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Response Surface Methodology Approach for Optimisation of Alkaline Hydrolysis of Jatropha Curcas oil via Microwave Assisted

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The production of fatty acid by alkaline hydrolysis method from *Jatropha Curcas* oil using microwave assisted irradation system has been investigated. This fatty acid is widely used as raw materials for biochemicals industry. The optimisation of alkaline hydrolysis variables such as temperature, catalyst concentration loading, reaction time and oil to solvent ratio was carried out using central composite design (CCD) in response to surface methodology (RSM) to achieve maximum free fatty acid yield (% FFA). Analysis of variance (ANOVA) analysis shows that the catalyst concentration are the most significant variance effecting the yield of % FFA, with $R^2 = 0.9827$ indicating good fitting of the suggested model. The highest fatty acids yield was 98 % achieved at the optimum condition of 95 °C, 1.75 M of ethanolic KOH concentration, 1:68 oil to solvent ratio and 15 min of reaction time in 3,000 W microwave power system. This study reports under optimised condition, fatty acids yield was significantly increased and this also showed the potential of *Jatropha Curcas* oil as feedstock for fatty acids production.

1. Introduction

Microwaves are electromagnetic energy, which has frequency and wavelength in the ranges of 300 MHz to 300 GHz, and 0.001 m to 1 m (Costa et al., 2013). Lately microwave irradiation is becoming worldwide popular method of heating which replace the conventional method because it proved to be clean, convenient and most important it affords higher yields and used in shorter time (Palma et al., 2013).. Microwave radiation causes molecular friction of electric dipole, which results in heating. Lipids have low specific heat, which makes them susceptible to this radiation. Microwave preheating can be used to substitute conventional heating results in fast pre-treating with less energy consumption. This also generates permanent pores in the oil that makes higher yield. This method of heating has been extended to almost all area of chemistry with the exception of the carbohydrate i.e. fatty acids but it is testified by the limited number of applications (Chiavaro et al., 2010).
Fatty acids (FA)s is an important components and precursors used in the preparation of a wide variety of products such as soaps, surfactants, lubricants, plasticizers, paints, coatings, pharmaceuticals, foods, agricultural, industrial and personal care products (Gunstone and Hamilton, 2001). Currently, these fatty acids have also become a low-cost and biodegradability raw material for polyol esters synthesis (Schuchardt et al., 1998). Conventional, fatty acids are obtained from the reaction of vegetable oils and/or animals fats with superheated steams (Patil et al., 1988). This reaction is carried out at 100 - 260 °C and 100 – 7,000 kPa using a 0.4-1.5 wt % water-to-oil ratio. Different variations of this technology have been used by industry (e.g. Twitchell process, the Colgate-Emery synthesis and the Eisenlohr process) (Twitchell, 1898). These processes are normally referred to as fat splitting. The main drawbacks of this process are the requirement of a distillation unit to further clean free fatty acids (FFA). Researchers have employed several methods to prepare FAs such as enzymatic hydrolysis using lipases from *Aspergillus niger, Rhizopus javanicus* and *Penicillium solitum* (Carvalho et al., 2009), *C.rugosa* (Serri et al., 2008) and

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subcritical water (Pinto and Lantas, 2006). Nowadays, researchers used potassium hydroxide catalyzed hydrolysis of esters sometimes known as saponification because of its relationship with soap making. There are two big advantages of doing this. The reactions are one-way rather than reversible, and the products are easier to separate (Salimon et al., 2011). On laboratory scale, typically potassium or sodium hydroxide in ethanol, refluxing for 1 h, and the FAs recovered after acidification of the reaction mixture. This is a sufficiently mild procedure that most FAs, including polyunsaturates, epoxides, and cyclopropenes, are unaltered.

The earliest known study involving microwave is pre-treatment of C18 fatty acids esterification (Melo-Junior et al., 2009). The results showed conversion up to 60 % in 60 min of reaction under relatively mild conditions and non-catalytic system. It has been proposed that in case of low power of high-frequency electromagnetic field the non-thermal activation of enzyme may be observed. The application of microwave in alkaline hydrolysis has so far rarely found. Therefore, the aim of this study was to investigate the efficiency of pre-treatment alkaline hydrolysis under microwave irradiation. The Response surface methodology (RSM) was applied to design the optimum operating conditions for the fatty acids production.

2. Methodology

2.1 Materials and chemicals

Jatropha curcas oil was purchased from Bionas Sdn Bhd, Malaysia. Potassium hydroxide pellets (purity of 99 %), isopropanol, phenolphthalein, sodium hydroxide and n-hexane were obtained from Merck, Darmstadt, Germany. Ethanol (purity of 96 %), anhydrous magnesium sulphate, Hydrochloric acid (HCl), Methanol dry (MeOH dry) and Toluene were purchased from Fisher Chemicals (UK). The Jatropha oil and all chemicals are of analytical grade and were used directly without any purification. Microwave treatments were carried out using a domestic microwave synthesis reactor (Fabricated by Dixson Company) with variable power levels of 3,000 W.

2.2 Preparation of fatty acids by microwave system

The fatty acid process was carried out as described by Salimon et al. (2011). Briefly, the batch mixture containing Jatropha curcas seed oil and ethanolic KOH was mixed in a 500 mL temperature-controlled reactor. The reactor vessel was placed in a microwave synthesis reactor. The contents in the reaction flask was stirred using mechanical stirrer. In addition, due to high temperature, a reflux system was established for condensing sample into reactor. After the reaction was completed, the sample was cooled and 200 mL water was added to the mixture to enhance separation of fatty acids. A 100 mL of hexane was added to extract the unsaponifiables. The aqueous alcohol phase, containing the soaps, was acidified to pH 1 with HCl 6N, and the FFA was recovered by extraction with hexane. The extract was washed with distilled water until neutral. The FFA-containing upper layer was dried with anhydrous magnesium sulphate, and solvent was evaporated in a vacuum rotary evaporator at 50 °C.

2.2 Determination of the free fatty acids (FFA)

Samples were taken from the reaction mixture according to experimental design and was used for analysis of free fatty acid concentration (FFA %). The FFA% from alkaline hydrolysis of Jatropha curcas seed oil was determined according to acid value test as reference method (AOCS, 1999). The FFA % was calculated by using Eq(1).

$$\% \text{ FFA} = M_W \times N \times (A-B) / W \qquad (2)$$

where N is normality of titrant, M_W is molecular weight of KOH, W is the weight of sample, A is volume of titrant used for sample, B is volume of titrant used for blank.

2.3 Design of experiments

The free fatty acids yield of alkaline hydrolysis was taken as response and influenced by various potential variables. The Design Expert software version 8 (INC,USA) was used to generate experiment value from central composite rotatable design (CCRD) procedure and analysed by Response Surface Methodology (RSM) and also for determined the effect of independent variables on response and optimise the alkaline hydrolysis. A 3^4 full factorial experiment design, 24 experiments with 6 replication at design centre were carried out randomly to estimate the error (total of 30 runs) was employed to generate the experiment data for RSM models. The variables include temperature (A), catalyst concentration (B), time (C) and oil to solvent molar ratio (D). The coded values were listed in Table 1.

Table 1: Experimental range and level coded of independent variables for the central composite design

Variables	Units	Type	Range and level (coded)				
			-2	-1	0	+ 1	+2
Temperature	Deg Celcius (^{o}C)	Factor A	50	65	80	95	110
Catalyst concentration	Molarity (M)	Factor B	1.5	1.75	2.00	2.25	2.50
Time	Minute (min)	Factor C	7.5	15.00	22.50	30.00	37.50
Oil to Solvent ratio		Factor D	58	68	78.00	88	98.00
FFA	Percentage (%)	Response	67.1				98

3. Result & Discussion

3.1 Optimisation of alkaline hydrolysed for increased fatty acids yield.

The optimal condition of the alkaline hydrolysis was chosen based on reaction of triglyceride with ethanol and KOH to produce glycerol and fatty acids. The initial results of optimal conditions are as follow: oil/ ethanol ratio, 1:68; KOH concentration, 1.75 M; time, 15 min; temperature 90 °C which is summarized in Table 2, which also shows experiment design and results of CCD for alkaline hydrolysis. The overall second-order as shown in Eq(2) describes the relationship between the variables and the free fatty acids yield in terms of coded values;

$$Y = +67.50 - 0.48A - 2.68B - 2.15C - 1.29D + 2.37AB + 0.20AC - 5.23AD + 1.16BC + 2.74BC + 0.35CD + 2.65A^2 + 6.00B^2 + 5.08C^2 + 6.86D^2 \qquad (2)$$

where *Y* is the predicted response, A-D are actual variables of predictor; temperature (A), catalyst concentration (B), time (C) and oil to solvent molar ratio (D). The positive sign in front of terms reveals synergistic effect while negative sign reveals the antagonistic effect that would indicate the influence of independents variables on the process (Saidi et al., 2013).

3.2 Analysis of Regression model and Statistical

Analysis of variance (ANOVA) for fatty acid yield was used in order to check the adequacy of the empirical model and the results were summarized in Table 2. To measure how well the suggested model fit the experiment data, the parameter such as R^2, *p*-value, F-value, and lack of fit were used (Ceylan, 2008).The actual values are obtained from response data of experimental runs while the predicted values were generated by using the approximation functions based on the quadratic model of CCD (Mazaheri, 2001) and tabulated in Table 3.

Table 2: Analysis of variance (ANOVA) for response surface quadratic model

Source of variance	Sum of squares	Degree of freedom (df)	Mean Square	*F*-Value	*P*-Value Prob>*F*
Model	3,352.67	14	239.48	60.96	< 0.0001
A-Temperature	5.56	1	5.56	1.41	0.2527
B-Catalyst Concentration	172.00	1	172.00	43.78	< 0.0001
C- Time	111.16	1	111.16	28.29	< 0.0001
D- Oil to alcohol ratio	39.91	1	39.91	10.16	0.0061
AB	89.54	1	89.54	22.79	0.0002
AC	0.66	1	0.66	0.17	0.6877
AD	437.33	1	437.33	111.32	< 0.0001
BC	21.51	1	21.51	5.47	0.0335
BD	120.18	1	120.18	30.59	< 0.0001
CD	2.00	1	2.00	0.51	0.4870
A^2	192.84	1	192.84	49.09	< 0.0001
B^2	987.94	1	987.94	251.47	< 0.0001
C^2	706.88	1	706.88	179.93	< 0.0001
D^2	1,292.31	1	1292.31	328.95	< 0.0001
Residual	58.93	15	3.93		
Lack of fit	58.67	10	5.87	112.83	< 0.0001

As according to Table 2, the p-value of the model is less than 0.0001 demonstrating high significance in predicting the response value and the suitability of the deduced model. The significance of all coefficients was established by P-values also shown in same table. Catalyst loading was the most important operating variable based on higher *F*-value compared to other factorial (Koochecki et al, 2009). Another critical determination are the corresponding coefficients of determination $R^2 = 0.9827$, adj-$R^2 = 0.9666$. They were consider relatively high, which indicate good agreement between experimental and predicted data as reported by Little and Hill (1978).

Table 3: Experimental design and results of CCD for alkaline hydrolysis

Run order	Temperature (°C); A	Catalyst concentration (M); B	Time (min); C	Oil to solvent ratio; D	Free Fatty Acids (% FFA)
1	80.00	2.0	22.50	78	67.6
2	80.00	2.0	22.50	78	67.7
3	80.00	2.0	7.50	78	93.3
4	50.00	2.0	22.50	78	78.0
5	80.00	2.5	22.50	78	84.8
6	95.00	2.25	15.00	68	91.7
7	95.00	1.75	15.00	68	98
8	80.00	2.00	22.50	78	67.1
9	65.00	1.75	15.00	88	95.5
10	95.00	2.25	30.00	88	83.9
11	65.00	2.25	15.00	88	91.0
12	80.00	2.00	22.50	98	91.7
13	95.00	1.75	30.00	88	73.8
14	80.00	2.00	22.50	78	67.5
15	65.00	2.25	30.00	88	91.5
16	95.00	2.25	30.00	68	91.9
17	80.00	2.00	22.50	78	67.7
18	65.00	1.75	30.00	68	88.9
19	80.00	2.00	22.50	78	67.6
20	80.00	2.00	22.50	58	97.1
21	65.00	1.75	30.00	88	93.8
22	95.00	1.75	30.00	68	95.4
23	110.00	2.00	22.50	78	77.1
24	80.00	1.50	22.50	78	97.1
25	65.00	2.25	30.00	68	74
26	65.00	1.75	15.00	68	97.1
27	65.00	2.25	15.00	68	80
28	95.00	1.75	15.00	88	84.3
29	80.00	2.00	37.50	78	81.2
30	95.00	2.25	15.00	88	83.1

$R^2 = 0.9827$

R^2 (Pred) $= 0.9008$

R^2 (adj) $= 0.9666$

3.3 Interaction between process variables

ANOVA results in table 2 shows interaction between variables and have significant effect on the yield of FFA. This were determined by *P*-Value < 0.0001 which are interaction between temperature and oil to solvent ratio and interaction between catalyst concentration and oil to solvent ration give most significant effect to the FFA yield. This also can be seen at Figure 1(a), the parallel lines connecting each other in interaction plot shows significant interaction. Therefore, instead of study single variable (as in conventional) the interactions will be investigated which is significance and important for a comprehensive optimisation study.

Figure 1(b) shows the effect of different reaction temperature and oil to solvent ratio on the FFA yield in three dimensional surface response. From the figure, at any point quantity of molar ratio from 68 to 88, the yield of FFA increase proportionally with reaction temperature but the yield augmented when the molar ratio was reduced from 88 to 68 at any constant temperature. The observed phenomena shows increasing reaction temperature enhance the reaction rate therefore enhance the FFA yield (Goyal et al., 2012). The effect of catalyst concentration and temperature shows in Figure 1(c). At low temperature (65 °C) and low catalyst concentration (1.75 M), shows the high yield but at higher temperature the yield become almost the same. Reaction temperature plays a crucial role in determination of reaction rate (Saka and Isayama, 2009).

Figure 1(d) represents the effect of oil to solvent ratio to catalyst concentration. Within the studied of molar ratio, increment in the ratio slightly enhance the yield but at some point the yield decrease when molar ratio increase. This figure also shows influence of catalyst concentration on FFA yield. It can be seen the yield increase at low amount of catalyst.

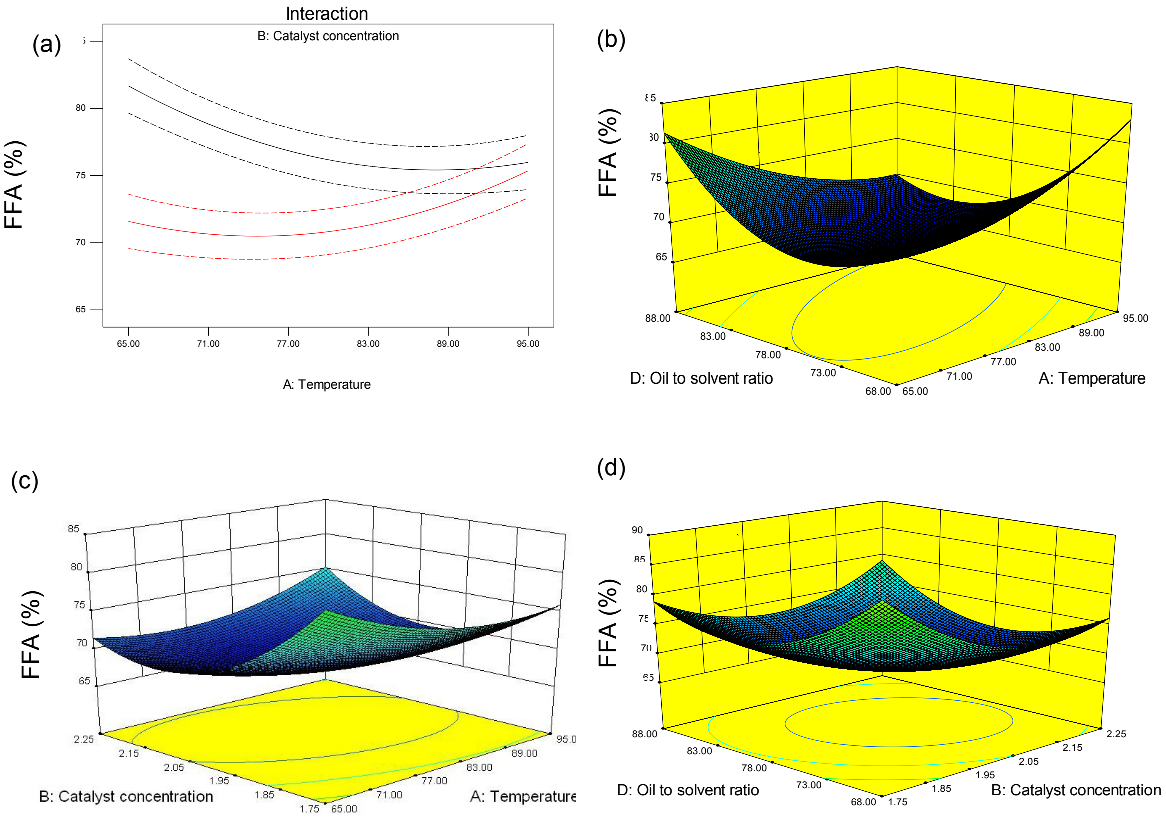

Figure 1: Interaction between (a) Interaction plot (b) Oil to solvent ratio and temperature (c) Catalyst concentration and temperature (d) Oil to solvent ratio and catalyst concentration

Conclusion

Microwave assisted for fatty acids production was carried out to determine the effect of various parameters on FFA yield. In order to optimise the yield, numerical feature of Design Expert software was applied to find the optimum combination condition which result in maximum yield. The highest FFA achieved (98 %) under optimum conditions of 95 °C, 1.75 M of ethanolic KOH concentration, 1:68 oil to solvent ratio and 15 min of reaction time. The model is validated by RSM with R^2 value = 0.9827.

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