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Deacidification of palm oil mill effluent using anion exchange resin

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ABSTRACT

This paper described the method to deacidify Palm oil mill effluent (POME) by substituting FFA contents to anion from exchange resins (Dowex Marathon A and Lewatit MP500). The deacidification was conducted in a fixed bed column reactor using two different effluents, collected from factory fat pit and cooling pond. Furthermore, the acid values were evaluated to calculate the quantity of FFA content. After deacidification, the acid values of POME from the two sources were lower than 1 mgKOH/g oil and with brighter color.

1. Introduction

Indonesia is the largest producer of palm oil in the world, as shown by its export figures and increasing large growing areas for palm plantation. For example, in 2018, the country produced 43,000,000 metric tons of palm oils and 55.5% were exported. Furthermore, it has been estimated that by 2020, palm oil plantation will cover approximately 12 million hectares after it has been found to be producing 35% of the world's palm oil in 2012, with India and China being the biggest importers.

The rapid development of plantation commodities in Indonesia, especially palm oil processing, has made consumers set high standards for the Crude Palm Oil (CPO) produced. About 41.4% of vegetable oils consumed in 2014 were originated from palm oil, surpassing other types such as rapeseed, sunflower, soybeans, coconut, peanuts, and cottonseed oils.

However, the CPO must adhere to many standards, including level of free fatty acid (FFA) composition because its high percentage is undesirable, as well as high carotene content which is around 200–500 ppm and causing reddish yellow crude palm oil. High FFA in CPO is due to several factors, such as:

- Overcooking in palm oil bunches processing.
- Untreated bunches in processing plants cause damages to litter which results in the breakdown of cell walls containing oil, therefore, the lipolytic enzyme (lipase) found in the protoplasm hydrolyzes the fat while releasing acid and forming FFA.
- The cleanliness of the processing plant is not maintained properly.

The most common practice implemented in lowering the FFA content in palm oil is through blending and this involves the mixture of CPO with high FFA level (>5%) with those with low level (<=4%). This process requires effective supervision in order to obtain the desired FFA level because CPO containing high level of FFA is stored in the residual tank and cannot be properly utilized.

Palm oil generates some undesirable by-products, especially POME which is formed from processing such as extraction, washing, and clarging. The by-product is the largest with a colloidal suspension containing 95–96% water, 0.6–0.7% of oil and fat, and 4–5% of total solids by Otti et al. [12]. It is a thick liquid, brownish in color, has a discharged temperature between 80 and 90 °C, and fairly acidic with a pH value of 4.0–5.0. Furthermore, improper management of POME and other solid wastes may rapidly deteriorate the surrounding environment. Hence, there is an urgent need for a sustainable management system to mitigate them.

POME was collected through a fat pit and cooling pond, however, the only components that could be recovered were oils and fat. The oil layer from the fat pit was separated and pumped back

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to the residual tank and due to the high FAA concentration, it cannot be reused directly. The POME was further transported into the cooling pond where it is allowed to react aerobically and the oils and fats contained were extracted and re-utilized. This material has a higher FFA content which must be reduced; therefore, an effective method is needed.

CPO with high FFA (more than 3.50% standard grade) is only traded in the local market. Furthermore, the availability of many companies in Indonesia producing with this grade leads to the saturation of the local CPO supply, and consequently, shortage in the global market. Furthermore, the saturation reduces the local price while the price for the global market rises due to lack of supply. Therefore, companies producing only low-grade CPO suffer more losses, while those with high grade benefit greatly.

Eychenne and Mouloungui [5] discovered that there is possibility of reducing the High FFA content in CPO through the use of alkalis, alumina treatment, distillation under vacuum condition, esterification, solvent extraction by Pirola et al [13], Rodrigues et al [14], Goncalves et al. [7], membrane system by Firman et al [6], Azmi et al [1], and Charanyaa et al. [3], and enzymatic amidation by Wang et al. [17]. Distillation is considered the most effective method to neutralize vegetable oils with high acidity, however, this operation is energy intensive. Moreover, Salam et al. [16] indicate that heating oil to high temperature under reduced pressure generates secondary reactions that alter their physicochemical characteristics and organoleptic properties. Furthermore, pretreatment with alkali prior to membrane filtration resulted in a very high reduction (ca. 90%) of FFA in the processed oils by Salam et al. [16]. These approaches, however, lead to high refining loss when applied to high-FFA oils.

Recent works from Eychenne and Mouloungui [5], Kitakawa et al [8,9,10], Russbueldt and Hoelderich [15], and Boffito et al. [2] have focused on utilizing ion exchange resins as adsorbent to remove FFA content, which simultaneously serves as catalyst for transesterification and esterification of several different raw oils. This operation was performed in a fixed bed or continuous stirred reactor because ion exchange resins can be employed in the either aqueous or non-aqueous system. Cation exchange resin acted as a catalyst in the esterification of the FFA, while anion-exchange resin catalyzes transesterification of triglyceride.

There are some resins utilization in the past, such as anionic Diaion PA306S and cationic Diaion PK208LH by Kitakawa et al. [9,10], anionic Amberlite A26 and A27 and cationic Amberlite 15 by Russbueldt and Hoelderich [15], Lewatit MP500, MP500A and MP600 by Eychenne and Mouloungui [5], acidic ion-exchange resin EBD-100, EBD-200 and EBD-300 Russbueldt and Hoelderich [15], Amberlite A15d (A15) and A46w (A46) by Boffito et al. [2]. Several triglycerides and diglycerides in the crude oil can be converted to fatty acid methyl ester by transesterification using anion-exchange resin catalyst; the remaining FFA in the solution can also be removed by adsorption on the same anion-exchange resin by Kitakawa et al. [9]. Therefore, Kitakawa et al. [10] not only the FFA but also the water contained in the feed oil was removed from the effluent by the adsorption on the anion-exchange resin. The anion-exchange resin with a lower cross-linking density and a smaller particle size was found to have produced a high reaction rate and high conversion by Kitakawa et al. [8].

The aim of this work therefore was to decrease acid value from palm oil waste obtained from the fat pit and cooling pond (with acid value greater than 18 mg KOH/g minyak) by deacidification. This process was conducted in a fixed bed column containing Dowex marathon A and Lewatit MP500 anion exchange resins to obtain palm oil with FFA less than 3.5 mg KOH/g oil. From the research mentioned above, there has been no research on the deacidification of palm oil waste using ion exchange, but Eychenne and Mouloungui [5], shown that Lewatit MP 500A gave excellent results in esterification of trimethylopropane (TMP) and erucic acid both fixed-bed and stirred reactors, the yield was between 87 and 99%. So, Lewatit MP 500A MP 500A has the potential as an ion exchange resin to reduce the levels of free fatty acids in palm oil waste. While Dowex marathon A resin is a high capacity, gel type 1, strong base anion exchange resin of uniform bead size distribution. It is a based on a styrene-divinyl benzene copolymer matrix with quaternary ammonium functional groups. Dowex marathon A resin is specifically designed to give high throughput and economical operation in both water and non-water applications. So, it is probable if dowex marathon A has the potential as an ion exchange resin in the deacidification process of palm oil waste.

2. Experimental

2.1. Materials

Two different samples were obtained from a crude palm oil industry in South Sumatera Indonesia. First Crude Palm Oil Waste sample was taken from the cooling pond (CPOW-CP) with high acid value (more than 35 mg KOH/g). The second sample was from the fat pit (CPOW-FP) with an acid value higher than 15 mg KOH/g. CPOW-CP was extracted from POME cooling pond using n-hexane. Dowex marathon A and Lewatit MP500 were used as active anion exchange resin.

The resins need to be activated by two-phase washing before being utilized. At first, they were supplied into the 2-bed volume of sodium hydroxide 4% at 40 °C at a flow rate of 1 L/hr to displace the chloride using hydroxyl ion. After this first washing, the resins were subjected to a 2-bed volume of water at a flow rate of 1 L/hr to eliminate remaining sodium hydroxide. The detailed physical properties of the different ion exchange resins are shown in Table 1.

2.2. Deacidification trial

Deacidification was performed using a column packed (d 50 mm and h 500 mm) with 1-liter resin at an average temperature of about 40 °C. Fatty oil and n-hexane were mixed in three variations of 2:3, 3:2, and 1:1 and each of them was supplied with a constant flow rate from the top of the column. The product obtained was separated from n-hexane by distillation and after the deacidification, resins were rinsed using methanol to eliminate FFA contaminant and regenerated using the same process as the activation method.

The CPOW sample obtained was very viscous, therefore, n-hexane solution was used to dissolve the oils in order to decrease the viscosity. This was important because lower viscosity produces good contact between fatty oils and resin, consequently, enhancing

Table 1
Physical Properties of the Resins.

Properties	Type of Resin	
	Dowex Marathon A	Lewatit MP500
Physical form	White to amber translucent beads	beige, opaque beads
Matrix	Styrene-DVB	Crosslinked Polystyrene
Functional group	Quaternary amine	quaternary amine type I
Total exchange capacity	1.3 eq/L (Cl-form)	1.1 eq/L(Cl-form)
Particle Size Uniformity coefficient	1.1 mm	0.62(±0.05) mm
Harmonic mean size	0.575 ± 0.050 mm	–

the deacidification process. However, the N-hexane was regenerated by distillation and could be reused for subsequent deacidification.

2.3. Analysis

The acid value was analyzed through the use of an acid-base titration method. This was conducted by transferring a half gram of sample into a conical flask containing 50 mL of neutralized ethanol and chloroform (1:1). The mixture was titrated with KOH (1 N) in ethanol to determine the acidity of the solution with the utilization of Phenolphthalein indicator to indicate titration endpoint when the solution turned from colorless to pink. These experiments were repeated at least two times to check the reproducibility of the obtained results.

3. Results and discussion

Reduction of FFA content in POME through ion exchange was observed when positively charged ion in FFA was swapped with negatively charged ion from anionic resins. This deacidification result for CPOW-FP using Lewatit MP500 resin could be examined in Table 2.

The process successfully lowered the acid value (AV) of all fatty oil to 0.5 mg KOH/g. The FFA was bound to the hydroxyl ion of the resin and separated by rinsing the resin with methanol. Even without regeneration, the resin still yielded AV oils for the next three batches albeit only in low composition. Lewatit MP500 used in this study was in hydroxyl form which is more enlarged than chloride form and thus has a higher contact surface area. Lewatit MP 500, apart from its ion exchange capacity, is also prominent for its effective adsorption and desorption of naturally occurring organic substances. Its performance was, therefore, not related to the nature of its functional groups, particle size, or ion exchange capacity, but appeared to be more founded on its adsorbing capacity action by Otti et al. [12].

Percent yield obtained between 85 and 87% by using column with d 50 mm and h 500 mm (h/d 10), similar with Eychenne and Mouloungui [5] on the use of columns with d 25 mm and h 200 mm (h/d 8). But by using column with d 30 mm and h 450 mm (h/d 15), Eychenne and Mouloungui [5] managed to achieve a yield of 99%. The greater the ratio of h/d, the greater the yield produced.

The effect of n-hexane on deacidification CPOW-FP using Dowex Marathon A resin before and after regeneration is shown in Table 3-4.

It was, however, found that CPOW-FP with initial acid value 24.24 mg KOH/g oil can be downgraded successfully using Dowex Marathon A resin (oil hexane ratio 1:1) up to more than 90%, with an acid value below 3.5 mg KOH/g oil even after the 4th batch. In the 5th batch, the value only reached 4.56 mg/g of oil or reduced by 81.17%. This was used as a regeneration indicator because the value obtained was more than 3.5 mg KOH/g oil. Therefore, a regenerated resin was employed for further deacidification for two batches. Meanwhile, when hexane composition was lowered (oil: n-hexane = 3: 2), the initial resin was effective until the third batch, while the regenerated resin was effectively utilized for another batch.

Table 2
Results of CPOW-FP Deacidification in Packed Bed Column with Lewatit MP 500.

Batch	AV before process	AV after process	Yield[1]
1	18.84	2.8	85.14
2	20.41	2.91	85.74
3	23.03	2.92	87.32

[1] The yield represents the efficiency of the deacidification and was calculated as: Yield = 100 − (final AV / initial AV) × 100. AV, acid values.

Both resins, Lewatit MP500 and Dowex Marathon A are macroporous ion exchange resins characterized by a large internal surface area, good mechanical stability, high chemical resistance, and ability to bind large organic ions. Therefore, the adsorption takes place due to the interaction between the pair of electrons on the nitrogen group of the resin and the hydrogen atom of the acid. Initially, Maddikeri et al. [11] find that an enhanced quantum of pair electrons of the nitrogen group of resin is present for possible interaction with the hydrogen of the acid group. However, Lewatit MP500 resin only has the ability to reduce FFA by 85%, while Dowex Marathon A resin has the ability to reduce FFA by more than 90%. Therefore, it is safe to conclude that Dowex Marathon A resin has more potential for expansion.

However, the performance of the resin decreased with the number of batches. This can be associated with the number of ions exchanged with FFA in the first batch causing the reduction of active ions in the resin for the next batch. It was also caused by some of FFA which remains bound to the resin even though it has been washed by using methanol to decrease the absorption of FFA compared to the previous batch.

The resin was saturated in order to decrease the binding power and cause the bondage of fewer FFA to its ions. However, those that cannot be bound were returned to the oil and found to have caused the declining quality of the oil in the next batch. The resin might also become less effective due to methanol washing and regeneration flow conducted co-currently with deacidification flow which caused the residual FFA to inhibit the next adsorption process. Therefore, backwash regeneration would be considered more effective.

Table 5 lists the result of WCPO-CP deacidification process with Dowex Resin and variation of oil: hexane ratios. The deacidification yield showed Dowex marathon A to have had higher activity than Lewatit MP500 and very effective even with raw materials with very high AV (more than 35). Therefore, it can be concluded that higher oil: hexane ratio leads to a greater decrease in acid value.

However, in contrast to the use of Dowex Marathon A and Lewatit MP500 resins, where the flow rate output of oil and n-hexane was slow, Amberlite IRA 900 has the ability to produce a higher flow rate output, thereby, making the overall deacidification process faster. It is also possible to employ the Amberlite resin in the deacidification of WCPO-CP with an acid value of 70 mg KOH/g oil to produce a value of 14.4 mg KOH/g oil in one flow and 1.1 with two flows. Contrarily, the utilization of Dowex Marathon A in WCPO-CP with the same acid value gave lesser output.

The deacidification of WCPO with an acid value greater than 40 mg KOH/g oil no longer becomes effective with the ion exchange method, because the process runs very slowly, and much of the oil produced remain in the resin. This accumulation of oil caused the resin to regenerate faster especially with more methanols when washing. Therefore, washing with excess methanol or a solution of oxidizing agent might be needed to overcome saturation for the resin.

Chasanov et al. [4] indicate that in addition to residual FFA content, adsorbed color body (pigment) and other impurities were not removed from the resin either by rinsing with methanol or sodium hydroxide solution. Consequently, the capacity of the resin gradually reduced to the point where the process was no longer efficient. In such case, the exhausted resin must be treated with a solution of an oxidizing agent which removed the adsorbed impurities to restore its capacity by Chasanov et al. [4]. Photographs of the feed and effluent solutions are as shown in Fig. 1a and 1b. The effluent

Table 3
Results of CPOW-FP Deacidification in Packed Bed Column with Dowex (Oil:n-hexane = 1:1). AV before process 24.24 mgKOH/g oil.

Batch	Initial Used Resin		Regenerated Resin	
	AV after process	Yield[1] (%)	AV after process	Yield[1] (%)
1	1.52	93.72	1.72	92.90
2	2.54	89.54	1.38	94.32
3	2.03	91.63	9.64	60.22
4	2.03	91.63		
5	4.56	81.17		

[1] The yield represents the efficiency of the deacidification and was calculated as: Yield = 100 − (final AV / initial AV) × 100. AV, acid values.

Table 4
Results of CPOW-FP Deacidification in Packed Bed Column with Dowex (Oil:n-hexane = 3:2). AV before process 24.24 mgKOH/g oil.

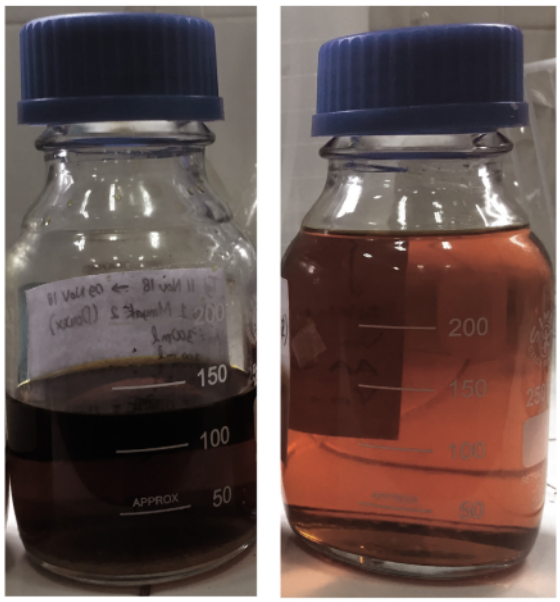
Batch	Initial Used Resin		Regenerated Resin	
	AV after process	Yield[1] (%)	AV after process	Yield[1] (%)
1	0.52	97.84	1.37769	94.32
2	1.57	93.52	15.49897	36.06
3	1.74	92.83	22.73183	6.22
4	4.62	80.95		

[1] The yield represents the efficiency of the deacidification and was calculated as: Yield = 100 − (final AV / initial AV) × 100. AV, acid values.

Table 5
Results of CPOW-CP Deacidification in Packed Bed Column with Dowex Marathon A.

Oil:Hexane Ratio	AV before process	AV after process	Yield[1]
2:3	38	2.5	93.42
1:1	35	0.6	98.29
3:2	39	0.6	98.46

[1] The yield represents the efficiency of the deacidification and was calculated as: Yield = 100 − (final AV / initial AV) × 100. AV, acid values.



(a) (b)

Fig. 1. Photographs of the feed (a) effluent solutions (b).

solution was transparent yellow in a single phase, thus the dark brown pigment in the feed oil did not flow out. This means the pigment was adsorbed on the anion-exchange resin (Dowex Marathon A) during the process of deacidification.

4. Conclusion

There is a possibility of conducting the deacidification process efficiently in a column packed with anion exchange resin (Dowex Marathon A and Lewatit MP500). The use of Dowex Marathon A obtained higher percent yield than Lewatit MP 500. This process has the capacity to decrease the acid value to 0.6 and also adsorb the oils pigment. However, regeneration with excess methanol or a solution of oxidizing agent might be needed to overcome the saturated resin problem.

CRediT authorship contribution statement

Fitri Hadiah: Conception and design of study, Analysis and/or interpretation of data, Drafting the manuscript, Revising the manuscript critically for important intellectual content, Approval of the version of the manuscript to be published. **Adhe Muhammad Rainaldi:** Acquisition of data. **Medias Indah Monica Sari:** Acquisition of data. **Muhammad Rico:** Acquisition of data. **Dwi Sinthiya Kusumawardani:** Acquisition of data. **Rianyza Gayatri:** Drafting the manuscript, Revising the manuscript critically for important intellectual content. **Tuty Emilia Agustina:** Conception and design of study, Approval of the version of the manuscript to be published. **Susila Arita:** Acquisition of data. **Tuti Indah Saria:** Acquisition of data.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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