Synthesis of mercaptoethyl ester of palm fatty acid distillate: 
Effects of dehydration methods

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Abstract. This research was aimed to evaluate the synthesis of mercaptoethyl ester of palm fatty acid distillate (PFAD) where water as a byproduct was removed by using vacuum distillation and azeotropic distillation. The reactions were done in a batch reactor using para-toluene sulfonic acid (pTSA) as a catalyst. The performances of the synthesis were evaluated by measuring the sulfhydryl content and yield of the product. Compared to dehydration by vacuum distillation, dehydration by azeotropic distillation gave lower sulfhydryl content and yield but faster reaction completion. Azeotropic distillation gave sulfhydryl content and yield in the range of 6–7% and 57–74%, respectively. Vacuum distillation gave sulfhydryl content and yield in the range of 7–9% and 75–85%, respectively.

1. Introduction

Mercaptoethyl ester of fatty acid (MEFA) is a raw material for the manufacture of organotin based polyvinyl chloride (PVC) thermal stabilizers. Thermal stabilizers are essential for PVC to avoid degradation during the extrusion process [1]. PVC thermal degradation is also known as dehydrochlorination since hydrochloric acid is released during the process. As a result of thermal degradation, PVC changes its color from clear to yellow, red, brown, and finally black. Along with the severity of degradation, the mechanical properties of PVC changes, and in the worst case, PVC could not be formed into the desired final product.

MEFA is produced from free fatty acid (FFA) and mercaptoethanol (ME). The common source of FFA is Tall Oil Fatty Acid (TOFA). TOFA is produced as a byproduct in the production of pulp from pine wood. It mainly comprises of unsaturated fatty acid, up to 90% of its weight consists of oleic and linoleic acid [2]. Recently, Putrawan et al. [3] found that MEFA could be synthesized from Palm Fatty Acid Distillate (PFAD), a byproduct of palm oil refining processes. As with TOFA, PFAD is also mainly composed of FFA. The reaction between PFAD and ME can be described as follows [3]:

\[
\text{RCOOH} + \text{HSCH}_2\text{CH}_2\text{OH} \rightleftharpoons \text{RCOOCH}_2\text{CH}_2\text{SH} + \text{H}_2\text{O}
\]
The important parameter for MEFA quality is sulfhydryl (SH) content. Sulfhydryl group is used as a quality parameter since this functional group will be converted into sulfur bounds which substitute allylic chlorine atoms, the initiation sites of thermal degradation of PVC bone [4].

During the reaction, the system must be dehydrated to shift the reaction toward the product side. There are several dehydration methods, including distillation, extraction, and adsorption. Based on operating pressure, distillation can be divided into atmospheric and vacuum distillations. Distillation can also be divided into azeotropic and ordinary distillations, whether it involves entrainer or not, respectively. The separation task of dehydration, in this case, is to remove water as a by-product while keeping ME in the liquid phase. The peculiarities of the separation are the small amount of water to be removed (less than 5% of the total mixture), the presence of sulfur compounds, the reaction temperature is mild, and the product is sufficiently sensitive and may decompose or polymerize at its normal boiling point. Atmospheric distillation is not appropriate to apply as removing water at the end of the reaction will boil and decompose the product. Extraction is faced with the problem of the difficulty in finding solvents that can separate water and ME which are both polar. Adsorption could not be applied since MEFA synthesis is done at temperatures significantly above room temperature. Synthesis of MEFA from PFAD is best to work at 70–80°C [3] where the adsorption capacities of most desiccants are low. Besides, most water desiccants are poisoned by sulfur compounds. Thus, only vacuum distillation and azeotropic distillation can be explored.

Vacuum distillation mentioned here is ordinary distillation which operates below atmospheric pressure. The operation at low pressure is expected to enable water vaporization at lower temperatures to prevent thermal decomposition. Both temperature and pressure can be set independently. At a determined temperature, keeping the pressure at a certain value is not beneficial because it will create an equilibrium which means that water is left in the liquid phase. Lowering pressure, however, lowers the difference in boiling temperatures between the light key and the heavy key components. Moreover, water is formed gradually during the reaction. To remove water completely, the pressure must be reduced gradually in order not to vaporize ME.

Azeotropic distillation uses an entrainer as a separating agent [5]. An entrainer forms a low boiling point azeotrope with water but immiscible with water when condensed. Two popular entrainers for water removal are benzene and cyclohexane. Benzenbaum et al. [6] performed azeotropic distillation using benzene as entrainer for the synthesis of copolymers at atmospheric pressure and temperatures up to 110°C within 1.5 hours. Azeotropic distillation has also been studied by Cane [7] at lower temperatures (60°C) to dehydrate ethanol using cyclohexane as entrainer. When an entrainer is added to the reaction mixtures of MEFA synthesis, it will bind the produced water during the reaction in the form of an azeotrope. Distilling the formed azeotrope will vaporize the azeotrope and, after condensation, separates into water and entrainer layers. The entrainer is then recycled and the dehydration cycle repeats.

Since the above mentioned two dehydration methods remove water in different ways while the effectiveness of water removal affects the reaction performance, both methods were thought to affect the reaction performance, i.e., the quality and yield of MEFA. It is the purpose of this research to study the effects of dehydration method on the quality and yield of product in the synthesis of MEFA from PFAD. The dehydration methods involved were vacuum distillation and azeotropic distillation. The synthesis was done in batch operations with para-toluene sulfonic acid (pTSA) as a catalyst. The quality of MEFA was measured as sulfhydryl content since this functional group takes an important role in stabilizing PVC.

2. Experiments

2.1. Materials
PFAD was obtained from a local palm oil refinery. Benzene (>99.7%) and cyclohexane (>99.5%) were purchased from Merck. pTSA with a purity of more than 99% was purchased from Fluka.
2.2. Procedure
For the reaction with vacuum distillation for removing water, the apparatus consisted of a jacketed beaker glass having a volume of 500 mL, a condenser, a condensate collector, and a vacuum system. The synthesis procedure referred to the previous work [3] that PFAD and ME were placed in the beaker and conditioned to the desired temperature by circulating hot water through the jacket, catalyst was added after the temperature achieved the desired value, the pressure was reduced gradually until full vacuum at 20 torr, the product was washed with water, and finally dried in vacuum. The reaction temperature was varied in the 60-90°C range.

For the reaction with azeotropic distillation for removing water, a Dean-Stark apparatus was used. The apparatus consisted of a boiling glass still with a volume of 500 mL which was connected to a condenser with a water trap at the bottom. At first, 80 g of PFAD was placed in the still. ME, entrainer, and catalyst with determined ratios were added into the still. The still was then heated using a mantle heater. After boiling, the entrainer and water vaporized as an azeotrope. The azeotrope separated into two liquid phases, i.e., water and entrainer, after condensed. Water was trapped in the water trap, the entrainer was recycled back to the still and the cycle of water removal repeated. The reaction was stopped when the water level in the water trap became constant. The product was then washed and dried.

The dehydration method affects the management of reaction temperature. For the vacuum distillation, the temperature could be set independently by controlling the hot water circulating through the reactor jacket. For the azeotropic distillation, once the entrainer-to-PFAD ratio was set, the reaction temperature was fixed by the bubble point of the reaction mixture. Each run was done twice. Excess in ME and catalyst-to-PFAD mole ratio were fixed for all runs at 10% and 1%, respectively. Acid, saponification, and iodine values were determined according to AOCS methods Cd 3d-63, Cd 3c-91, and Cd 1d-92, respectively [8]. Sulfhydryl (SH) content was determined by iodine titration [9]. IR spectra were measured using spectrophotometer Shimadzu IR-Prestige-21.

3. Results and Discussion
3.1. Characteristics of FFA and MEFA
The PFAD used had acid, saponification, and iodine values of 181 mg KOH/g, 203 mg KOH/g, and 53 g I/100 g, respectively. High acid value ensured that PFAD is mostly composed of FFAs. Analogous to MET (mercaptoethyl tallate), a MEFA derived from TOFA, MEP (mercaptoethyl palmate) is used here to name MEFA synthesized from PFAD. Figure 1 shows the IR spectra of PFAD, ME, and MEP. Because most of PFAD components are FFAs, the characteristics of PFAD spectra are the same as those of carboxylate acids which characterized by the existence of a strong broad O–H stretching band in the 3500–2500 cm⁻¹ range and the C=O stretching band at near 1700 cm⁻¹. Unsaturated FFAs have a typical peak at 3050 cm⁻¹ showing the existence of =C–H stretching band (between 3100-3000 cm⁻¹). The =C–H peak in PFAD was not very sharp because half of PFAD components are saturated fatty acid. ME was characterized by the existence of a weak –SH stretching band near 2550 cm⁻¹ and a strong broad O–H stretching band in the 3600–3000 cm⁻¹ range. It is clearly shown that the spectra of MEPs obtained using the vacuum distillation and azeotropic distillation were similar. The broad O–H stretching band is significantly reduced in MEP spectra and an –SH stretching band was found at near 2550 cm⁻¹. The spectra of MEPs using both dehydration methods were identical to that of MET. This convinced that MEPs could be synthesized regardless of the methods used to remove water as a side product.

3.2. Sulfhydryl content and yield of MEP with vacuum distillation as a dehydration method
Figure 2 shows the sulfhydryl content and yield of MEP obtained at various reaction temperatures when vacuum distillation was used to remove water. Both sulfhydryl content and yield increased with temperature. However, the increase in both performance indicators declined as temperature increased. Higher temperature increased the reaction rate. However, it also increased the volatility of ME. Higher temperature increased the possibility for ME to leave from the liquid phase where the reaction occurred. At all temperatures, a perfect reaction with a 100% yield could not be achieved. The sulfhydryl content
was also still significantly lower than the theoretical value. The theoretical value of sulfhydryl content is 9.6 with was predicted based on palmitic and oleic acids. As mentioned previously, it is due to the existence of side reactions [3], among them are the formation of thioesters [11], co-polymerizes [6], and the attachment of double bonds by ME [10].

![Figure 1. IR Spectra of FFA and MEFA.](image)

**Figure 1.** IR Spectra of FFA and MEFA.

![Figure 2. Sulfhydryl content (a) and yield (b) of MEP in vacuum distillation.](image)

**Figure 2.** Sulfhydryl content (a) and yield (b) of MEP in vacuum distillation.

### 3.3. Sulfhydryl content and yield of MEP with azeotropic distillation as a dehydration method

At first, the performances of benzene and cyclohexane as entrainers were compared. The synthesis was done at an entrainer-to-PFAD weight ratio of 3.0. The sulfhydryl contents of MEPs obtained using benzene and cyclohexane as entrainers were (6.9±0.1)% and (6.7±0.2)%, respectively. Statistical tests showed that this difference in sulfhydryl content was not significant. As explained earlier, the role of entrainer is to dehydrate the reaction mixture by forming an azeotrope with water. The azeotrope composition of water-benzene and water-cyclohexane systems are almost the same, i.e., 9%-wt water, with azeotrope temperature in the 69–70°C range [14]. For the same entrainer-to-PFAD ratio, therefore, the capacities of the entrainers are almost the same and the extents of the reactions become the same. Since benzene is known to be carcinogenic, cyclohexane is considered to be more favorable.

The effects of entrainer-to-PFAD ratio were then studied using cyclohexane as entrainer. Figures 3a and 3b show the effects of entrainer-to-PFAD ratio on the sulfhydryl content and yield of MEP, respectively. When using vacuum distillation to remove water, the reaction temperature could be
regulated independently. In contrast to the case, when using azeotropic distillation, the reaction temperature was fixed by the entrainer-to-PFAD ratio since entrainer-to-PFAD determines the bubble point of the reaction mixture. The reaction temperature observed for each entrainer-to-PFAD ratio is shown at the top of each bar in figure 3. Both sulphydryl content and yield were low at the entrainer-to-PFAD ratio of 1. It is due to the high reaction temperature at this entrainer-to-PFAD ratio. The reaction between PFAD and ME occurs in the liquid phase. At the entrainer-to-PFAD ratio equals to 1.0, the reaction temperature was high (91°C). Although the normal boiling point of ME is higher than 90°C, i.e., 157°C [13], with the existence of cyclohexane, ME starts vaporizing at 90°C. Loss in one of reactant due to distillation made the extent of reaction low. A significant increase in sulphydryl content was found when the entrainer-to-PFAD ratio increased from 1.0 to 2.0. Higher entrainer-to-PFAD ratio resulted in lower reaction temperature which could keep ME in the liquid phase. A further increase in the entrainer-to-PFAD ratio to 3.0 did not increase the sulphydryl content and yield significantly. It is due to the long reaction time necessary at this entrainer-to-PFAD ratio. The reaction times at the entrainer-to-PFAD ratio of 3.0 were 4.0 hours and those at the entrainer-to-PFAD ratios of 1.0 and 2.0 were 3 hours. Longer reaction time increased the quantity of side products which lowered the sulphydryl content and yield of MEP.

![Figure 3](image1.png)

**Figure 3.** Sulphhydryl content (a) and yield (b) of MEP in azeotropic distillation.

![Figure 4](image2.png)

**Figure 4.** Comparison of dehydration methods in sulphhydryl content (a) and yield (b).

3.4. Effects of dehydration methods on reaction performance

The performances of reaction involving the two dehydration methods in the downstream were compared in figure 4. Each point in the graph is also provided with reaction temperature. Higher sulphhydryl content and yield were obtained when water was dehydrated using vacuum distillation. Using azeotropic
distillation, there is a tendency that ME is also carried in the vapor phase since ME is soluble in benzene and cyclohexane. In other words, the azeotrope formed is, in fact, a ternary system. When the vapor phase is condensed, some ME is left in the condensate trap since it is miscible with water. This made the concentration of ME in the reaction mixture depleted, and less product is obtained. In vacuum distillation, reaction temperature could be set independently using a temperature controller. It is possible using vacuum distillation to control reaction mixture from 60 to 80°C. Using azeotropic distillation, however, the reaction mixture is fixed by the entrainer-to-FFA ratio. It is not possible to have reaction temperatures lower than the boiling point of the entrainer used. The lowest reaction temperature observed during the experiment was 78°C when using cyclohexane as an entrainer at an entrainer-to-FFA ratio of 3.0. It is a little bit lower than the normal boiling point of cyclohexane since the atmospheric pressure during the experiments was 60 to 80 mmHg lower than 1 atm. The advantage of azeotropic distillation is shorter reaction time, 3 to 4 hours. By using vacuum distillation, the reaction needed 6 hours for completion. The minimum sulfhydryl content technically required and the minimum yield of MEP to be economic as raw materials for PVC thermal stabilizer are also shown in figure 4. It could be seen that azeotropic distillation could not satisfy these requirements. On the other hand, the MEP by vacuum distillation at 70°C and 80°C could be accepted by both requirements.

4. Conclusions
Mercaptoethyl ester of palm fatty acid distillate has been synthesized using two dehydration methods: vacuum distillation and azeotropic distillation. Compared to vacuum distillation, dehydration by azeotropic distillation gave lower sulfhydryl content and yield but faster reaction completion. Azeotropic distillation gave sulfhydryl content and yield in the range of 6–7% and 57–74%, respectively, which are still lower than the minimum requirement. Vacuum distillation gave sulfhydryl content and yield in the range of 7–9% and 75–85%, respectively, and satisfied the minimum requirement.

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