A Decrease in the Number of Palm Oil Acids from Fatpit Station using The Ion Exchange Method

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Abstract

Crude Palm Oil (CPO) is a vegetable oil that contains free fatty acids. Free fatty acids (FFA) number below 5% affect the price of this commodity. This study aims to reduce the FFA in CPO from the Fatpit station using the ion exchange method by means of the anion resin Amberlite IRA 900 and Lewatit Monoplus M500. The decrease in acid number occurs due to the exchange of OH- ions in anion resins and OH- ions in the FFA constituent bonds present in CPO. The reduction process using n-hexane solvent with a ratio of 1:1, 1:2, 2:3 and 3:2. The results indicate that the resin anion via monoplus M500 is more consistent in reducing the acid level lowered by the Amberlite IRA anion resin. 900 equal to 87% with 3 repetitions. The n-hexane solvent has an effect on the process of reducing the acid number, where the optimal ratio is using a ratio of 3:2. Regeneration of anion resin does not have a positive effect on the process of decreasing the acid number. The ion exchange capacity of the resin via monolus M500 was 0.67 mL mol/g, while for Amberlite IRA 900 resin it was 0.29 mL mol/g. Decreasing the number of acids contained in CPO can use the ion exchange method by taking into account the ion exchange medium, the type of solvent and the form of the ion exchange.

Keywords: CPO, FFA, de-acidification, anion resin, n-hexane

INTRODUCTION

Coconut plantation commodities are the mainstay of Indonesia's national income and foreign exchange, which can be seen from the export value of plantation commodities where in 2015 the total plantation exports reached US $ 23,933 billion or equivalent to IDR
311,138 trillion (assuming 1 US $ = Rp 13,000). The rapid development of plantation commodities, especially palm oil processing, makes consumers set high standards for the processing of palm oil in this case known as Crude Palm Oil (CPO). During the period of 2014 crude palm oil fulfilled approximately 41.4% of the vegetable oil needs the rest of the world comes from rape seed oil, sunflower, soybean, coconut oil, peanut, and cottonseed oil [1]. One of the parameters set by consumers before buying CPO is the levels of free fatty acids or Fat Fatty Acid (FFA) contained therein. Crude Palm Oil (CPO) is a vegetable oil which has a high content of free fatty acids or FFA and high enough carotene levels, ranging from 200-500 ppm, this high carotene content causes reddish yellow crude palm oil.

Several studies carried out in order to reduce the number of acids with the aim to control the increase in the number of acids contained in oils such as adsorption using natural zeolite Lampung [2], adsorption using ion exchange resins [3], Deasidification using anion exchange resin [4-7], esterification [8-10], Transesterification [11,12]. Research to reduce acid levels is usually part of the process for manufacturing final products such as cooking oil, biodiesel or to restore the function of the product before it is used like used cooking oil.

The process of reducing the acid number using the ion exchange method with the help of anion resin can obtain optimum results. In addition to simple ways of working, the application of this system can be adapted to the processing of palm oil. The resin in this process serves to break the bond of free fatty acids by exchanging OH-ions contained in CPO with OH + ions in anion resins. The breaking of the bonds results in the process of increasing the acid number which can be controlled by factors that cause the increase in the number of acids left behind in the anion resin. In addition, the oil (CPO) which is derived by using this method has a better level of brightness than before.

MATERIALS AND METHODS

Materials

The raw material used in this study is crude palm oil with acid values ranging from 18 mg KOH/g of oil to 24 mg KOH/g of oil. The raw material is obtained from one of the palm oil mills in the province of South Sumatra. In addition to Crude palm Oil, n-hexane chemicals and resin Amberlite IRA 900 anion and Lewatit Monoplus M500 are used in the process of reducing acid levels. Before use, the resin is activated by using 4% NaOH solution to convert chloride ions to hydroxyl ions.

The use of n-hexane as a solvent in the process of reducing the number of acids with the following considerations first, n-hexane is the lightest solvent in lifting oil and volatile lift (boiling point between 65-70°C) making it easier to reflux [13]. Viscosity of n-hexane was 0.294 cP while the viscosity of CPO at an average temperature of 55°C was 23.2 cP. With a large difference, n-hexane is easier to dissolve CPO with the same composition [14].

Methods

The process of decreasing the acid number using 2 columns containing Amberlite IRA 900 resin and Lewatit Monoplus M500 with a volume of 225 mL each. Before being used the resin is activated first by using 450 mL NaOH solution which functions to replace chloride ions to hydroxyl ions. After that, do a rinse by using distilled water to clean the remaining NaOH in the resin column.

Next procedure each column containing resin with a mixture of oil and n-hexane using a ratio of 1:1. The process of flowing oil mixed with hexane is carried out from the top of the column containing the resin by placing it into a measuring flask. Open the bottom of the measuring flask slightly so that the mixture of oil and hexane in it comes out slowly and enters between Amberlite IRA 900 or Lewatit Monoplus M500 resins. To get the results of the process of decreasing the acid number, open the bottom of the column and put the result in a reagent bottle. The process ends when the mixture of oil and n-hexane is used up and nothing else comes out through the bottom of the column. When finished the acid number can be measured and the resin rinsed using 225 mL of methanol to clean the resin inside the column. Repeat until the amount of acid produced ≥ 5 mg KOH/g of oil, if achieved indicates the resin in the column is time to regenerate.

In the same way, the process of decreasing the acid number is continued by using a ratio of 2:3, 3:2 and 1:2 between oil and n-hexane. The final step is to distillation the mixture of oil and n-hexane to determine the oil recovery in crude palm oil (CPO) after the acid number has been successfully reduced.

Data Analysis

To find out the number of acids contained in crude palm oil before and after the reduction process is calculated using the equation:

\[
\text{Acid Value} = \frac{\text{mL KOH} \times X \times \text{KOH} \times 56.1}{\text{sample (gram)}}
\]  

\[
\text{mL KOH} = \text{is the amount of KOH that is used up when measuring acid numbers}
\]
N KOH = KOH normality used
Gram sampel = The number of oil samples taken
a constant = 56.1

To calculate the capacity of the ion exchange resin Amberlite IRA 900 and Lewatit Monoplus M500 is calculated using the equation:

\[
KT = \frac{\Delta \text{DAN} \times V \text{oil} \times p \text{oil}}{BM \text{ KOH} \times V \text{resin}}
\]  

\[
\Delta \text{DAN} = \text{Difference between acid numbers after and before the decline (mg KOH/g)}
\]

\[
V \text{oil} = \text{The amount of oil used in the process (mL)}
\]

\[
p \text{oil} = \text{Density CPO (0.89 g/mol) 55°C}
\]

Molecular Weight KOH = 56.09 g/mol

V Resin = The amount of resin used in the process (g)

RESULT AND DISCUSSION

The process of decreasing the acid number in crude palm oil (CPO) obtained from the fatpit station in the process of palm oil processing is carried out by the ion exchange method using Lewatit Monoplus M500 anion resin and Amberlite IRA 900. The solvent used is n-hexane with a ratio of 1:1; 2:3; 3:2; 2:1; 1:2 to oil. The catalyst used in the process of decreasing the crude palm oil acid number is Amberlite IRA 900 resin and Lewatit shown in Table 1.

Table 1. Specification Amberlite IRA 900 Resin and Lewatit Monoplus M500

<table>
<thead>
<tr>
<th>Specification</th>
<th>Amberlite IRA 900</th>
<th>Lewatit Monoplus M500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuctional group</td>
<td>Trimethyl ammonium</td>
<td>Quaternary amine, type I</td>
</tr>
<tr>
<td>Total Exchange Capacity</td>
<td>≥1.00 eq/L (Cl-form)</td>
<td>1.3</td>
</tr>
<tr>
<td>Moisture holding capacity</td>
<td>58 to 64 % (Cl-form)</td>
<td>-</td>
</tr>
<tr>
<td>Uniformity coefficient</td>
<td>≤ 1.80</td>
<td>Max 1.1</td>
</tr>
<tr>
<td>Harmonic Mean size</td>
<td>0.650 to 0.820</td>
<td>0.62</td>
</tr>
<tr>
<td>Volume Change</td>
<td>Cl- 25%</td>
<td>OH- ≤ 20</td>
</tr>
</tbody>
</table>

This acid reduction process begins by determining the type of anion resin that is most effective in reducing the acid number of the raw material used. The process is carried out by inserting the resin into the column, then oil with a high acid number is flowed into the column, after that the calculated volume is obtained and measuring the acid number.

Lewatit Monoplus M500 resin 225 mL with the same total volume is able to reduce the acid number from 18, 20, 24, 24 mg KOH g of oil to 2.1, 2.19, 3.55, 16.52 mg KOH/g of oil, meanwhile Amberlite IRA 900 resin decreases the acid number with a result of 1.59, 1.21, 12.87, 12.65 mg KOH/g oil.

Based on Figures 1 and 2, the decrease in acid number when seen from the percentage decrease, the Amberlite IRA 900 resin is superior because it can reduce acid number up to 92% while the Lewatit Monoplus M500 resin percentage reduction is only 87%. When viewed from the endurance in decreasing the acid number of Lewatit Monoplus M500 resin, it can last up to 3 decreasing cycles before regeneration is better than Amberlite IRA 900 resin which only reaches 2 decreasing cycles.

The difference in results is due to, first the total exchange capacity value for Amberlite IRA 900 ≥ 1.00.
for resin passing through monoplus M500 at least 1.3 eq/L. Besides that the thing that affects the process of decreasing the acid number is the volume change where for Amberlite IRA 900 resin is ≤ 25% while for Lewatit Monoplus M500 resin is max 20%. This figure shows the large capacity of the resin to exchange ions after activation in order to reduce the acid number. The greater the volume change value, the greater the opportunity to exchange OH ions in Crude Palm Oil (CPO).

Second, the value of Harmonic mean size for Amberlite IRA 900 resins is 0.650 mm to 0.820 mm while for Lewatit Monoplus M500 resins is 0.620 mm. With the smaller size of the resin making the cross-sectional area larger so that the process of decreasing the acid number becomes longer. This causes the Lewatit Monoplus M500 resin to have a longer down cycle than the Amberlite IRA 900 resin.

In a study conducted by Maddikeri [3] the process of adsorption in removing fatty acids using ion exchange resins where the process is the interaction between hydrogen from the acid group with the exchange of electrons derived from the resin used (Indion 810, Indion 850 and Indion 860). Indion 860 has a greater adsorption capacity compared to Indion 810 and Indion 850 because of the total indion exchange capacity of 860 4.2 mol/kg dry resin. This is in line with research conducted to reduce the acid number of CPO, where the total capacity exchange of Lewatit Monoplus M500 resin is 1.3 eq/L while the Amberlite IRA 900 resin is 1 eq/L.

Figure 3 illustrates the relationship between the ratio to the decrease in Crude Palm Oil (CPO) acid value with an initial acid number of 24 mg KOH/g of oil which is divided into 4 cycles.

The lowest ratio in reducing acid number is in the ratio of 3:2. In this condition the use of hexane is the least compared to the others but is able to produce optimal results and can last up to 3 cycles with stable results. In this condition, hexane can play a role in which its function is to dissolve the oil to be flowed into the resin, the fatty acids contained in the oil can be bound to the optimum by the resin so as to reduce the acid number properly.

Different with 1:2 ratio, this composition is the greatest use of hexane. It could be that this condition makes the hexane dissolve too much oil so that the fatty acids contained in the oil are not bound by the resin. It is natural that this ratio has a longer cycle because the resin workload is lighter at this ratio.

In a study conducted by Hadiah [5], the process of decreasing acid numbers by deacidification method using a ratio between hexane and raw materials was 1:1. The results obtained by using this comparison can reduce the number of acids derived from Kapok Seed Oil (AV 18.12) Bagilumbang (AV 13.20), Candle nut Oil (AV 10.80) to 0.5.

After each ratio is unable to reduce the acid number to < from 5 mg KOH/g of oil, regeneration is carried out to restore the ability of the resin in ion exchange by using a 4% NaOH solution at 40 °C. The regeneration process is carried out by flowing 4% NaOH solution into the column containing the resin, functioning to replace OH-ions on the resin surface.

In a study conducted by Partuti [15], in which resins that have been regenerated can be used again for further ion exchange. The higher the concentration the faster ion exchange time. According to Saroso [16], the resin regeneration process is very influential by paying attention to the purpose of the ion exchange itself. Tonnage greatly influences whether the resin can provide maximum results after the regeneration process is complete.
performed. This could be related to the regeneration process which emits soap scum for all ratios which should not have happened. This can be interpreted that there is still residual oil attached to the oil surface resulting in a decrease in the ability of ion exchange in decreasing the acid number.

In the process of decreasing the number of acids there is a breakdown of fatty acid bonds to break the cycle of the formation of fatty acids. The severed ties are actually contaminated oil, causing a decrease in the volume of palm oil which has reduced acid levels. Figure 5-8 shows the volume of oil obtained after the process of decreasing the number of crude oil in each ratio used from cycle 1 to cycle 4.

Figure 5. Oil Recovery Ratio 1:1

Figure 6. Oil Recovery Ratio 2:3

The ratio with hexane composition more than oil such as Figure 6 and Figure 8 get the volume of oil, this happens because the process of decreasing the acid number through the sidelines of the resin is smoother and can be quoted entirely. Inversely proportional to Figure 5 and Figure 7, the resulting volume of oil is obtained less in the same cycle because not all of the oil is dissolved in hexane so that when it passes through the resin OH-ion exchange does not occur, but also other substances that come attached to result in reduced capacity resin in ion exchange.

Figure 7. Oil Recovery Ratio 3: 2

Figure 8. Oil Recovery Ratio 1:2

To find out the ion exchange capacity of Amberlite IRA 900 and Lewatit Monoplus M500 resin, a decrease in acid number was measured by stirring the resin and oil with a constant rotation and varying the sampling time. Tables 2 to table 5 were measured for ion exchange capacity using oil with an acid number of 20.84 mg KOH/g of oil with a rotation of 40 rpm and a resin volume of 5 g.

The capacity of ion exchange at 5 minutes can be seen in Tables 2 and 3 where the ion exchange capacity for Lewatit Monoplus M500 resins is 0.68 mL mol/gr while for Amberlite IRA 900 resins the ion exchange capacity is 0.45 mL mol/gr. Because the reduction process is not visible, the sampling time is changed to 2 minutes as shown in Tables 4 and 5. The results of the change in time result in an exchange capacity for Lewatit Monoplus M500 resin of 0.67 mL mol/g while Amberlite IRA 900 resin 0.05 mL mol/g.
### Table 2. Measurement of Ion Exchange Capacity in Monoplus M 500 Lewatit Resin with a Time of 5 Minutes

<table>
<thead>
<tr>
<th>No</th>
<th>Minute to</th>
<th>AA End (mg KOH/g of oil)</th>
<th>Δ Decline (mg KOH/g of oil)</th>
<th>Ion Capacity (mL mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>18.3</td>
<td>2.54</td>
<td>0.48</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>17.26</td>
<td>3.58</td>
<td>0.68</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>17.20</td>
<td>3.64</td>
<td>0.69</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>17.13</td>
<td>3.71</td>
<td>0.71</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>17.06</td>
<td>3.78</td>
<td>0.72</td>
</tr>
</tbody>
</table>

### Table 3. Measurement of Ion Exchange Capacity in Amberlite IRA 900 Resin with a Time of 5 Minutes

<table>
<thead>
<tr>
<th>No</th>
<th>Minute to</th>
<th>AA End (mg KOH/g of oil)</th>
<th>Δ Decline (mg KOH/g of oil)</th>
<th>Ion Capacity (mL mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>19.49</td>
<td>2.38</td>
<td>0.45</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>19.06</td>
<td>2.82</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>19.45</td>
<td>2.43</td>
<td>0.46</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>19.25</td>
<td>2.62</td>
<td>0.50</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>19.40</td>
<td>2.47</td>
<td>0.47</td>
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</table>

### Table 4. Measurement of Ion Exchange Capacity in Monoplus M 500 Lewatit Resin with 2 Minutes

<table>
<thead>
<tr>
<th>No</th>
<th>Minute to</th>
<th>AA End (mg KOH/g of oil)</th>
<th>Δ Decline (mg KOH/g of oil)</th>
<th>Ion Capacity (mL mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>14.04</td>
<td>8.42</td>
<td>0.67</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>14.13</td>
<td>8.33</td>
<td>0.66</td>
</tr>
</tbody>
</table>

### Table 5. Measurement of Ion Exchange Capacity in Amberlite IRA 900 Resin with 2 Minutes

<table>
<thead>
<tr>
<th>No</th>
<th>Minute to</th>
<th>AA End (mg KOH/g of oil)</th>
<th>Δ Decline (mg KOH/g of oil)</th>
<th>Ion Capacity (mL mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>18.81</td>
<td>3.65</td>
<td>0.29</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>18.58</td>
<td>3.88</td>
<td>0.31</td>
</tr>
</tbody>
</table>

### CONCLUSION

The percentage decrease in acid number for Amberlite IRA 900 Resin (92%) is greater than that of Lewatit Monoplus M500 resin (84%) with 2 cycles of decrease in acid acid Amberlite IRA 900 resin and 2 Lycelet resin in Lewatit Monoplus M500 resin. The regeneration process carried out on both types of resins did not cause a positive effect. However, the ratio of oil to hexane which has economic value is at a ratio of 3:2 where this ratio is able to reduce the number of acids with a consistent rate of 2 mg KOH/g of oil for 3 times the decline atayu cycle. To get optimal results in reducing the acid number after regeneration, it is recommended that the regeneration process uses a backwash system so that all solids that can interfere with the ion exchange process on the resin surface are lost.

### REFERENCES


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