Purification of crude turpentine oil through acid degumming using phosphoric acid

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Abstract. The production of bio-based materials is one of the accomplishments of the Sustainable Development Goals (SDGs), especially responsible consumption and production (SDG 12). One way to produce raw materials for the pharmaceutical industry is by utilizing waste from turpentine condensate. This study focused on turpentine waste derived from pine resin in the Trenggalek pine plantation area of East Java, Indonesia. Degumming is one of the preliminary treatments generally applied for oil refining, while acid degumming is a method of degumming. This research studied mass transfer and chemical reactions on the degumming of turpentine with phosphoric acid solutions. An amount of 100 mL of turpentine and 10 mL of 50% phosphoric acid solution was placed in a three-necked flask and stirred. The batch process was carried out at a temperature range of 40-80°C and stirred at 200 rpm for 30-120 minutes. Every 30 minutes, a 2 mL sample was taken from a three-neck flask to measure the refractive index and determine the gum concentration in the turpentine oil. Stirring the substance for two hours at 80°C resulted in the best gum removal at 44.9%.

1 Introduction

The circular economy makes an important contribution to achieving the Sustainable Development Goals (SDGs), especially responsible consumption and production (SDG 12). One of several strategies is regenerative, biobased production [1], and efficient use of natural resources [2]. Indonesia is a country rich in natural resources. Indonesia's forests rank third in the world. Some of the forest areas managed by Perum Perhutani are forest areas classified as pine company class. In 2022, domestic turpentine sales volume will be 1,088 tons, while abroad it will be 9,840 tons [3]. Turpentine derivative products can be processed and processed further into products that have higher sales value and usability. The turpentine processing process is carried out by tapping pine tree sap, then processing it by evaporation to collect the steam, the resulting steam when separated from the water will become

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turpentine. Turpentine derivative products can be used as paint materials, glue materials, ink materials, paper materials, and so on [4].

To improve the quality of the turpentine oil produced, it is necessary to purify the crude oil. Refining crude oil will remove unpleasant tastes and odors, unattractive colors, and extend the shelf life of the oil before consumption or use as raw materials in industry. Degumming is the process of separating unwanted gum which can reduce the stability of products resulting from processing vegetable oils. This process is carried out by adding water, steam, or phosphoric acid, then the impurities are separated from the oil, a centrifuge is carried out [5].

Turpentine oil often called spirits of turpentine is a liquid that evaporates easily, is colorless (clear), has a distinctive odor (hard), and is flammable. Turpentine oil comes from distilling pine sap. The amount of turpentine oil contained in pine resin ranges from 10-17.5%. Fresh sap will produce a higher percentage of turpentine. The pine tree that is widely cultivated in Indonesia is the *Pinus merkusii* type. Turpentine oil has long been used as thinner, printer ink solvent, printing industry, paint solvent, and metal polish, but now turpentine oil is used as an additive in the cosmetics (perfume) industry, insect repellent, antifungal, and disinfectant, as well as the pharmaceutical industry because it has more value, and high economy [6,7]. Derivatives of turpentine and monoterpene from essential oils have antioxidant, antibacterial, antifungal, and anticancer properties [8,9].

Gum is an impurity found in turpentine and makes the oil cloudy and allows precipitation to occur. This condition will cause problems during the storage process and disrupt the subsequent oil refining process. The oil refining process for edible oil generally consists of 4 purification stages which include the gum separation process (degumming), the free fatty acid separation process (neutralization), the bleaching process, and the odor removal process (deodorization) [10]. Degumming (separating gum) is the process of separating sap or mucus which consists of phosphatides, proteins, carbon residues, carbohydrates, water, and resin. These compounds are separated in the water phase so that they can be separated by precipitation, filtration, or centrifugation. The phosphatide components form mucus and are undesirable because the triglycerides will hydrate, causing an emulsion and making the oil dark during storage. Phosphatides that are dissolved in oil can be separated by channeling hot water vapor into the oil so that they are separated from the oil, while phosphatides that are not soluble in water can be separated by adding phosphoric acid [11]. Superheated steam at around 120-200°C can separate the turpentine and resin components [12]. With the addition of this water, phospholipids will lose their lipophilic properties and become lipophobic so they can be separated from the oil. Meanwhile, non-hydratable phosphatides must first be converted into hydratable phosphatides by adding an acid solution followed by a neutralization process. In general, the acids used in the degumming process are phosphoric acid and citric acid [11,13,14].

In the acid degumming process, gum mass transfer occurs from liquid phase I (oil) to liquid phase II (phosphoric acid solution). This mass transfer takes place if there is contact between liquid phase I and liquid phase II which can be done in a stirred flask. The rate of mass transfer in each phase is influenced by the concentration gradient that exists in each phase. The mass transfer will occur from high concentration to low concentration. Phase transfer between the phases of two films occurs at the liquid-liquid phase boundary. According to the two-film theory, mass transfer between phases consists of three steps, namely mass transfer from liquid phase I to the phase boundary through the liquid phase I film, mass transfer at the phase boundary which is considered to be very fast, and mass transfer from the phase boundary to the liquid phase II through liquid phase film II [15]. Up to now, there was no research has been found on the degumming of crude turpentine oil using phosphoric acid. This research aimed to study the degumming kinetics of turpentine oil and determine the regime that influences the extraction rate.

2 Material and Methods

The research materials used in the turpentine degumming process are the following crude turpentine oil (was purchased from PT. Perhutani Anugerah Kimia Trenggalek, East Java, Indonesia), phosphoric acid (H_3PO_4) solution (85%), and distilled water. Crude turpentine oil is a by-product of processing pine sap into gum resin and turpentine. During the turpentine degumming process, a specific procedure was followed to extract the impurities present in crude turpentine. This process involved mixing 100 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 a duration of 30 to 120 minutes. During the process, every 30 minutes, 2 milliliters 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 experimental procedure is shown in Figure 1.

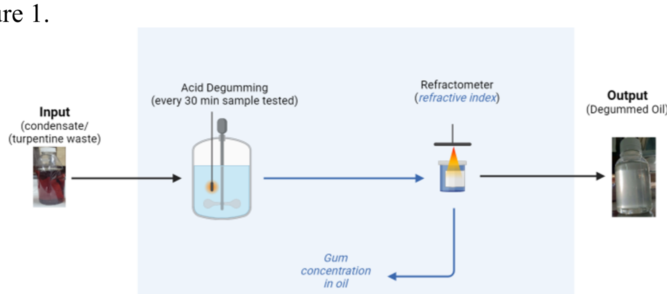


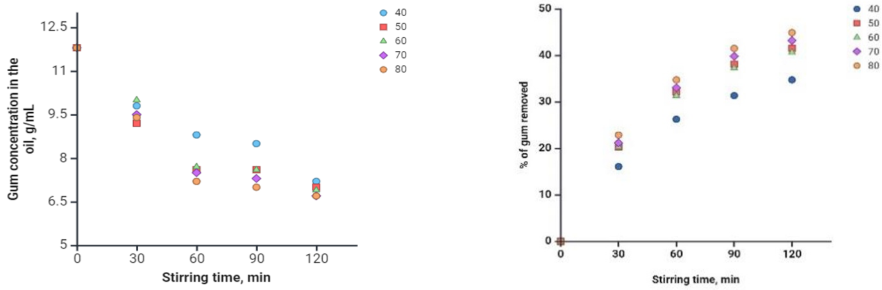
Fig. 1. Experimental procedure. This figure was created with BioRender.com under agreement number " XV26ST1350 ".

3 Results and Discussion

Mass transfer between phases in this study consists of 3 steps: 1) Gum moves from the oil to the water phase; 2) Gum in the water phase reacts with phosphoric acid to form phosphate gum, and 3) Gum phosphate from the water phase moves to gum phosphate in the solid phase. The process of degumming turpentine oil with phosphoric acid involves a reaction mechanism that starts with the transfer of gum that is 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 phase and the phosphoric acid phase 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. In degumming of 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 [16].

3.1 The effect of stirring time

The effect of stirring time on the degumming process is shown in Figure 2. Increasing the stirring time leads to a decrease in the concentration of remaining gum in the oil (Figure 2a), or increasing the percentage of gum removed (Figure 2b). "Condensate turpentine", which is also known as crude turpentine oil, has a high concentration of gum. The mixture of crude turpentine oil and phosphoric acid requires enough time to ensure that the gum from the oil phase gets transferred to the phosphoric acid solution phase. "Condensate turpentine", which is also known as crude turpentine oil, has a high concentration of gum. The mixture of crude turpentine oil and phosphoric acid requires enough time to ensure that the gum from the oil phase gets transferred to the phosphoric acid solution phase.



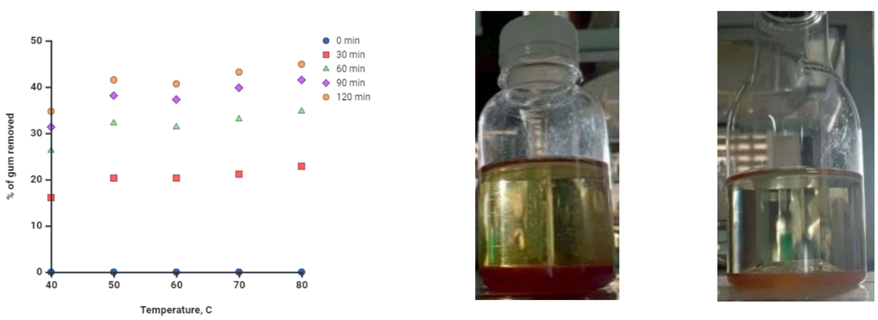
(a) (b)

Fig. 2. The effect of stirring time on gum concentration (a), and % of gum removed (b)

Figure 2 illustrates the impact of stirring time on the degumming process. The concentration of gum in purified turpentine oil (Figure 2a) is inversely proportional to the amount of gum removed (Figure 2b). A longer contact time between crude turpentine and phosphoric acid results in more gum being removed and therefore a lower concentration of gum in the purified turpentine oil. Similarly, for the extraction of bioactive components from microalgae, it is crucial to determine the optimal contact time that can yield better results [17-19].

3.2 The effect of temperature

The effect of temperature on the percentage of gum removed can be observed in Figure 3.



(a) (b) (c)

Fig. 3. (a) The effect of temperature on the percentage of gum removed, (b) Photo image of the turpentine condition after 24 hours of settling from the degumming process at 40°C, (c) at 80°C

The study found that increasing the process temperature leads to a higher amount of removed gum. After conducting a thorough analysis, it was discovered that the optimal condition for achieving the highest gum removal yield was at a temperature of 80°C for 120 minutes. With this condition, an impressive 44.9% of gum was successfully removed. The results indicated that an increase in the process temperature led to a significant increase in the amount of gum removed. This finding suggests that temperature plays a crucial role in gum removal during the process, and it could be used to optimize the process for maximum efficiency. The condition of the turpentine after settling for 24 hours from the degumming process at two different temperatures, 40°C, and 80°C, is shown in Figures 3b and 3c.

Figures 3b and 3c show that the degumming at a temperature of 80°C is much clearer than the degumming at 40°C. It shows that the temperature of the degumming process has a very significant effect on the turpentine yield. An increase in the degumming temperature can reduce the viscosity and surface tension of the emulsion (gum) [20].

4 Conclusion

Crude turpentine oil can be purified using the acid degumming method with phosphoric acid. The phosphoric acid concentration was 50%, with a ratio of acid to crude oil of 1/10 v/v. 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, with a percentage of gum taken at 44.9%.

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