Optimization of Wax Esters Production from Palm Fatty Acid Distillate and Oleyl Alcohol Over Amberlyst 15 by Response Surface Methodology

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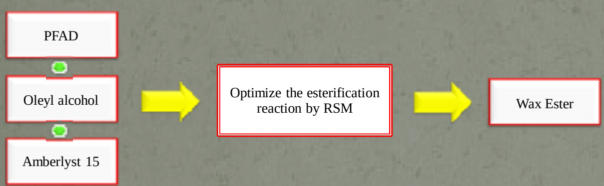
Abstract

The synthesis of wax esters using palm fatty acid distillate and oleyl alcohol catalyzed by Amberlyst 15 was carried out. Response surface methodology (RSM) base on a five-level, three-variable central composite design (CCD) was used to evaluate the interactive effects of synthesis, of amount of catalyst (21.6 – 38.4% w/w), reaction time (18 – 102 minute) and molar ratio (fatty acid distillate to oleyl alcohol, 1:1.16 – 1: 2.84) on the percentage conversion of fatty acid distillate. The optimum conditions derived via RSM were : amount of catalyst 33% w/w, reaction time 95 minute and substrate molar ratio 1:2.7. The actual experimental conversion was 81.52% under optimum condition, which compared well to the maximum predicted value of 80.50%.

Introduction :

Palm fatty acid distillate (PFAD) is by-product of crude palm oil refinery. The main component of PFAD is free fatty acid and also have glyceride, squalene, sterols, vitamin E and other substance. At room temperature, PFAD is a light brown solid and melting to brown liquid on heating. Mostly, PFAD is used for raw material in oleochemical industry such as laundry soap industry and animal feed. But, the other way to increase value of PFAD is synthesis of wax ester.Wax ester are long chain ester that are including of fatty acid and long chain alcohol with more than 12 carbon atom of chain lengths. This compounds have used in many application due to their potential such as excellent wetting behavior at interface and non greasy feeling when applied on skin surface. The wax ester is one of many ingredient in cosmetic, pharmaceutical, lubricants, plasticizer and other chemical industries. Animal, vegetables and mineral can be generated natural waxes such as beeswax and canuba wax. But they are more expensive and limited in access. So, the synthesized waxes from low raw material cost is interesting. Wax esters can be produced by esterification of palm fatty acid distillate (PFAD) and oleyl alcohol using heterogeneous acid catalyst. The classical optimization is varying one parameter while the other parameter keeping constant at one time. But this method cannot evaluatethe variables relationship and the response. Response surface methodology (RSM) is statistical technique for solve this problem. RSM have many advantages such as reducing number of experimental run. RSM has successfully been applied to optimize the wax ester synthesis and biodiesel.

Methodology:



A five-level-three-factor central composite design (CCD) was employed in this study, requiring 20 experiments. The independent variables to optimize wax esters synthesis were catalyst concentration (C), oleyl alcohol-to-PFAD ratio(O) and reaction time (T). The actual and coded levels of the independent variables are given in table 1.

Table 1 Range of independent variables for central composite design

Variables	Symbols	Levels				
		-1.68 (-α)	-1	0	1	1.68 (α)
Amberlyst 15 concentration (%w/w)	C	21.6	25	30	35	38.4
Oleyl alcohol-to-PFAD ratio (mol)	O	1.16	1.50	2	2.5	2.84
Reaction time (min)	T	18	35	60	85	102

Results and Discussion :

Model fitting and ANOVA

The quadratic polynomial model for percentage conversion to predict the predicted values were obtained from the model fitting technique using SPSS software version 12 and were correlated to the observed value. From the software, the quadratic polynomial is given below:

$$\text{Conversion}(\%) = 23.068 - 0.22\,C + 27.812\,O + 0.349\,T + 0.006\,C^2 - 3.843\,O^2 + 0.058\,CO - 0.001\,CT - 0.094\,OT$$

Where C is the amount of Amberlyst 15; O is the molar ratio; T is the time

The computed F value (0.848) is lower than the tabular $F_{(0.05, 5, 5)}$ value (5.05) at 5% confidence level which indicated insignificant lack of fit of the model and also showed the model are suitable to describe the experiment. In addition, the regression model for data was found to be highly coefficient of determination (R^2=0.980).

Effect of parameters

From the Fig.1a, the molar ratio of oleyl alcohol is more effective the the amount of catalyst on the percentage conversion of synthetic esters. The molar ratio of oleyl alcohol and time (Fig. 1b) and the amount of catalyst and time (Fig. 1c) are similar effect on the wax esters. It's indicated that the highly percentage conversion of synthetic esters as a results of increasing these variables.

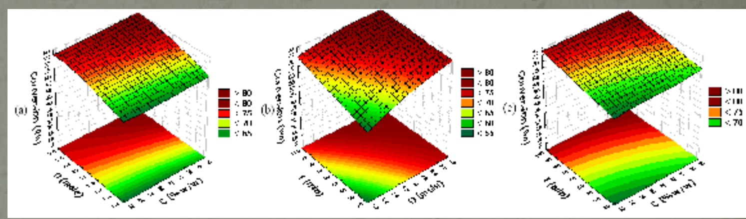


Fig. 1 Response surface plot showing of two variable and their effect on the synthesis of wax ester. Other parameter is constant; (a) 60 minute of time, (b) 30% of amount of catalyst, (c) 2 mol of oleyl alcohol to PFAD

Optimization of reaction

The optimum conditions were 33% of amount of Amberlyst 15, 2.7 mol of oleyl alcohol to PFAD and 95 minute of reaction time. And it gave 81.52 of actual and 80.55 of predicted percentage conversion.Comparison of actual and predicted conversion indicated good correspondence between both value, and shown that empirical models derived from RSM can be used to describe the relationship between the factors and response in wax esters synthesis.

Characterization of wax esters

The esterification reaction to synthesis wax esters from palm fatty acid distillate and oleyl alcohol by Amberlyst 15 was identified this ester by gas chromatograph (GC). Methyl lurate (R_t 3.98 min) was added to sample for determination of wax ester yield. The composition of wax esters by optimization of RSM are present in fig. 2 and table 2.

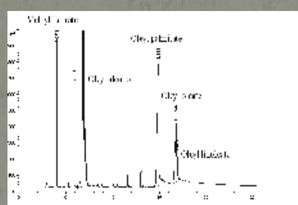


Fig. 2 Chromatogram of wax esters at the optimum condition of esterification reaction

Table 2 Composition of wax esters synthesized from PFAD at optimum condition

Wax esters	Retention time (min)	Percentage yield (%)
methyl laurate (IS)*	4.071	-
Oleyl palmitate	14.888	49.34
Oleyl oleate	16.794	26.59
Oleyl linoleate	16.907	4.61
Total	-	80.54

Conclusions and discussions :

PFAD, by-product from palm oil refinery industry, is suitable to synthesize wax esters. The central composite design and response surface methodology in esterification reaction indicate the increasing trend of percentage conversion of PFAD due to increasing level of each parameter. The response surface graphs show the effect of molar ratio of oleyl alcohol and time are higher than amount of catalyst. The optimum condition of esterification reaction was obtained at 2.70:1 of molar ratio of oleyl alcohol-to-PFAD, 33% of Amberlyst 15 catalyst amount and 95 min of reaction time. At the optimum conditions, it gave more than 80% of percentage conversion of PFAD. In addition, the GC was applied to calculate the percentage yield of wax esters product in this point. The total percentage yield of wax esters was 80.15%. In addition, utilization of by-product such as PFAD will lead not only to a value-added application, but also to a zero-waste strategy in palm oil refinery industry.

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Reference :

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