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Abstract. In this research, polyalkyd resins were prepared from palm oil by polycondensation reaction. A two-step method viz., alcoholysis and esterification were conducted to synthesize polyalkyd resins. Response surface methodology was used to optimize the reaction parameters for esterification like reaction temperature, reaction time, catalyst concentration, acid anhydride to mono-glyceride ratio and agitation speed. The optimum condition was used to prepare various types of polyalkyds using different types of acid anhydrides such as, maleic anhydride, succinic anhydride, phthalic anhydride, 3,4,5,6-tetrahydrophthalic anhydride and cis-1,2-cyclohexanedicarboxylic anhydride. Result analyses through RSM revealed a desirability of 0.985 for the reaction time of 88.64 min. Moreover, 91.5% fractional conversion was achieved actually, which is close to the predicted value. The analysis revealed that 3,4,5,6-tetrahydophthalic anhydride-based resin showed improved resinous property than others due to the high degree of crosslinking.

1. Introduction

There are a huge number of vegetable oils available in the world. Nearly, 4000 botanical species have been identified in the planet, from which oil can be extracted [1]. These vegetable oils can be utilized to produce polymers and polymeric materials [2]. Many useful polymers like, polyesters, polyurethanes, polyamides, etc. have been prepared from different vegetable oils and studied in previous investigations [3]. The polymerization techniques and methods with different features of the prepared polymers are also highlighted. Moreover, palm oil along with other vegetable oils has been studied for the preparation of different kinds of polymers, especially polyalkyds.

The common process to prepare polyesters is the two-steps method includes alcoholysis followed by esterification [4,5]. In alcoholysis process, the oils or triglycerides are subjected to alcoholysis to produce mono-glycerides (as partial glycerides), catalysed by various acid or base catalysts such as, PbO, NaOH, CaO, Ca(OH)$_2$, CaCO$_3$, para-toluene sulphonic acid (PTSA), etc. After this, the mono-glycerides are subjected to polymerization process with different acid anhydrides such as, aliphatic acid anhydride (glutaric anhydride, maleic anhydride, succinic anhydride, etc.) and aromatic acid anhydrides (phthalic anhydride) to produce polyalkyd based resin [6,7].

The aim of this study was to optimize the reaction parameters for esterification process using palm

oil. In the previously published article, the esterification was performed using different kind of vegetable oils, but optimization of the reaction parameters, especially for pal oil-based polyalkyd preparation yet not documented. Moreover, a solution based on the analysis was suggested which may help to predicts the reaction parameters for other kinds of vegetable oil to be used for the same purpose.

2. Experimental

2.1. Materials
Palm oil was provided by Malaysian Palm Oil Board (MPOB). Glycerol and calcium oxide were procured from Aladdin Chemistry Co. Ltd., Shanghai, China. Methyl ethyl ketone peroxide and 3,4,5,6-tetrahydrophthalic anhydride (Molecular weight: 152.16 g/mol; chemical formula: $C_8H_8O_3$) was purchased from Aladdin chemical corporation, Shanghai China. Sulphuric acid was purchased from Fisher scientific, USA. Maleic anhydride (MA) was purchased from ACROS, USA. Cobalt napthenate and styrene were purchased from Sigma Aldrich, USA

2.2. Optimisation of esterification process using RSM
The solutions for the desired response and the corresponding set of optimum experimental conditions for the esterification process were suggested by response surface methodology (RSM). The minimum numbers of experimental runs were predicted by central composite design. The total numbers of experiments were based on five (5) different factors at various distinct settings, which suggest 50 runs including 32-full factorial distinct points, ten (10) runs at unique axial points and eight (8) constant runs at center points. The primary analysis with crude oil helped to find out the range of the parameters. The experimental factors and pre-assumed range of values for polyesterification reaction are presented in table 1. The factors are selected from the previous study based on polyalkyd preparation [8]. Table 2 represents the fifty (50) experimental runs as suggested by central composite design.

Table 1. Experimental factors and pre-assumed range of values for esterification.

Factors	Units	Low	High	-α	α
(A) Temperature	Celsius	220	260	192.432	287.568
(B) Time	Min	30	180	-73.3811	283.381
(C) Agitation	rpm	300	1000	-182.445	1482.44
(D) Molar ratio	Unit less	0.1	0.5	-0.175683	0.775683
(E) Catalyst concentration	wt.%	0.02	0.08	-0.0213524	0.121352

Table 2. Analysis of variance for response surface quadratic model.

Source	Sum of squares	df	Mean Square	F value	p-value Prob>F
Model	15594.52	20	779.73	31.82	<0.0001
A-Temperature	2691.36	1	2691.36	109.83	<0.0001
B-Time	312.03	1	312.03	12.73	0.0013
C-Agitation	196.32	1	196.32	8.01	0.0084
D-Molar ratio	246.78	1	246.78	10.07	0.0036
E-Catalyst concentration	34.20	1	34.20	1.40	0.2470
Residual	710.62	29	24.50		
Lack of Fit	710.43	22	32.29	1159.21	<0.0001
Pure Error	0.19	7	0.028		
Cor Total	16305.14	49			
	Std. Dev.		4.93	R-Squared	0.9389
	Mean		51.24	Adj R-Squared	0.9270
	C.V. %		9.62	Pred R-Square	0.8982
	PRESS		1660.42	Adeq Precisior	27.790

The optimized data, obtained from RSM analysis, was used further in the preparation of different types of polyalkyds by using SA, MA, PA, TPA and CDA through esterification process. The name tags for the formulated resins using SA, MA, PA, TPA and CDA are SAR, MAR, PAR, TPAR and CDAR, respectively. Further, esterification was also carried out with TPA and MA at different ratios to find the effects of aromatic and aliphatic acid anhydride content on the resinous properties. The name tags for the samples containing 0, 50, 75 and 100% MA are MA0, MA50, MA75 and MA100, respectively.

3. Results and discussion

3.1. Factor analysis

Preparation of polyalkyds involves alcoholysis and esterification process. The alcoholysis process is usually completed within one or two hours after the reaction temperature is reached [9]. The screening and selection of the range of reaction parameters were performed by using crude oil for esterification process. The esterification process was optimized with the help of design expert software (DES). The completion of esterification process was determined by the acid value of the products. The reduction in acid value with respect to time is useful to calculate the fractional conversion of the alkyd resins. The variations of response were found to be significant due to the changes of reaction conditions, which is satisfying the usefulness of RSM application as well as indicating the importance of different factors. The minimum number of experimental runs was predicted by using central composite design. A full factorial central composite design matrix was used for five factors in against for a single response, acid value. The response for the individual run was the input in the system. Eventually, a solution was suggested by RSM, containing a set of reaction parameters. These parameters were economic, and the reaction based on that condition was the optimum with the highest desirability.

Analysis of the effects of different variables showed the significance of their contributions to the reaction. The analysis of variance (ANOVA) was generated after the computational tasks. A quadratic model of reduced order was formulated using the Equation (1) to find the values for different coefficients for the characteristics of the reaction. The process variables such as, temperature, time, catalyst concentration, molar ratio and agitation speed in the predictive model are designated as A, B, C, D and E, respectively. The results obtained from the predictive model indicate that the aforementioned factors are responsible for the main linear effects. The "Model F-value" of 31.82 implies the model is significant and there is only a 0.01% chance that a "Model F-Value" could occur due to noise. Additionally, the values of "Prob > F" less than 0.0500 indicates model terms are also significant. In this case A, B, C, D, BC, A^2, B^2, D^2 are significant model terms. Table 2 shows the statistical analysis of the variables. From these data a modified model was proposed by excluding the insignificant terms from the general predictive equation as mentioned below. From the analysis, it was found that the esterification process can be elucidated by the equation of the empirical model, with more than 93% overall system variability, as indicated by the R-Squared value of 0.9389. It was performed by the multivariate regression analyses. Thus, the general equation becomes as follows (equation (1)):

$$Y = 28.38 + 8.90A + 3.03B + 2.40C - 2.69D +$$
$$5.08BC + 20.27A^2 + 6.12\ B^2 + 7.22D^2$$

(1)

Where, Y is the fractional conversion. The main linear effects of the different factors such as, temperature, time, agitation and molar ratio are denoted, respectively as A, B, C and D. The linear interaction effect for time and agitation are indicated by BC, whereas quadratic effects can be denoted as A^2, B^2, D^2, which corresponds to respective factors or variables. The "Pred R-Squared" of 0.8982 is in reasonable agreement with the "Adj R-Squared" of 0.9270. Usually, signal-to-noise ratio is desirable more than 4. The signal to noise ratio was found to be 27.790, which signifies adequate signal.

3.2. Process analysis

Different solutions for the esterification reaction were obtained by the predictive equation as stated earlier (equation (1)). RSM was used conveniently for this process, as it can give different choices to fix the response at different reaction conditions. Different interactions between different factors for the esterification process were evaluated by solving the equation. The conversation of alkyd resin at any of the points of interactions of two variables was calculated assuming the other parameters to be set at their mean value, zero. To understand the effects of different parameters on esterification process, the interactions of two individual factors and their 3-D responses were examined by the graphs generated with the help of DES.

Figure 1 represents the 3-D plots of agitation vs. temperature (figure 1(a)), agitation vs. time (figure 1(b)) and agitation vs. catalyst concentration (figure 1(c)), respectively. It is clear from the figure that, the interaction between agitation and temperature has much effect than that of others. The acid value changes sharply due to high temperature and high agitation. As the temperature and agition varied the fatty acids in the palm oil reacted with the glycerol and presence of acid also varied the product. Therefore, the acid valuse chages. However, the interaction for agitation vs. time and agitation vs. catalyst concentration was found to be almost a flat trend, indicatiing less affecting contribution in terms of variation of responses. Figure 1 represents the 3-D responses of catalyst concentration vs. molar ratio (figure 1(d)), catalyst concentration vs. temperature (figure 1(e)) and catalyst concentration vs. time (figure 1(f)). Sharp changes were observed in the curves of catalyst concentration and temperature, indicating good interaction. The higher catalyst concentration and the higher temperature was found to be responsible for a higher value of the response, whereas the molar ratio and time showed less affection to the reaction process, as observed from the nearly flat trend during the reaction. This is because of hgiher percentage of catalyst at higher temperature can stimulate more reactions to get affected on the response. The significant and quick changes observed in the case of molar ratio and temperature. This response was sharp and steady due to changes in temperature and molar ratio. This is happened so because, the reaction is mode dependent on the molar ratio of fatty acid and glycerol percentage or ratio. Therefore, if the molar ratio of the reactant changes, the development of the product also changes. The other responses were insignificant as predicted due to the quadratic effect of molar ratio. Finally, the time and temperature, which is also important and an indication for the sharp changes of the acid value. For a batch reaction system, the extent of reaction or conversion is higher with time at low reaction temperature [10] and seems to be a first order reaction kinetics. As the temperature increases the response was found to be increasing up to temperature around 235°C and further increasing of temperature affects the response slowly and behaves like a second order reaction kinetics [11]. The reversible nature of esterification reaction is probably the reason for slow responses at a higher temperature.

Among the process variables, the molar ratio of PA to monoglyceride and catalyst concentration is very important. These parameters need to be controlled to achieve a higher yield and conversation of oil to alkyd with high purity. It was found that the maximum conversion can be achieved by increasing the catalyst concentration up to a certain level for a molar ratio. It was also found that, at the lower molar ratio with higher catalyst concentration the conversion remains still high. However, the industrial importance in the manufacturing process is always depreciated to use of the high amount of catalyst. Thus, optimization of this process found to be a significant analysis and can be used for the manufacturing process at a larger scale.
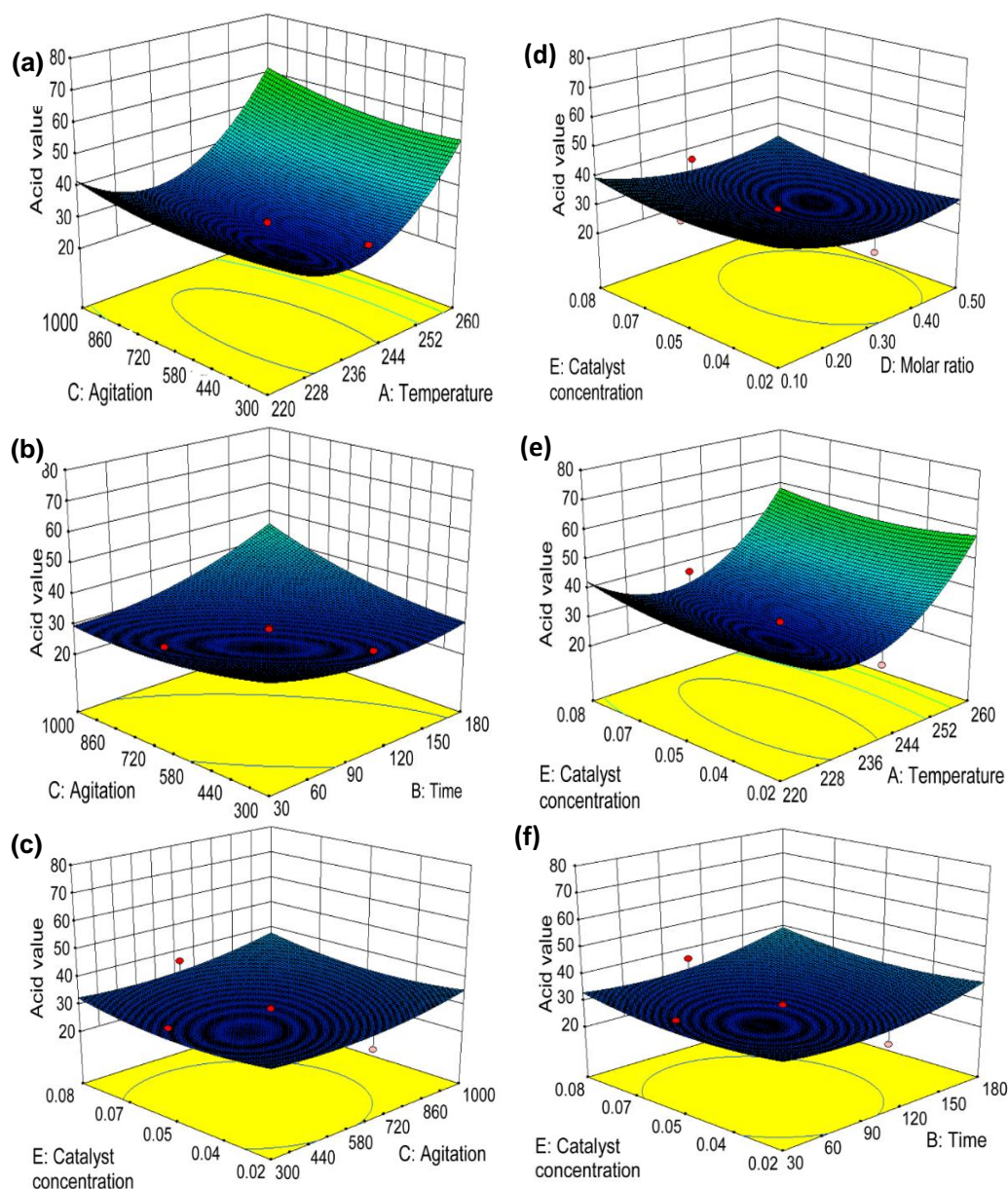
Figure 1. 3-D curves of agitation vs. temperature (a), agitation vs. time (b) and agitation vs catalyst concentration (c), catalyst concentration vs. molar ratio (d), catalyst concentration vs. temperature (e) and catalyst concentration vs time (f).

3.3. Process optimization

The optimization of the process is required not only to ensure or detect the optimum reaction parameters for a higher yield or desired response, but also to confirm high quality products with faster drying time, acceptable colour, low manufacturing cost, etc. The drying time is important for product quality. Additionally, it is always considered to reduce the product cost by reducing the reaction time and temperature. The optimization of the process was carried out by the optimization tool of the design expert software, while the criteria function helped to input the desired value to achieve a targeted response.

The best solutions were obtained by solving equation 1 and it was targeted to achieve the desired responses. There were a number of solutions available as suggested by the design expert software. The best one was considered based on the economic value of the process by evaluating different factors,

individually and their effects on the response. Nearly, 91.5% of fractional conversion was achieved which is indicating a good fit of the model with the experimental statistical analysis. A comparison with the previous work showed an improvement in the reaction time and almost like the conversion rate, although a very few works related to palm oil-based alkyds and esterification were performed [8].

Several solutions were proposed by the software, although the best one was considered for further experiments. However, the solutions of optimization process for different sets of reaction parameters are presented in table 3, whereas the best solution was chosen as follows: reaction temperature = 240°C, reaction time = 88.64 min, agitation speed = 584.20, molar ratio = 0.35:1, catalyst concentration = 0.04 at response 27.12 of acid value with the highest desirability of 0.985. The optimum parameters are listed in table 4. The values for the other solutions were found to be very close to each other. Finally, to confirm the optimization process, the optimum experimental run was carried out, which was found similar to the values as suggested earlier by the software. In the previous investigation, the optimization of the esterification process was carried out with four factors [8]. The optimization process was considered by the dehydration process by NaHSO$_4$ in the presence of NaOH and PbO as the catalysts for alcoholysis. In a different work, castor oil-based esterification process was analyzed and nearly 97% of the reaction was completed in 2 h and 30 min in the range of temperature of 230 to 240°C [11]. The major differences from these works to the current study was the dehydration process and uses of different catalyst (CaO), which reduced the reaction time almost 50% with higher desirability and lower acid value. Moreover, agitation was found to be influential regarding the properties of the polyalkyds. Several research works were carried out for the transesterification of different vegetable oils for the production of biodiesel, and RSM was used [12,13] for the optimization process. The reported results were found different from this current work due to the high activation energy required for the establishment of the equilibrium reaction between PA and glyceride oil for polyalkyd preparation [8].

Table 3. The solutions suggested by RSM for the esterification process.

Number	Temperature	Time	Agitation	Molar ratio	Catalyst concentration	Acid value	Desirability
1	240.00	88.64	584.20	0.35	0.04	27.12	0.985
2	240.00	88.55	586.81	0.35	0.04	27.12	0.985
4	240.00	88.10	584.83	0.35	0.04	27.12	0.985
4	240.00	88.40	587.40	0.35	0.04	27.12	0.985

Table 4. The optimum solution suggested by RSM.

Parameters	Optimum values
Fractional conversion (%)	91.5
Reaction temperature (^{o}C)	240°C
Reaction time (min)	88.64
Agitation speed (rpm)	584.20
Molar ratio of PA: MG	0.35
Catalyst concentration (wt.%)	0.04
Desirability (%)	0.985
Response (Acid value)	27.12

4. Conclusion

Palm oil was used to prepare polyalkyds through alcoholysis and esterification process. The crude oil was subjected for the dehydration process to increase the unsaturation. It was found that the usage of H$_2$SO$_4$ improves the unsaturation of oil as maximum as 165%. After performing a preliminary screening of the reaction parameters, the esterification process was optimized through RSM. Result analyses revealed very high desirability of 0.985 through RSM analyses. Moreover, 91.5% fractional conversion was achieved, which is close to the predicted value. The optimum reaction conditions were used to formulate different types of polyalkyds using different acid anhydrides, viz., SA, MA, PA,

TPA and CDA. The properties of the resins were found to be dependent on the types of acid anhydrides. Among the resins, the TPA-based resin was found to be the best in terms of different resinous properties.

Acknowledgment

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