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Original Article

Effect of design parameters on esterification pretreatment by modified reactive distillation of high free fatty acid oil with ethanol

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Abstract

To treat high free fatty acid (FFA) feedstock, the reduction of FFA by esterification was investigated in a modified continuous reactive distillation column. In the study, the molar ratio of ethanol to crude palm oil was 8:1 and the reaction temperature was 80±5 °C with Amberlite-15 catalyst and feed rate of 4.27 ml/min. To study effects of design parameters, effects of the mass ratio of Amberlite-15 catalyst to activated carbon (from 1.19to 5.26), the initial concentration of FFA in feedstock, the feed location, the catalyst distribution, and the residence time were examined experimentally The Taguchi method and sensibility analysis showed that residence time had the largest effect on FFA conversion while the initial FFA content and the amount of catalyst were secondary.

Keywords: crude palm oil, esterification, reactive distillation, amberlite-15 catalyst, ethanol

1. Introduction

The limited supply of fossil fuels is a concern that has motivated the research and development of alternative fuels. These include biofuels such as biodiesel, which can be produced from vegetable oils or animal fats. Since the prices of feedstocks share the main portion of biodiesel production cost (Kapilakarn & Peugtong, 2007), low-cost feedstocks should be considered. The Office of Agricultural Economics (2016) reported that the cost of crude palm oil (CPO) is approximately half that of refined palm oil (RPO)and in comparison to other alternative bio-oils,CPO is indeed relatively low-cost feedstock (Chai, Tu, Lu, & Yang, 2014). However, it contains over 5% free fatty acids (FFA), which can induce saponification during direct transesterification. Hence, esterification, a generally reversible reaction, is necessary to reduce the initial high FFA content to an appropriate level for transesterification (Alptekin, Canakci, & Sanli, 2011; Chai *et al.*, 2014; Javidialesaadi & Raeissi, 2013; Kombe, Temu, Rajabu, & Mrema, 2011). The esterification reaction of FFA and ethanol with acid-catalyst to produce ethyl ester and water is shown in Equation1.

$$FFA + Ethanol \overset{H^+}{\rightleftharpoons} Ethyl\ Ester + Water \qquad (1)$$

Due to the different boiling points of water-ethanol and ethyl ester, a reactive distillation (RD) column which combines chemical reaction with separation by distillation in a single vessel can be used to increase product conversion (Kirbaslar, Baykal, & Dramur, 2001; Sert & Atalay, 2011). Immediate separation of the products beneficially shifts the equilibrium of a reversible reaction. Both RD and thermally coupled RD have been studied by simulations (Banchero & Gozzelino, 2015; Gomez-Castro, Rico-Ramirez, Segovia-Hernandez, & Hernadex-Castro, 2011). Normally, conventional esterification of FFA to biodiesel process requires the molar ratio of alcohol to FFA at about rang of 5:1 to 9:1 (Chongkhong, Tongurai, & Chetpattananondh, 2009; Marchetti & Errazu, 2008;) while in theoretical, the reaction requires only one mole of alcohol per mole of FFA as shown in Equation 1. For economic consideration, the excess alcohol needs to be recycled. A more recycle alcohol requires more

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energy. The RD approach also can decrease the consumption of alcohol and the overall costs of operation (Prasertsit, Mueanmas, & Tongurai, 2013). Moreover, using heterogeneous catalyst such as Amberlite-15 in the esterification reaction is convention to separate catalyst after the reaction (Marchetti, Miguel, & Errazu, 2007).

Therefore, the purpose of this work was to demonstrate use of an RD column, to reduce FFA in CPO by esterification of ethanol with activated carbon-Amberlite-15 catalyst bed in order to reduce catalyst separation problem. The effects of catalyst distribution, initial FFA content, feed location, Amberlite-15 to activated carbon ratio and residence time were examined experimentally.

2. Materials and Methods

2.1 Materials

CPO containing approximately 5-10% FFA was obtained from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops (Thailand). Ethanol (95% wt.) was purchased from Merck; Amberlite-15 from Sigma Aldrich; and activated carbon from Qualitech Supply, Songkhla, Thailand. Sodium Hydroxide was obtained from LobaChemiePvt, Ltd., while phenolphthalein was from QReC, New Zealand.

2.2 Experimental setup

The esterification process was performed in a reactive distillation column as shown in Figure 1.Two or three glass tubes (each 300 mm in height and 45 mm in inner diameter) were connected vertically in series, both with Amberlite-15and activated carbon packing inside. The lower end of the bottom tube was connected to a reboiler, and the top end of the upper tube to a condenser. The RD column, the re-boiler and the CPO were all concurrently preheated up to the desired reaction temperature of 80±5°C. Along its height, the column was heated to 80°C by heating tape. The ethanol feed rate was 4.27 ml/min, while the ethanol to oil molar ratio was 8:1 in the feed into the RD column. After the process reached the steady state, samples (50 ml each) were typically withdrawn from the reboiler every hour. In the first part the effect of each parameter was considered separately as the conditions were shown in Table 1.

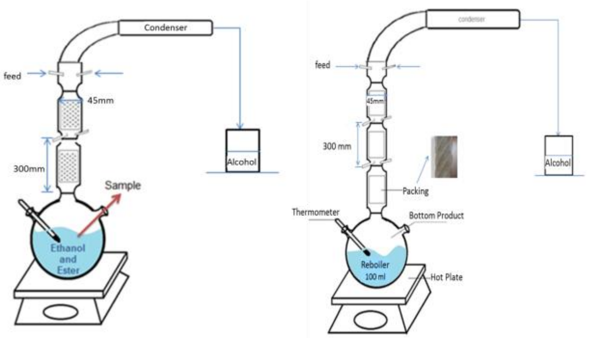


Figure 1. Simple reactive distillation column.

2.3 Analysis

2.3.1 Remaining of FFA

The bottom product sampling from the reboiler was washed with distilled water to terminate the reaction. After separating alcohol phase from the ethyl ester product, the product was titrated with sodium hydroxide (NaOH) using phenolphthalein indicator to determine the amount of remaining FFA.

2.3.2 Compare design parameters on FFA conversion

The effects of design parameters were examined quantitatively by Taguchi method as two-level-three-parameter arrays, L_4 (2^3), which had four conditions. This method provides which parameter has the strongest effect on the FFA conversion and provided interaction between each pairs of parameters. The parameters were residence time (t) of 3.3 and 3.6 minutes, Amberlite-15 to activated carbon to ratio (R) of 1 and 1.1 and initial FFA content (F) of 6.5 and 7.05. Comparing the effects of parameters was also done by sensibility analysis which considered the change of response (FFA conversion) over dimensionless number of parameter. The dimensionless number was ratio of the range of each variable and its maximum value,

$$\frac{x_{\max} - x_{\min}}{x_{\max}}$$

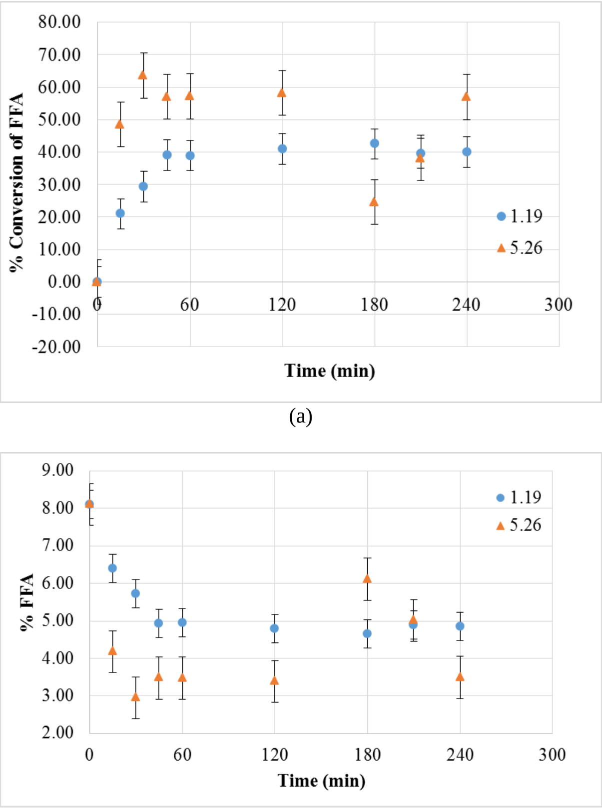
Table 1. Experimental conditions

No. Set	Parameter condition				
	Amberlite-15: Activated carbon ratio	Initial FFA	Feed location	Catalyst distribution	Residence time (min)
1	1.19 to 5.26		Upper part	Along 60 cm-height column	7
2	1.19	5.1 to 8.1	Upper part	Along 60 cm-height column	7
3	1.19	5.1	Middle part, Upper part	Along 90 cm-height column	7
4	1.19	5.1	Upper part	Along whole 90 cm- height column, upper part, lower part	7
5	1.19	5.1	Upper part	Along whole 60 cm-height	2, 6, 11

3. Results and Discussion

3.1 Effect ofamberlite-15 catalyst to activated carbon mass ratio

The experiment was performed in a 60 cm height column. Figure 2 shows that increasing the Amberlite-15 catalyst to activated carbon mass ratio from 1.19 to 5.2 increased conversion of FFA significantly. This is consistent with the results of Ozbay, Oktar, and Tapan (2008), as increasing the amount of Amberlite catalyst increased the surface area for reaction. Higher acidity would carbocate intermediate bulk causing faster reactions with the alcohol. The experiments also showed that the conversion rate of FFA increased sharply in the first 60 minutes, and then gradually slowed down to stay at the steady state (Farag, Maghraby & Taha, 2011; Marchetti *et al.*, 2007; Sert & Atalay, 2011). At 180-240 minutes, the FFA increased in the experiment with 0.19% mass ratio of activated carbon to catalyst, probably because hydrolysis dominated over esterification (Fu, Chen, Lv, Yang, & Yuan, 2015; Park, Wang, Kim, & Lee, 2010;Prasertsit, Phoosakul, & Sukmanee, 2014**)**, so the conversion of FFA decreased.



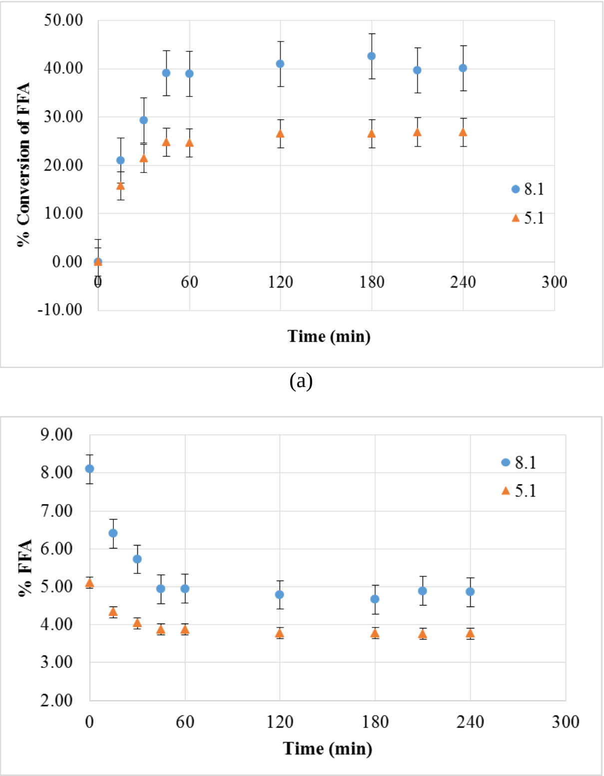
(a)

(b)

Figure 2. Effects of activated carbon to catalyst mass ratio on (a) % conversion of FFA, and (b) FFA content, with activated carbon to catalyst mass ratios1.19and 5.26, in a 60 cm height column, at 80±5 °C. The ethanol to oil molar ratio was 8:1 and the residence time was 7 minutes (P-value = 0.0005).

3.2 Effect of initial free fatty acid content

The experiment was performed in a 60 cm height column. Figure 3 shows effects of initial FFA content. During the first 60 minutes of the esterification, the conversion of FFA increased from 26.83 to 40.03 % as the initial FFA content was changed from 5.1 % to 8.1 %, in accordance with the law of mass action (Levenspiel, 1999; Onanong, Witoon, & Metta, 2011).Both initial concentrations of FFA provided the steady-state in about 120 minutes.



(a)

(b)

Figure 3. Effects of initial free fatty acid content on (a) conversion of FFA, and (b) FFA content, in a 60 cm height column at 80±5 °C. The ethanol to oil molar ratio was 8:1 and activated carbon to catalyst mass ratio was 0.84 (P-value = 0.00028).

3.3 Effect of feed location

To study effects of the feed location in a 90cm height column, both reactants were fed in at the upper or the middle part of the column, under otherwise similar conditions as shown in Figure 4. The results show that the feed location did not significantly affect the conversion of FFA (53.75% and 53.28 %) as illustrated in Figure 5. This was different from the previous work which feed at the upper of 60 cm height column gave conversion greater than feed at the lower column (Thummasaneh *et al.*, 2016). In this case studied, the modified distillation provided heat along the column, maintaining the column temperature at 80^{o}Cas the bottom temperature of 80 ^{o}C provided less vapor of ethanol and water as reflux back to the column. Therefore, only feed at the lower part, significantly, gave a smaller conversion since a shorter contact area of reactant and catalyst while feeding at the middle part or upper part, insignificant amount of ethanol-water vapor was distributed in the entire column and the contact area of reactant and catalyst in the reaction zone did not differ between the two cases, and was not enough to reduce the FFA (Thakore & Bhatt, 2007).

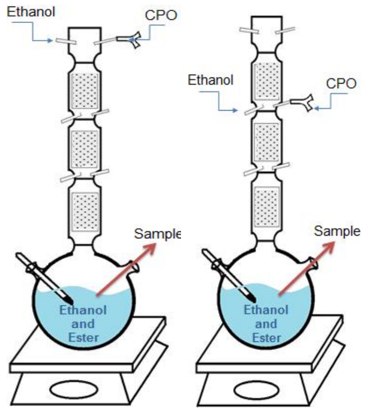
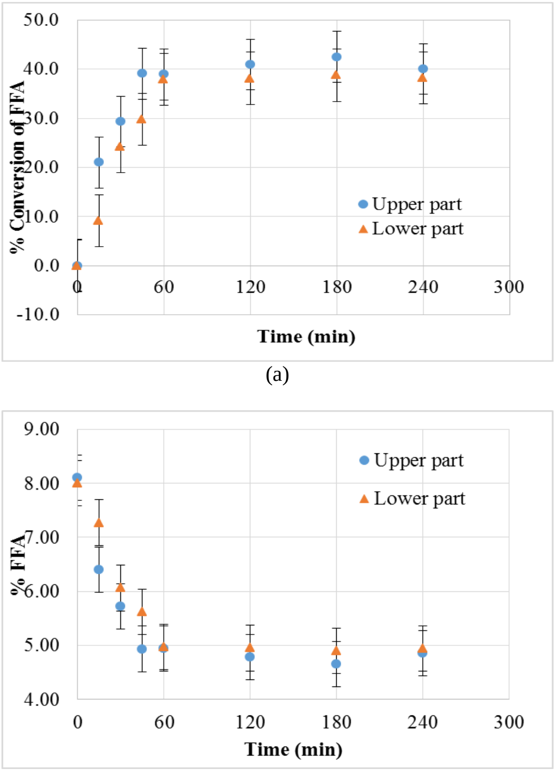


Figure 4. Alternative feed locations into the reactive distillation column.



(a)

(b)

Figure 5. Effects of feed location into the reactive distillation column on (a) conversion of FFA, and (b) FFA content at 80±5 ^{o}C, with ethanol to oil molar ratio of 8:1, and with activated carbon to catalyst mass ratio 0.84 (P-value = 0.3445).

3.4 Effect of distribution of catalyst

The study of catalyst distribution within the 90 cm height column and feeding from the top of column is depicted in Figure 6. The conversions of FFA were 26.83, 13.72 and 10.62 % with the catalyst distributed along the whole column, its upper part only, and its lower part only, respectively. This is because distributing the catalyst along the whole column provided the most active catalyst sites to the reaction.

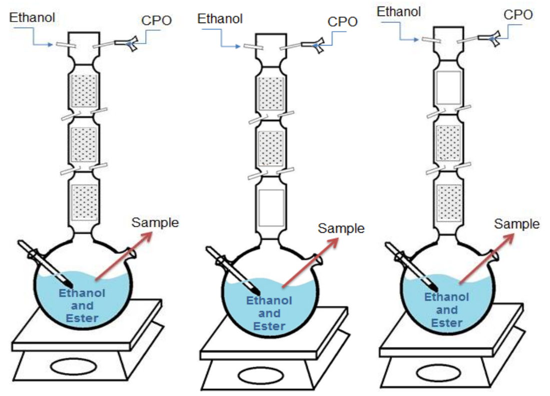
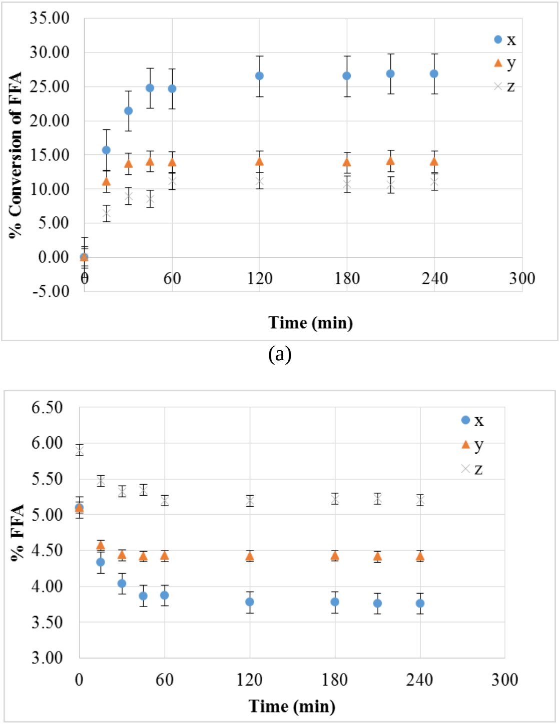


Figure 6. Alternative distributions of catalyst in the reactive distillation column.



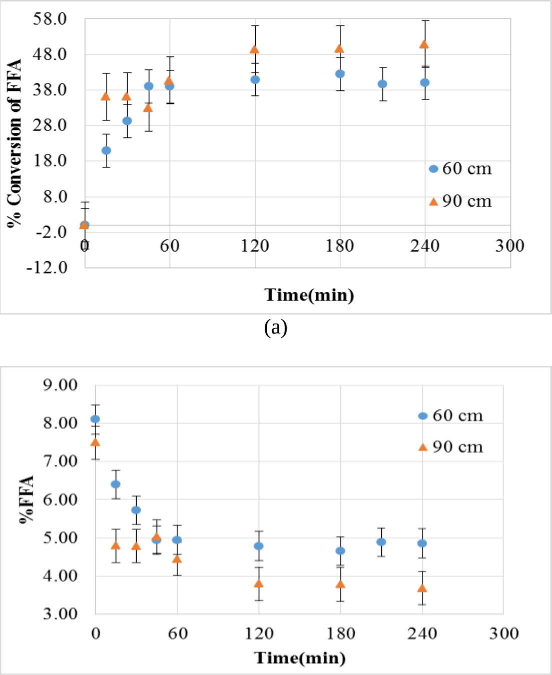
(a)

(b)

Figure 7. Effects of the distribution of catalyst in the reactive distillation column on (a) conversion of FFA, and (b) FFA content. The symbols indicate (x) along whole column, (y) in upper part, and (z) in lower part of the column. Operation was at 80±5 ^{o}C, with ethanol to oil molar ratio 8:1, and with activated carbon to catalyst mass ratio 0.84 (P-value = 3.09e-6).

3.5 Effects of residence time

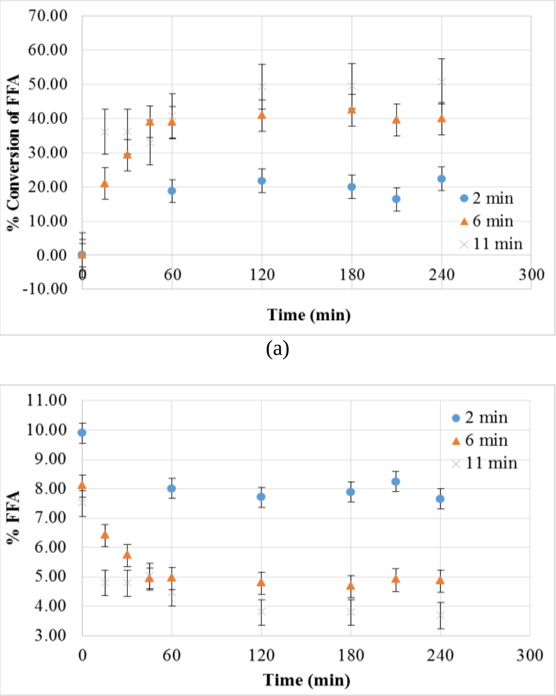
Figure 8 shows the effects of residence time, manipulated by varying the column height from 60 to 90 cm. The conversion of FFA increased from 40.03 to 50.93 % with the height increase because the reactants had longer contact times with the catalyst (Fogler, 2013; Ratanawilai, 2014). The results also agree with Figure 9, where residence time was manipulated through the feed flow rate to a 60 cm height column (from 8.33 ml/min to 4.67 ml/min).Longer residence times in the RD column consistently gave higher conversion of the FFA.



(a)

(b)

Figure 8. Effects of residence time manipulated by varying the column height on (a) conversion of FFA, and (b) FFA content. The feed flow rate was 4.67 ml/min, at 80±5 ºC, with ethanol to oil molar ratio 8:1, and with activated carbon to catalyst mass ratio 0.84 (P-value =0.0010).



(a)

(b)

Figure 9. Effect of residence time manipulated by varying the feed flow rate on (a) conversion of FFA and (b) FFA content. Column was operated at 80±5 ºC, with ethanol to oil molar ratio 8:1, and with activated carbon to catalyst mass ratio 0.84 (P-value = 0.0021).

3.6 Comparison of design parameters

The effects of residence time (t), Amberlite-15 to activated carbon ratio (R), initial free fatty acid (F) content, and their interactions were studied by the Taguchi method as shown in Table 2. The residence time (t) had the strongest effect on reduction of free fatty acids, and the interaction R x F was also comparatively large in its effect. The next ranked effects were from initial FFA content and the interaction t x R. The mechanistic reasons have already been discussed. This shows that increase FFA conversion can do by increasing

Table2. Orthogonal array analysis of factors by Taguchi method.

Experiment	Conditions			Response(% conversion)
	Residence time, t (minutes)	Activated carbon to Amberlite ratio, R	Initial FFA content, F	
1	t_1=3.3	R_1= 1	F_1 = 6.5	y_1 =28.92
2	t_1=3.3	R_2 =1.1	F_2 =7.05	y_2 =33.90
3	t_2=6.1	R_1= 1	F_2 =7.05	y_3 =24.26
4	t_2=6.1	R_2 =1.1	F_1 = 6.5	y_4 =10.62
Independent variable				Effect
Effect of t	$\|(y_1+y_2)/2-(y_3+y_4)/2\|$= 31.41 - 17.44 = 13.98			13.98
Effect of R	$\|(y_1+y_3)/2-(y_2+y_4)/2\|$= 26.59 - 22.26 = 4.33			4.33
Effect of F	$\|(y_1+y_4)/2-(y_2+y_3)/2\|$= 19.77 - 29.08 = 9.31			9.31
Effect of txR	$\|(y_1+y_4)/2-(y_2+y_3)/2\|$= 19.77 - 29.08 = 9.31			9.31
Effect of txF	$\|(y_1+y_3)/2-(y_2+y_4)/2\|$= 26.59 - 22.26 = 4.33			4.33
Effect of RxF	$\|(y_1+y_2)/2-(y_3+y_4)/2\|$= 31.41 - 17.44 = 13.98			13.98

residence time by reducing feed flow rate since increasing column height (same amount of catalyst) dues higher capital cost. However if the FFA input contains high FFA, catalyst ratio should be increased rather than increasing residence time. Effects of size of design parameters also were compared by sensibility analysis as shown in Table 3. This result shows that the residence time also had the largest effect on the conversion and the next ranked parameter was the initial FFA content.

Table 3. Analysis of factors by variable ratio.

Effect	Conversion of FFA Difference (a, in %)	Dimensionless (b) $\frac{x_{\max}-x_{\min}}{x_{\max}}$	% Variable ratio $\frac{a}{b}$
Residence time	50.89 – 21.15 = 29.74	$\frac{11-2}{11}=0.82$	$\frac{29.74}{0.82}=36.27$
Initial of FFA	40.03 – 26.83 = 13.20	$\frac{8.10-5.10}{8.10}=0.37$	$\frac{13.20}{0.37}=35.67$
Mass ratio of activated carbon to catalyst	59.10 – 40.03 = 19.07	$\frac{0.84-0.19}{0.84}=0.77$	$\frac{19.07}{0.77}=24.77$

4. Conclusions

To consider the effect of design parameters in the pretreatment of FFA in CPO by modified reactive distillation with fixing the molar ratio of ethanol to crude palm oil at 8:1, the reaction temperature at 80±5 ^{o}C, feed rate of 4.27 ml/min. the Amberlite-15 catalyst mixing with activated carbon in the mass ratio of 5.26 containing in the whole RD column and resident time of 7 minutes provided the highest 59.10% conversion of FFA. Since the column temperature in the modified RD was uniform along the column, the feed location did not significantly affect the conversion. During both Taguchi and sensibility analyses with the feed location was at the upper part of the RD column, the residence time (either controlled by feed flow rate or by height of packed column) had the largest effect on FFA conversion, followed by the initial FFA content and Amberlite-15 catalyst to activated carbon mass ratio.

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References

Alptekin, E., Canakci, M., & Sanli, H. (2011). Methyl ester production from chicken fat with high FFA. Bioenergy Technology (BE). *Proceeding of World Renewable Energy Congress*, Sweden, May 8-13, 2011.

Banchero, M., & Gozzelino, G. (2015). Nb_2O_5-catalyzed kinetics of fatty acids esterification for reactive distillation process simulation. *Chemical Engineering Research and Design, 100*, 292-301.

Chai, M., Tu, Q., Lu, M., & Yang, J. Y. (2014). Esterification pretreatment of free fatty acid in biodiesel production, from laboratory to industry. *Fuel Processing Technology, 125*, 106-113. doi:10.1016/j.fuproc.2014.03.025

Chongkhong, S., Tongurai, T., & Chetpattananondh, P. (2009). Continuous esterification for biodiesel production from palm fatty acid distillate using economical process. *Renewable Energy, 34*(4), 1059-1063. doi:org/10.1016/j.renene.2008.07.008

Farag, H. A., Maghraby, A. E., & Taha, A. N. (2011). Optimization of factors affecting esterification of mixed oil with high percentage of free fatty acid. *Fuel Processing Technology, 92*(3), 507-510. doi: 10.1016/j.fuproc.2010.11.004

Fogler, S. H. (2013). *Elements of chemical reaction engineering*. New York, NY: Pearson International.

Fu, J., Chen, L., Lv, P., Yang, L., & Yuan, Z. (2015). Free fatty acids esterification for biodiesel production using self-synthesized macro porous cation exchange resin as solid acid catalyst. *Fuel, 154*, 1-8.doi:org/10.1016/j.fuel.2015.03.048

Gomez-Castro, F. I., Rico-Ramirez, V., Segovia-Hernandez, J. G., & Hernadex-Castro, S. (2011). Esterification of fatty acids in a thermally coupled reactive distillation column by the two-step supercritical methanol method. *Chemical Engineering Research and Design, 89*(4), 480-490. doi:10.1016/j.cherd.2010.08.009

Javidialesaadi, A., & Raeissi, S. (2013). Biodiesel production from high free fatty acid-content oils: Experimental investigation of the pretreatment step. *APCBEE Procedia, 5*, 474-478. doi:10.1016/j.apcbee.2013.05.080

Kapilakarn, K., & Peugtong, A. (2007). A comparison of costs of biodiesel production from transesterication. *International Energy Journal, 8*(1), 1-6.

Kirbaslar, I. S., Baykal, B. Z., & Dramur, U. (2001). Esterification of acetic acid with ethanol catalysed by an acidic ion-exchange resin. *Turkish Journal of Engineering and Environment Science, 25,* 569-577.

Kombe, G. G., Temu, K. A., Rajabu, M. H., & Mrema, D. G. (2011). High free fatty acid (FFA) feedstock pretreatment method for biodiesel production. *Proceeding of Second International Conference on Advances in Engineering and Technology*, 176-182. Retrieved from https://www.mak.ac.ug/documents/Makfiles/aet2011/Kombe.pdf

Levenspiel, O. (1999). *Chemical reaction engineering* (3rd Ed.). Hoboken, NJ: Wiley.

Marchetti, J. M., Miguel, V. U., & Errazu, A. F. (2007). Heterogeneous esterification of oil with high amount of free fatty acids. *Fuel, 86,* 906-910. doi:10.1016/j.fuel.2006.09.006

Marchetti, J. M., & Errazu, A. F. (2008). Comparison of different heterogeneous catalysts and different alcohols for the esterification reaction of oleic acid. *Fuel, 87*(15-16), 3477-3480. doi:10.1016/j.fuel.2008.05.011

Office of Agricultural Economics. (2016, May 15). Palm oil. Retrieved from http://www.oae.go.th/ewt_news.php?nid=21803&filename=news

Onanong,J., Witoon, T. & Metta, C. (2011). Production of mesoporous silica adsorbent from natural solid wastes. *Kasetsart Engineering Journal, 24*(75), 103-120. Retrieved from http://www.anchan.lib.ku.ac.th/kukr/bitstream/003/23599/1/kejv024n075a001.pdf

Őzbay, N., Oktar, N., & Tapan, N. A. (2008). Esterification of free fatty acids in waste cooking oils (WCO): Role of ion-exchange resins. *Fuel, 87*(10-11), 1789-1798. doi:10.1016/j.fuel.2007.12.010

Park, J. Y., Wang, Z. M., Kim, D. K., & Lee, J. S. (2010). Effects of water on the esterification of free fatty acids by acid catalysts. *Renewable Energy, 35*(3), 614-618. doi: 10.1016/j.renene.2009.08.007

Prasertsit, K., Mueanmas, C., & Tongurai, C. (2013). Trans-esterification of palm oil with methanol in a reactive distillation column. *Chemical Engineering and Processing: Process Intensification, 70,* 21-26. doi:10.1016/j.cep.2013.05.011

Prasertsit, K., Phoosakul, P., & Sukmanee, S. (2014). Use of calcium oxide in palm oil methyl ester production. *Songklanakarin Journal of Science and Technology, 36*(2), 195-200. Retrieved from http://rdo.psu.ac.th/sjstweb/journal/36-2/36-2-8.pdf

Ratanawilai, S. (2014). *Catalyst in industry, catalyst and industrial*. Songkhla, Thailand: Prince of Songkla University.

Sert, E., & Atalay, F.S. (2011). Esterification of acetic acid with butanol: Operation in a packed bed reactive distillation column. *Chemical and Biochemicak Engineering Quarterly, 25* (2), 221-227.

Thakore, B. S., & Bhatt, I. B. (2007). *Process design of distillation columns. Introduction to process engineering and design* (pp. 378-565). New Delhi, India: Tata McGraw-Hill.

Thummasaneh, P., Prasertsit, K., Ratanawilai, S., Thipkonglat, S., & Ongrattana, T. (2016). Free fatty acid reduction for biodiesel production in reactive distillation column. *International Conference on Advanced Material Science and Environmental Engineering (AMSEE)*. Chiang Mai, Thailand, June 26-27, 2016, 89-96