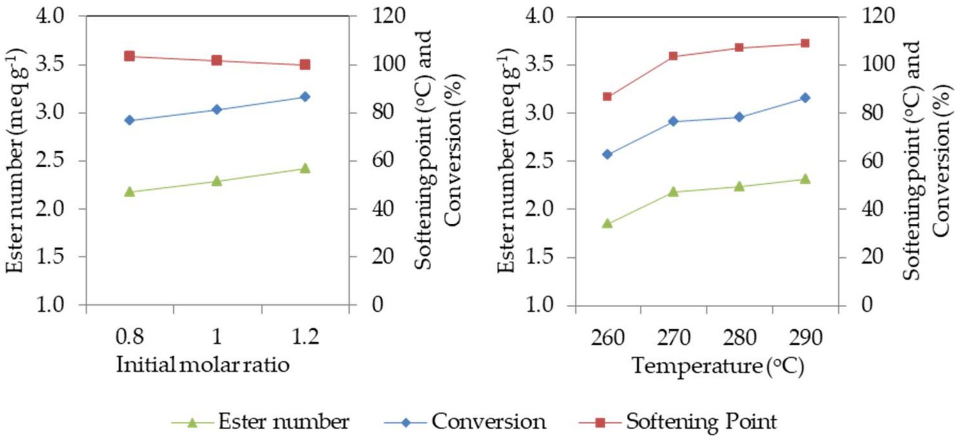


Figure 2. FT-IR spectra of (**a**) pentaerythritol (**b**) rosin ester (**c**) rosin.

3.2. The Effect of Different Conditions

3.2.1. Initial Molar Ratio of Pentaerythritol to Rosin (in the Mole of OH/COOH)

The effects of changing the initial pentaerythritol to rosin are shown in Figure 3a. From the mass balance, a pentaerythritol molecule can consume four resin acids. An excess of pentaerythritol caused a faster reaction and reached a higher conversion of rosin. The shifting of the molar ratio from 0.8 to 1.2 caused a rapidly increasing rosin conversion from 76.67 to 86.59%. This indicates that excessive pentaerythritol facilitates a higher reaction rate of rosin esterification.



(**a**) (**b**)

Figure 3. The conversion of rosin, ester number and softening point of RPE versus (**a**) molar ratio of pentaerythritol to rosin, at 270 °C and (**b**) temperature, with the ratio of 0.8 in 4 h reaction time.

One of the factors that affect the softening point is the molecular complexity [7]. In this work, the more complex the obtained ester, the higher softening point. Rosin has a softening point of 82 °C. After rosin reacted with pentaerythritol and formed a more complex molecule, tetra-ester, the softening point increased. Commercially, rosin pentaerythritol ester has a softening point specification between 95 °C and 105 °C [24]. Increasing the molar ratio from 0.8 to 1.2 had no significant effect on the softening point; it caused a minor decrease in the softening point from 103 °C to 100 °C. An excess of pentaerythritol was suspected to only speed up the reaction, which produced monoesters. Similar results were observed in the esterification of rosin with glycerol. Zhang et al. [21] found that a higher amount of glycerol increased the conversion of rosin, but lowered the softening point.

3.2.2. Temperature

Increasing temperature caused an increase in the rosin conversion, ester number, and softening point (Figure 3b). Changing the temperature from 260 °C to 270 °C caused rosin conversion to increase rapidly from 62.72% to 76.67%, and the softening point to increase rapidly from 87 °C to 103 °C. Upon changing the temperature from 270 °C to 280 °C, the conversion slightly increased from 76.67% to 78.35%, and the softening point increased to 107 °C. When the reaction was carried out at 290 °C, the conversion of rosin reached 86.37%, but the softening point only increased to 109 °C, corresponding to a minor increase in the ester number. In fact, with the ratio of 0.8, the maximum rosin conversion achieved was 80%. This indicates an increase of rosin decarboxylation at a higher temperature. Hind et al. [8] observed that the approximation of 0.03 to 0.05 mole of carbon dioxide per mole of rosin was produced during the esterification of rosin and glycerol at 285 °C to 290 °C.

3.3. Evaluations of Kinetic Model

Data-fitting was performed on all data by fitting pre-exponential factors and activation energies (in E/R value) to the experimental data by minimizing SSE. The concentration of each component was calculated by the Runge-Kutta method and minimization was conducted using Solver in Microsoft Excel. As seen in Table 1, the activation energy increases in order $E_2 < E_3 < E_4 < E_5 < E_1$. It is apparent that the decarboxylation step required the highest activation energy to break the COOH bond, resulting in the slowest reaction rate. The formation of tetra-ester consumed more extensive energy to break chemical bonds than tri-, di-, and monoester due to steric hindrances. Thus, higher activation energy is required to attack a larger atom or group. However, the reaction rate constant is determined by the activation energy and the pre-exponential factor. The pre-exponential factor increased in the order of $A_2 < A_3 < A_4 < A_5$, though, the reaction rate decreased in the order of $k_2 > k_5 > k_4 > k_3$ (Table 2). This indicates that there are collisions with insufficient energy and orientation.

Table 1. Kinetics parameters of esterification of rosin and pentaerythritol.

Ref	Reaction	A (kg mol^{-1} min^{-1})	E (kJ mol^{-1})	SSE
This work	1st	5.16×10^{18} *	233.00	0.1553
	2nd	7.07×10^{4}	65.81	
	3rd	1.82×10^{8}	107.97	
	4th	4.41×10^{9}	119.88	
	5th	5.49×10^{10}	129.13	
[11]		1.44×10^{6} **	88.867	
[22]		4.76×10^{8}	118.46	

Note: * in (min^{-1}), ** in (L mol^{-1} min^{-1}).

Table 2. Kinetic constants of esterification of rosin and pentaerythritol.

Kinetic Constant (kg mol^{-1} min^{-1})	Temperature (°C)			
	260	270	280	290
k_1	0.0001	0.0002	0.0005	0.0013
k_2	0.0252	0.0332	0.0432	0.0556
k_3	0.0048	0.0075	0.0116	0.0176
k_4	0.0079	0.0130	0.0210	0.0334
k_5	0.0122	0.0209	0.0351	0.0578

Note: k_1 (min^{-1}).

The calculated results from the proposed model for esterification at 270 °C with the ratio of 0.8 are shown in Figure 4. Comparison of the experimental data and the calculated results from both mol ratio (a) and temperature (b) variation showed that the proposed model showed good fits (Figure 5). Furthermore, the proposed model accuracy could also be measured by the coefficient of determination (r^2) which gives the value of 0.9985. The correlation coefficient (r) and the coefficient of determination (r^2) are correct measures of the model accuracy when the intercept is zero and the slope is 1 [25]. Statistically, the model can be accepted if the $r^2 \geq 0.8$ [26]. The fitted line of the acid number obtained from experimental data and the calculated results from the proposed model is seen in Figure 6a. The intercept is 0, and the slope is close to 1 (0.9995), so the regression analysis can measure the model accuracy.

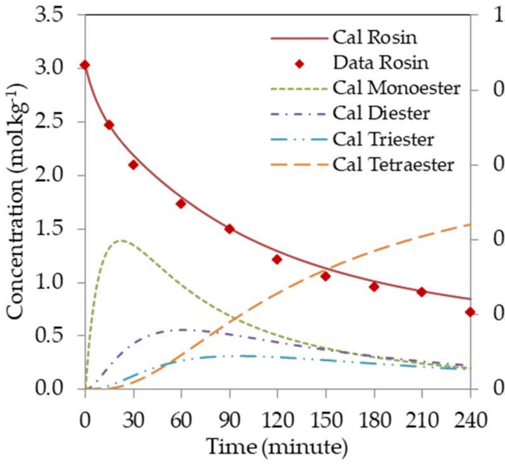
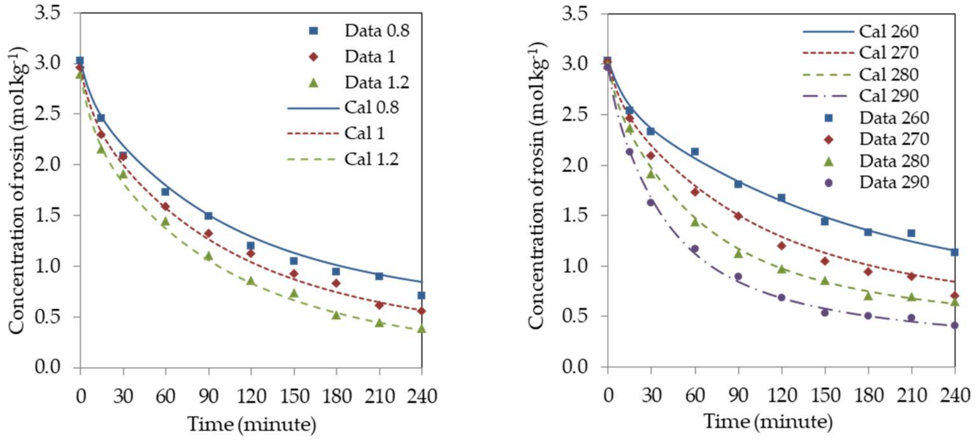


Figure 4. The evolution of calculation results obtained from the proposed kinetics model at 270 °C, with the ratio of 0.8.

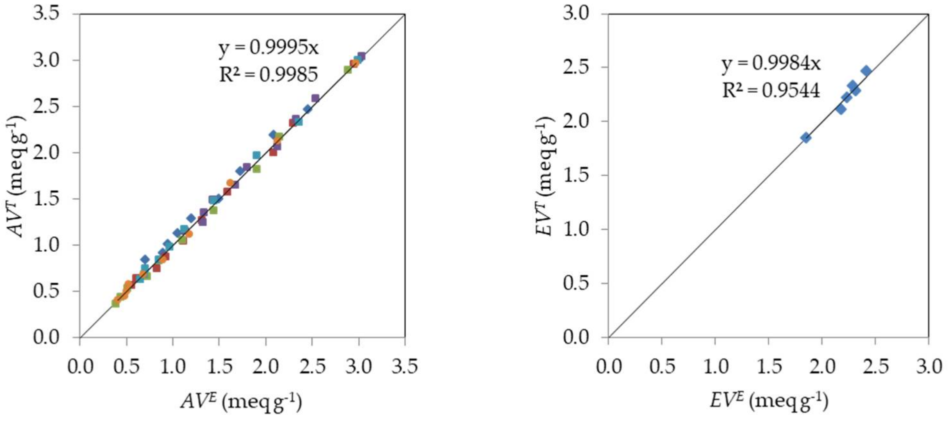


(**a**) (**b**)

Figure 5. The concentration of rosin during the reaction (**a**) at 270 °C and several initial ratios of pentaerythritol to rosin (**b**) at several temperatures with the initial ratio of 0.8.

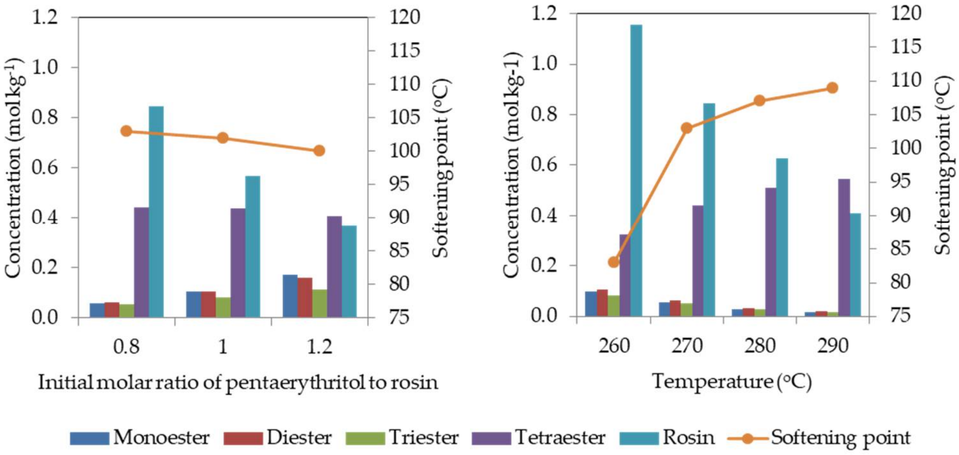
A similar result was obtained from fitting the ester number data (Figure 6b) which proved that the proposed model is fitted to the experimental data and is acceptable. MAPE is another accuracy measurement. MAPE of the acid number and the ester number are 3.5079 and 1.5645, respectively, which indicates a good agreement between the experimental data and the proposed model (MAPE < 10) [23].

It is interesting to describe the correlation between the calculated composition of ester as predicted by the proposed model and the experimental softening point data. Figure 7 shows a correlation between the softening point and the ester composition as mainly dominated by tetra-ester. As shown in Figure 7a, changing the ratio from 0.8 to 1.2 caused a minor decrease in the tetra-ester concentration which is also followed by the decrease of their corresponding softening point value. The higher concentration of tetra-ester (shown as a purple bar) caused a higher softening point. From Figure 7b, one could infer that increasing the temperature from 260 °C to 270 °C rapidly increased both the tetra-ester concentration as well as the softening point. There was no significant effect on the increase of softening point when the temperature was raised from 280 °C to 290 °C. Apparently, at a higher temperature, the decarboxylation of rosin increased, as indicated by the saponification and acid number. Again, this finding agrees well with our model prediction as shown by the high activation energy for the decarboxylation step.



(**a**) (**b**)

Figure 6. Fitting data of (**a**) the experimental acid number (AV^E) and the predicted acid number (AV^T) and (**b**) the experimental ester number (EV^E) and the predicted ester number (EV^T).



(**a**) (**b**)

Figure 7. Predicted concentration and experimental softening point (**a**) at 270 °C and several initial molar ratios of pentaerythritol to rosin (**b**) at several temperatures with the initial ratio of 0.8 in 4 h reaction time.

4. Conclusions

The kinetic study of rosin esterification with pentaerythritol has been investigated by varying mole ratios as well as reaction temperatures. Our experimental results showed that changing the initial molar ratio of pentaerythritol to rosin (in the mole of OH/COOH) from 0.8 to 1.2 had a minor effect on the softening point while increasing the temperature from 260 °C to 290 °C gave a notable increase in the softening point. However, the temperature increase from 280 °C to 290 °C, caused a minor effect to the softening point. This minor increase is due to the decarboxylation of rosin as a side reaction.

A kinetic model which describes rosin esterification with a pentaerythritol mechanism has also been proposed (Figure 1). The model consists of a reaction series that includes the formation of mono-, di-, tri-, and tetra-ester as well as the inclusion of rosin decarboxylation as a side reaction. The kinetics parameter of each reaction step was obtained which gave activation energy ranging from 65.81 to 233 kJ mol^{-1}. In general, the proposed model could capture the experimental data well both from the mole ratio and temperature variations. Additionally, our model also accurately predicts the correlation between tetra-ester formation and the softening point where a higher tetra-ester generally led to a higher softening point. Hence, the proposed model can be expected to serve as a tool for the reactor design of tetra-ester production from pine rosin and pentaerythritol.

Author Contributions: Conceptualization, M.P.W.H. and R.; Data curation, M.P.W.H.; Formal analysis, M.P.W.H.; Investigation, M.P.W.H.; Methodology, M.P.W.H. and R.; Supervision, R. and M.M.A.; Validation, R. and M.M.A.; Visualization, M.P.W.H.; Writing—original draft, M.P.W.H.; Writing—review & editing, R. and M.M.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: Financial support from Lembaga Pengelola Dana Pendidikan (LPDP) Ministry of Finance of the Republic of Indonesia is gratefully acknowledged for scholarship to M.P.W.H. We would also like to thank Gunawan Marga Widada from PT Perhutani Anugerah Kimia (PAK) Trenggalek, East Java for kind supply of materials in this work.

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

References

1. Kugler, S.; Ossowicz, P.; Malarczyk-Matusiak, K.; Wierzbicka, E. Advances in Rosin-Based Chemicals: The Latest Recipes, Applications and Future Trends. *Molecules* **2019**, *24*, 1651. [CrossRef] [PubMed]
2. Maiti, S.; Ray, S.S.; Kundu, A.K. Rosin: A renewable resource for polymers and polymer chemicals. *Prog. Polym. Sci.* **1989**, *14*, 297–338. [CrossRef]
3. Silvestre, A.J.D.; Gandini, A. Rosin: Major sources, properties and applications. In *Monomers, Polymers and Composites from Renewable Resource*; Elsevier: Amsterdam, The Netherlands, 2008; pp. 67–88.
4. Liu, S.; Xie, C.; Yu, S.; Xian, M.; Liu, F. A Brønsted-Lewis acidic ionic liquid: Its synthesis and use as the catalyst in rosin dimerization. *Cuihua Xuebao Chin. J. Catal.* **2009**, *30*, 401–406. [CrossRef]
5. Huang, Y.; Chen, X.; Deng, Y.; Zhou, D.; Wang, L. A novel nickel catalyst derived from layered double hydroxides (LDHs) supported on fluid catalytic cracking catalyst residue (FC3R) for rosin hydrogenation. *Chem. Eng. J.* **2015**, *269*, 434–443. [CrossRef]
6. Wang, L.; Chen, X.; Liang, J.; Chen, Y.; Pu, X.; Tong, Z. Kinetics of the catalytic isomerization and disproportionation of rosin over carbon-supported palladium. *Chem. Eng. J.* **2009**, *152*, 242–250. [CrossRef]
7. Board, N. *Modern Technology of Paints, Varnishes & Lacquers*, 2nd ed.; Asian Pasific Business Press Inc.: Delhi, India, 2007.
8. Hind, J.D.; Kanno, T.T.; Miner, C.S. Esters of rosin acids and glycidyl ethers. *J. Am. Oil Chem. Soc.* **1970**, *47*, 3–4.
9. Yu, S.; Zhang, H. Preparation of Rosin Pentaerythritol Ester Over an Fe_3O_4-Supported ZnO Catalyst. *Catal. Lett.* **2020**, *150*, 3359–3367. [CrossRef]
10. Pathak, Y.V.; Dorle, A.K. Study of rosin and rosin derivatives as coating materials for controlled release of drug. *J. Control Release* **1987**, *5*, 63–68. [CrossRef]
11. Ladero, M.; de Gracia, M.; Trujillo, F.; Garcia-Ochoa, F. Phenomenological kinetic modelling of the esterification of rosin and polyols. *Chem. Eng. J.* **2012**, *197*, 387–397. [CrossRef]
12. Xu, Z.; Lou, W.; Zhao, G.; Zhang, M.; Hao, J.; Wang, X. Pentaerythritol rosin ester as an environmentally friendly multifunctional additive in vegetable oil-based lubricant. *Tribol. Int.* **2019**, *135*, 213–218. [CrossRef]
13. Comyn, J. Surface characterization of pentaerythritol rosin ester. *Int. J. Adhes. Adhes.* **1995**, *15*, 9–14. [CrossRef]
14. Sarma, G.V.S.; Kumar, G.V.S.; Vijay, M.; Ramesh, K.V. Kinetic studies of esterification of butanoic acid with cyclohexanol. *Mater. Today Proc.* **2021**, *46*, 737–739. [CrossRef]
15. Chowdhury, A.; Sarkar, D.; Mitra, D. Esterification of Free Fatty Acids Derived from Waste Cooking Oil with Octanol: Process Optimization and Kinetic Modeling. *Chem. Eng. Technol.* **2016**, *39*, 730–740. [CrossRef]
16. Murad, P.C.; Hamerski, F.; Corazza, M.L.; Luz, L.F.L.; Voll, F.A.P. Acid-catalyzed esterification of free fatty acids with ethanol: An assessment of acid oil pretreatment, kinetic modeling and simulation. *React. Kinet. Mech. Catal.* **2018**, *123*, 505–515. [CrossRef]
17. Rani, K.N.P.; Neeharika, T.S.V.R.; Vardhan, G.H.; Kumar, T.P.; Devi, B.L.A.P. The Kinetics of the Esterification of Free Fatty Acids in Jatropha Oil using Glycerol based Solid Acid Catalyst. *Eur. J. Sustain. Dev. Res.* **2020**, *4*, em0116. [CrossRef]
18. Tarakcı, M.I.S.; Ilgen, O. Esterification of Oleic Acid with Methanol Using $Zr(SO_4)_2$ as a Heterogeneous Catalyst. *Chem. Eng. Technol.* **2018**, *41*, 845–852. [CrossRef]
19. Olagbende, O.H.; Falowo, O.A.; Latinwo, L.M.; Betiku, E. Esterification of Khaya senegalensis seed oil with a solid heterogeneous acid catalyst: Modeling, optimization, kinetic and thermodynamic studies. *Clean. Eng. Technol.* **2021**, *4*, 100200. [CrossRef]

20. Kopyshev, M.V.; Khasin, A.V.; Minyukova, T.P.; Khassin, A.A.; Yurieva, T.M. Esterification of pentaerythritol by carboxylic acids. *React. Kinet. Mech. Catal.* **2016**, *117*, 417–427. [CrossRef]
21. Zhang, D.; Zhou, D.; Wei, X.; Liang, J.; Chen, X.; Wang, L. Green catalytic conversion of hydrogenated rosin to glycerol esters using subcritical CO_2 in water and the associated kinetics. *J. Supercrit. Fluids* **2017**, *125*, 12–21. [CrossRef]
22. Smith, T.L.; Elliott, J.H. The kinetics of esterification of resin acids. *J. Am. Oil Chem. Soc.* **1985**, *35*, 692–699. [CrossRef]
23. Moreno, J.J.M.; Pol, A.P.; Abad, A.S.; Blasco, B.C. El índice R-MAPE como medida resistente del ajuste en la previsiońn. *Psicothema* **2013**, *25*, 500–506.
24. Duncan, D.P.; Cameron, T.B. Rosin Pentaerythritol Ester Preparation Improvement. U.S. Patent WO 4548746, 22 October 1985.
25. Li, J. Assessing the accuracy of predictive models for numerical data: Not r nor r2, why not? Then what? *PLoS ONE* **2017**, *12*, e0183250. [CrossRef]
26. Oraegbunam, J.C.; Oladipo, B.; Falowo, O.A.; Betiku, E. Clean sandbox (*Hura crepitans*) oil methyl esters synthesis: A kinetic and thermodynamic study through pH monitoring approach. *Renew. Energy* **2020**, *160*, 526–537. [CrossRef]