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Kinetic Study of the Degumming Process of Crude Turpentine Oil Using Phosphoric Acid

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ABSTRACT

Degumming, a critical preliminary step in oil refining, is crucial in removing impurities from turpentine, mainly through the acid degumming method. In this study, we investigate degumming turpentine's mass transfer and chemical reaction using phosphoric acid solutions, which provide valuable insights for real-world applications. The experiment used 100 ml of turpentine and 10 ml of 50% phosphoric acid solution at varying temperatures (40℃ to 80℃) and stirring times (0 to 120 minutes) in a stirred three-neck flask. The degumming process of turpentine follows a chemical regime, and the model provides a constant value for the mass transfer coefficient ($K_{cp}a$). The continuous reaction rate in the acid phase (k) increases with temperature. This relationship can be represented by the equation provided.

$$-\ln k = \frac{10424.9942}{RT} + 10.347$$

The equation is valid within the temperature range of 313 K to 353 K, with a coefficient of determination (R^2) of 0.9428.

1. Introduction

Indonesia is rich in natural resources, with extensive pine forests contributing to turpentine production. Two thousand twenty-two domestic and export sales reached 1,088 and 9,840 tons, respectively [1]. Turpentine, a by-product of pine resin, is widely used in industries such as paints, adhesives, and pharmaceuticals due to its valuable derivatives [2]. Additionally, superheated steam drying can be applied to resinous wood to release turpentine and prevent resin overflow during subsequent processing [3].

Purifying crude oil is essential to enhance turpentine oil's quality. Refining crude oil will eliminate unpleasant tastes, odors, and unattractive colors and extend the oil's shelf life before consumption or use as raw materials in the industry. Degumming is separating unwanted gum, which can reduce product stability when processing vegetable oils. This process is carried out by adding water, steam, or phosphoric acid. A centrifuge separates the impurities from the oil [4].

Turpentine oil, also known as spirits of turpentine, is a colorless, fast-evaporating liquid with a distinct, pungent odor. It is flammable and is obtained by distilling pine sap. The turpentine oil content in pine resin ranges from 10-17.5%, with fresh sap producing a higher percentage. The widely cultivated pine tree in Indonesia is of the *Pinus merkusii* type. Turpentine oil has historically been used as a thinner printer ink solvent, paint solvent, and metal polish. Nowadays, it is also used as an additive in the cosmetics (perfume) industry, as an insect repellent, antifungal, disinfectant, and in the pharmaceutical industry due to its high value and economic benefits [5],[6]. Derivatives

of turpentine and monoterpene from essential oils have antioxidant, antibacterial, antifungal, and anticancer properties [7],[8].

Gum is an impurity found in turpentine that makes the oil cloudy and causes precipitation. It can lead to storage problems and disrupt the oil refining process. The oil refining process typically consists of four purification stages: gum separation (degumming), free fatty acid separation (neutralization), bleaching, and odor removal (deodorization) [9]. Degumming removes sap or mucus containing phosphatides, proteins, carbon residues, carbohydrates, water, and resin. These compounds are separated in the water phase using precipitation, filtration, or centrifugation. The phosphatide components form mucus and are undesirable because they cause the triglycerides to hydrate, resulting in emulsion and darkening of the oil during storage. Phosphatides dissolved in oil can be removed by channeling hot water vapor into the oil, while those not soluble in water can be separated by adding phosphoric acid [10],[11].

The compounds in oil known as phosphatides consist of two types: hydratable phosphatides (HP) and non-hydratable phosphatides (NHP). Hydratable phosphatides can be easily separated by adding water at a low temperature of around 40°C. When water is added, phospholipids lose their ability to dissolve in oil and can be separated from it. On the other hand, non-hydratable phosphatides need to be converted into hydratable phosphatides by adding an acid solution and then neutralizing it. Typically, phosphoric acid [10],[11], and citric acid are used in degumming [12], [13],[14].

During the acid degumming process, gum is transferred from liquid phase I (oil) to liquid phase II (phosphoric acid solution). This transfer occurs when the two phases come into contact, which can be achieved in a stirred flask. The concentration gradient influences the mass transfer rate in each phase, with mass moving from high concentration to low concentration. The transfer between the two phases occurs at the liquid-liquid phase boundary. According to the two-film theory, mass transfer between phases involves three steps: mass transfer from liquid phase I to the phase boundary through the liquid phase I film, fast mass transfer at the phase boundary, and mass transfer from the phase boundary to the liquid phase II through liquid phase film II [15]. This study aimed to determine the optimal stirring time and temperature for the acid degumming of crude turpentine oil while also examining the kinetics involved in the process.

2. Research Methodology

2.1. Materials

The materials used included crude turpentine oil, standard turpentine oil (commercial), 85% technical-grade phosphoric acid solution (H_3PO_4), and distilled water. Technical-grade phosphoric acid reduced solvent costs, enabling its industrial application. Commercial standard turpentine oil was used as a benchmark to evaluate the degumming process results. The crude turpentine oil was purchased from PT. Perhutani Anugerah Kimia Trenggalek, East Java, Indonesia. Crude turpentine oil is a by-product of processing pine sap into gum resin and turpentine, as shown in Fig. 1.

2.2. Procedures

The turpentine degumming process with phosphoric acid was carried out in a stirred batch reactor equipped with a water bath to maintain the operating temperature. The equipment included a thermometer and a UV-Vis spectrophotometer to determine gum concentration.

One hundred mL of crude turpentine with 10 mL of 50% phosphoric acid in a three-necked flask. The temperature range used in the experiment was between 40°C and 80°C. The stirring speed used was 200 rpm for 30 to 120 minutes. The temperature range (40°C and 80°C) was selected to study the temperature dependence of the mass transfer rate, while the stirring speed of 200 rpm ensured consistent mixing throughout the experiment. During the process, every 30 minutes, 2 milliliter samples of the mixture were collected. The refractive index was measured with a refractometer to calculate the concentration of gum remaining in the turpentine solution.

The research data was used for a numerical evaluation to determine the mass transfer constant. A mathematical modeling mechanism determines $K_{cp}a$, K_i, and k values. Equation (1) represents the rate of change of gum concentration in the oil phase (C_{GM}) due to mass transfer across the phase boundary, while equation (2) models the gum transfer between the two phases (oil and acid), and equation (3) captures the rate of gum removal from the acid phase. The temperature functions for K_i

and *k* are obtained using the Sum of the Square of the Error (SSE) method with Matlab 2016 software. The tools fminsearch and ode15s are used in the following steps:

1. Input data used: C_{gm} (40°C, 50°C, 60°C, 70°C, and 80°C), V_m, V_b
2. Trial: $K_{cp}a$, *Ki* (40°C, 50°C, 60°C, 70°C, and 80°C), *k* (40°C, 50°C, 60°C, 70°C, and 80°C)
3. Calculate C_{gm}, C_{gb}, and C_b using equations (1), (2), (3):

$$(dC_{GM})/dt = -\alpha C_{GM} + K_{cp}a.C_{GB} \quad (1)$$

$$(dC_{GB})/dt = (\alpha C_{GM} - K_{cp}a.C_{GB}).V_M/V_B - k(C_{GB}.C_B) \quad (2)$$

$$(dC_B)/dt = -k.(C_{GB}-C_B) \quad (3)$$

4. Calculate the SSE of all
5. If SSE still needs to be at a minimum, return to step 2. If SSE was at a minimum, the calculation was complete, and $K_{cp}a$, Ki, and k were obtained for each temperature.

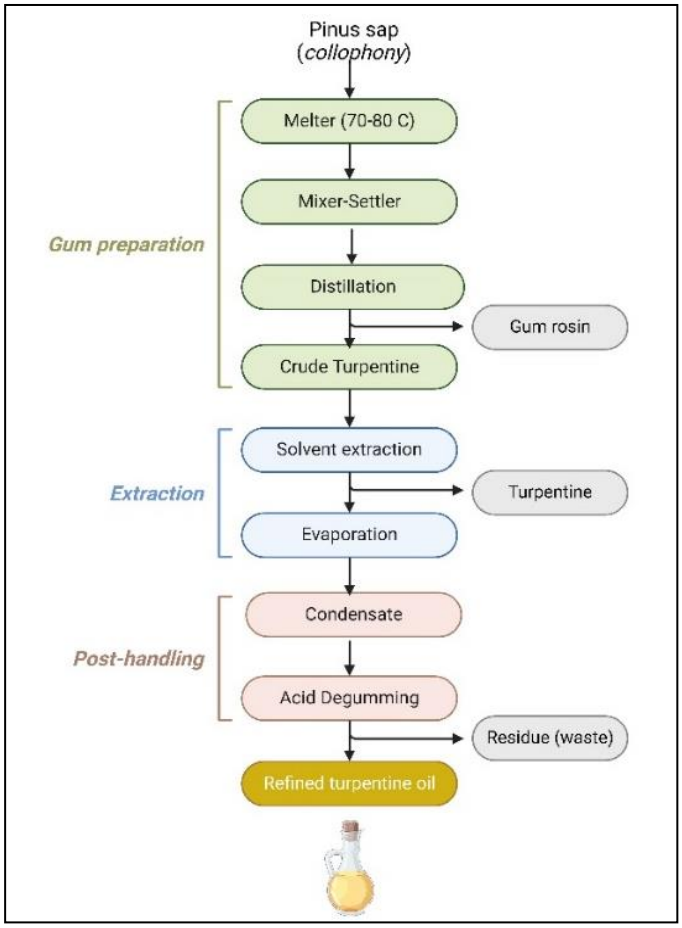

Fig. 1. Gum resin (*Gondorukem*) and Turpentine Production Process Flow Diagram. This figure was created with BioRender.com under agreement number "YZ26SJHXH4 ".

3. Results and Discussion

3.1. The effect of stirring time and temperature

Like bioactive extraction from microalgae [17],[18], determining the optimal contact time in the degumming process is crucial to enhance the efficiency of gum removal. The effect of stirring time and temperature on the degumming process has been investigated. The relationship between gum concentration in the oil phase and stirring time at various temperatures can be seen in Fig. 2.

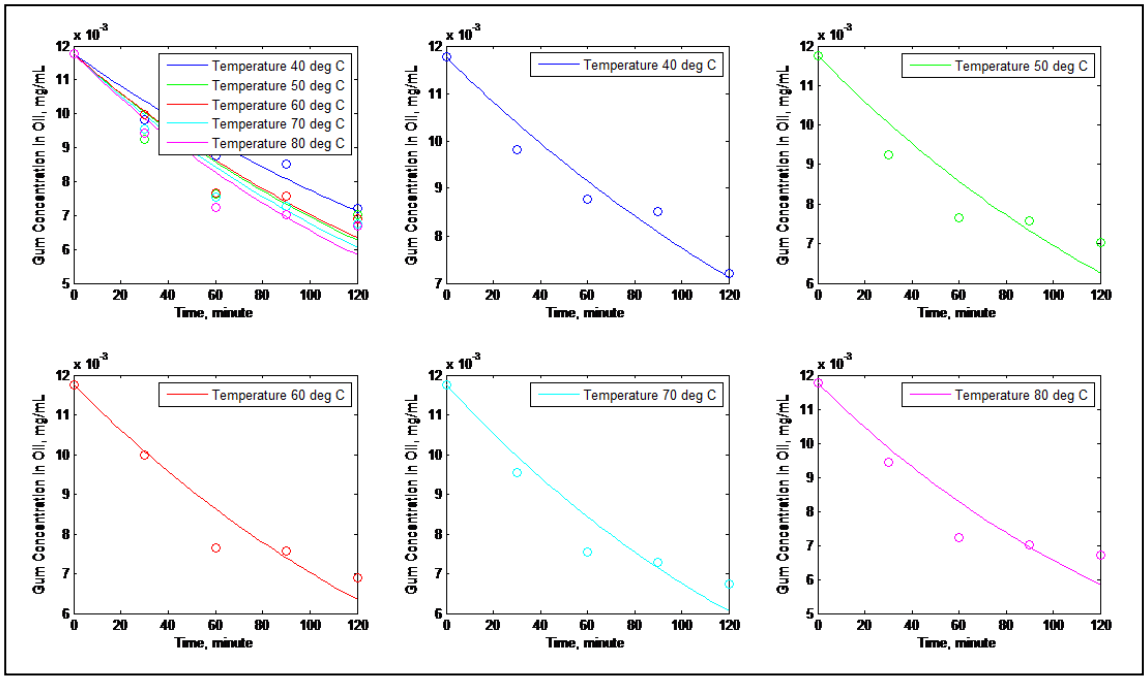

Fig. 2. Relationship between gum concentration (in the oil phase) and stirring time at different temperatures

Fig. 2. shows that the longer the degumming time, the lower the concentration of gum remaining in the oil. The higher the temperature for the same time, the lower the gum concentration will be. Figure 2 also illustrates the impact of stirring time on the degumming process. A longer contact time between crude turpentine and phosphoric acid results in more gum removal. The mixture of crude turpentine oil and phosphoric acid needs sufficient time to ensure that the gum from the oil phase is transferred to the phosphoric acid solution phase. Similarly, for bioactive components from microalgae extraction, it is crucial to determine the optimal contact time that can yield better results [17],[18],[19].

The results show that higher process temperatures led to a significant increase in the amount of gum removed. Temperature is a crucial factor in gum removal during the process and can be utilized to optimize the process for maximum efficiency. After a thorough analysis, it was determined that the optimal condition for achieving the highest yield of gum removal was at a temperature of 80°C for 120 minutes. Increasing the degumming temperature can decrease the viscosity and surface tension of the emulsion [20].

3.2. Kinetics of acid degumming

The mass transfer in this study involves three main steps: 1. Gum moves from the oil phase to the water phase. 2. Gum in the water phase reacts with phosphoric acid to form phosphate gum. 3. Phosphate gum from the water phase moves to solid gum phosphate. In the first step, the rate of gum transfer from the oil to the water phase is driven by diffusion, which increases with temperature due to lower viscosity and surface tension. In the second step, phosphoric acid facilitates the conversion of non-hydratable phosphatides to hydratable ones, and the rate of reaction increases with temperature, as reflected in the increasing values of k. The third step, where phosphate gum settles in the acid phase, is affected by temperature and stirring efficiency.

Degumming turpentine oil with phosphoric acid involves a reaction mechanism that starts with transferring gum bound to the oil phase to free gum in the phosphoric acid phase. Once the transfer is complete, the gum settles in the phosphoric acid phase. This transfer occurs when the oil and phosphoric acid phases come into contact in a stirred tank. The presence of phosphoric acid can convert non-hydratable phosphatides into hydratable phosphatides, allowing the gum to be separated from the oil [12]. In degumming crude palm oil (CPO), the optimum conditions were the use of 0.06% phosphoric acid (w/w), while citric acid is 0.04% (w/w), at 90°C for 20 min, with agitation vigorously [21]. Compared to degumming crude palm oil, which required only 0.06% phosphoric acid at 90°C for 20 minutes, turpentine oil degumming appears to require higher temperatures and longer durations, possibly due to differences in oil composition and gum structure.

The research involves varying temperatures with a stirring speed of 200 rotations per minute (rpm). One experiment was conducted for a specific duration, resulting in a single data point.

A computer program was developed using Hooke-Jeeves and Runge-Kutta minimization techniques to solve numerically. The Hooke-Jeeves method, used for optimization, and Runge-Kutta, used for solving differential equations, were employed to minimize the error between the experimental data and calculated results, ensuring accurate determination of the constants $K_{cp}a$, K_i, and k. The optimal values for the constants $K_{cp}a$, K_i, and k can be determined by minimizing the sum of squared errors (SSE) between the calculated results and the experimental data. The values of the optimization result parameters can be seen in Table 1. The increase in k with temperature, as seen in Table 1, indicates that the reaction rate accelerates with higher thermal energy, reducing the activation energy required for gum removal. The significant jump in k at 80°C suggests a threshold temperature where the degumming process becomes much more efficient.

Table 1. Optimization result parameters for degumming turpentine oil at different temperatures (Units: $K_{cp}a$ [1/min], Ki [dimensionless], k [1/min])

Component	Value				
T, C	40	50	60	70	80
Kcpa			10.6		
Ki	6.55	8.49	8.19	8.87	9.43
k	1.49E-03	3.37E-03	4.53E-03	5.47E-03	1.26E-02
SSE			1.82E-02		

From the remaining gum concentration data in turpentine oil as a function of time, a gum mass balance calculation was carried out to obtain the constant (k). Then, the value of k is evaluated as a function of temperature, as shown in Fig. 3.

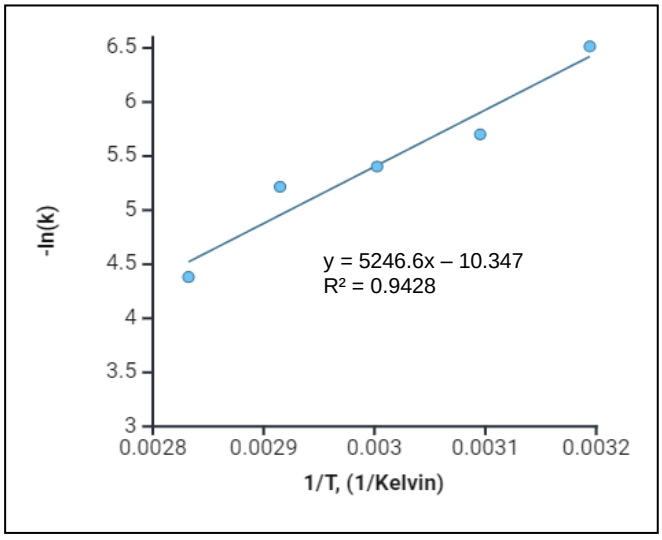

Fig. 3. Relationship between ln k and 1/T

Fig. 3. demonstrates that an increase in temperature is associated with a higher value of the reaction rate constant. According to Arrhenius' law, elevated temperatures increase reaction rates, enhancing the continuous. When the activation energy is approximately 40 kJ/mol, a rising temperature of 11°C doubles the reaction rate [22]. After performing linear regression calculations, the obtained values were (Ea/R)=-5,246.6 K, the activation energy, Ea=10,424.9942 cal/mol, and Arrhenius constant, A= exp (10.347) with an R^2 of 0.9428. The activation energy (Ea = 10,424.99 cal/mol) suggests that the energy required for gum removal is moderate, consistent with similar oil degumming processes. The Arrhenius constant (A = exp(10.347)) provides insight into the frequency of successful molecular collisions at various temperatures, further confirming the temperature dependence of the process.

Subsequently, we conducted a thorough analysis to evaluate the alignment between the observed gum concentration and the theoretical predictions. This assessment provided valuable insights into

the discrepancies and consistencies between our expected and actual data. The results of this analysis are presented in Fig. 4.

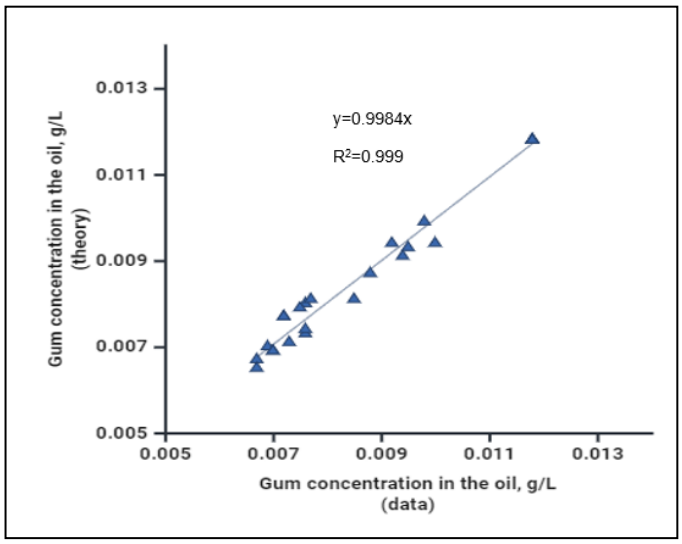

Fig. 4. Relationship between theoretical and research data gum concentration

After analyzing the data and theory in Fig. 4., the gum concentration was evaluated, yielding excellent results with R^2=0.999. The data analysis and theory presented in Fig. 4. focused on assessing the gum concentration. The results were impressive, with an R^2 value of 0.999, indicating a strong consistency between the actual data and the theoretical predictions. This research demonstrates that the acid degumming process follows a well-defined chemical reaction regime when implemented with phosphoric acid (technical grade). This process involves the removal of undesirable components from oils, enhancing their quality and making them more suitable for further refining and use.

4. Conclusion

The research on degumming turpentine waste using phosphoric acid concluded that the higher the temperature and the longer the stirring time, the purer the turpentine oil results. The best degumming conditions were at a temperature of 80 °C and a stirring time of 2 hours at a speed of 200 rpm. The degumming process of crude turpentine using phosphoric acid solution follows a chemical regime.

Notation

C_{GM} = gum concentration in the oil phase (mg/mL)
C_{GB} = gum concentration in the acid phase (mg/mL)
C_B = phosphoric acid concentration (% wt)
K_i = equilibrium constant
$K_{CP}a$ = mass transfer coefficient (1/minute)
k = the constant of the reaction rate (1/minute)
V_M = oil volume (mL)
V_B = phosphoric acid volume (mL)
ρ = density (g/mL)
μ = viscosity (kg/m.s)
N = rotation of the stirrer, rpm
D = diameter of stirrer, mm
T = Temperature (K)

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