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Optimization of Epoxidation of *Camelina sativa* Seed Oil Derived Unsaturated Fatty Acid using Response Surface Methodology

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Abstract—*Vegetable oils are as a potential feedstock due to their inherent quality of renewability, biodegradability and environment-friendly than conventional mineral oil. In this perspective, Camelina sativa may be considered as a potential feedstock for biofuels and industrial chemicals. Its oil contains 82.3% of an unsaturated fatty acid comprising of 48.7% of polyunsaturated fatty acid which can be chemically modified to industrial chemicals and for bio-lubricant base stocks. With this objective, the present study was envisaged so as to optimize the reaction conditions for preparation of its epoxidized fatty acid by response surface methodology (RSM) using central composite design (CCD). The experimental parameters such as molar ratios of unsaturated fatty acid to formic acid and also to hydrogen peroxide along with reaction time and temperatures were evaluated for obtaining desired epoxy moiety in Camelina oil. The optimized reaction conditions for epoxidation of Camelina oil derive unsaturated fatty acid was the molar ratio of unsaturated fatty acid to formic acid and to hydrogen peroxide were estimated to be 1:0.75 and 1:1.5, respectively at the reaction temperature of 47°C with the reaction time of 6 hrs. These reaction conditions resulted in high oxirane oxygen content yield (8.11 %) with >88% modification of the unsaturated double bond to oxirane in Camelina oil, which may be used as bio-lubricants base stocks.*

Keywords*: Camelina oil, Central composite design (CCD), Epoxy fatty acid, Oxirane oxygen content.*

1. INTRODUCTION

The increasing demand for crude petroleum, exhaustion of fossil fuel reserves and environmental pollution are the major key factors for the search of alternative bio-based products. Vegetable oils produced from natural resources may serve as alternative resources of fuels and chemicals. Several vegetable oils are rich in unsaturated fatty acid responsible for poor shelf life. The unsaturated C=C may be chemically modified to introduce various functionality to derive bio-based product.

Camelina sativa is an alternative oilseed crop for fuels and chemicals. The oil content varies from 29 to 41% by weight [1]. The fatty acid composition of Camelina oil reveals that it contains up to 90% of unsaturated fatty acid with an average of 5.8 double bonds per triglyceride. The percentage of unsaturated fatty acid and double bonds per triglyceride of Camelina oil is higher than that of soybean oil (84% and 4.6, respectively) [2]. The iodine value of Camelina oil is >140gI2/100g which may be suitable feedstock to introduce functional group for various industrial applications.

The unsaturated fatty acid is may act as a precursor to introduce different functionality groups, i.e. epoxides and hydroxyl. Epoxidation is the key step to chemically modify the fatty acids for various applications such as plasticizers, stabilizers and biocompatible lubricants [3-4]. Commercially available epoxidized soybean oil (ESO) [5] has been produced in-situ epoxidation with peroxyacetic acid in sulfuric acid, which acts as a catalyst. ESO have used as plasticizers application which was used for food packaging bags. The literature reported that the epoxidation of vegetable oils is mostly catalyzed by a mineral acid, enzymes and ion exchange resins. Cai [6] et al. reported the epoxidation of Sunflower, Soybean, Corn oil and in presence of peroxyacetic acid and sulfuric acid. Somidi [7] et al. studied that the heterogeneous sulfated-SnO2 catalyst was used for epoxidation of Canola oil. On a small-scale manufacture, the epoxidation of karanja oil,

soybean oil was conducted in the presence of a cationic ion exchange resins such as Amberlite IR-120H [8] and KU-2×8 [9] respectively.

The present article discusses the optimization of reaction condition for Performic acid catalyzed epoxidation of Camelina oil using response surface methodology.

2. MATERIALS AND METHODS

2.1 Preparation of unsaturated fatty acid

The unsaturated fatty acid was prepared from Camelina oil. The oil was saponified with potassium hydroxide solution followed by phosphoric acid treatment to obtain free fatty acids. In typical experiments, 100 g of Camelina oil was mixed with 80 ml of water, 60 ml of ethanol, 30 g of KOH refluxed till a transparent solution is observed. It was followed by addition of H_3PO_4 and washed with water till mixture was free from acid. The fatty acid mixture was dried under vacuum. Further, unsaturated fatty acid was obtained by using Urea inclusion method [10]. For this, the fatty acid mixture (40 g) was mixed in methanol (400 ml) in a conical flask (1000 ml) and the mixture was boiled at 65 °C underwater bath followed by slow addition of urea (30 g) after this the reaction mixture placed to cool at 7-8 °C for overnight. The saturated fatty acid forms a complex with Urea (Urea+SFA complex) and was removed by water washing.

2.2 Preparation of Epoxidized fatty acid

The epoxidation of Camelina-based unsaturated fatty acid as shown in Fig. 1. The reaction of epoxidation was conducted in a flat bottom flask where 15 g of unsaturated fatty acid was added formic acid (98-100%) under ice bath at 4°C. Then 30% aqueous solution of hydrogen peroxide was slowly added dropwise with continuous stirring and reaction was preceded up to the desired temperature. The product was cooled to room temperature, washed with distilled water and dried under vacuum to obtain colourless transparent, viscous liquid.

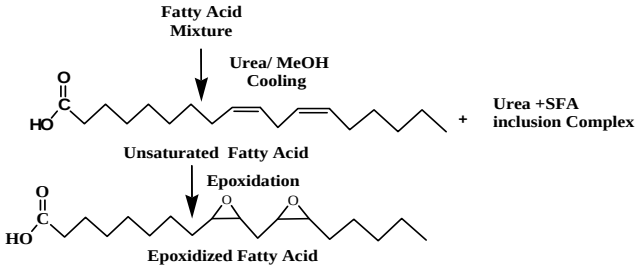

Fig. 1 The process of preparation of epoxy fatty acid from unsaturated fatty acid of Camelina oil

2.3 Process Optimization

The reaction conditions of epoxidation of camelina-based unsaturated fatty acid were optimized by using design expert software version 10. The experimental design for epoxidation reaction was carried out by using 2-level Central composite design (CCD) with three independent variables such as molar ratio of unsaturated fatty acid to a formic acid of 0.5-01, molar ratio of unsaturated fatty acid to hydrogen peroxide of 1-2, temperature 40-45 °C etc.

3. RESULTS AND DISCUSSION

Physicochemical properties of saponified Camelina oil based free fatty acid was evaluated where the iodine value = 143 gI_2/100g and acid value = 212 mg KOH/g. Further Camelina oil based unsaturated fatty acid was characterized for physicochemical properties where iodine value 162 gI_2/100g which implies the presence of high unsaturation moiety and acid value = 212 mg KOH/g in the oil.

Epoxidation of unsaturated fatty acid was carried out at RSM optimized condition with two molar ratio of unsaturated fatty acid : formic acid and also with hydrogen peroxide was 1:0.75:1.5 stirring at 600 rpm, reaction temperature at 46.7 °C and time for 6 hr. Resulting the maximum percentage of oxirane oxygen content is 8.1 which shows the extent of epoxy content up to >88% conversion of the double bond moiety and the epoxidized fatty acid was characterized for physicochemical properties where iodine value decreases from 162 to 9.49 gI_2/100g which further depicted >94% conversion during epoxidation of unsaturated fatty acid and its acid value 178 mg KOH/g.

3.1 Process Optimization by Response Surface Methodology (RSM)

3.1.1 Model analysis

Response Surface Methodology (RSM) has been used to analyze the experimental findings for optimization of process variables and generated the following second-order polynomial Eq. (1)

Oxirane oxygen content wt%

$$=+7.75 + 0.79 \times A + 0.73 \times B + 0.47 \times C - 0.76 \times A \times B + 0.26 \times A \times C - 0.11 \times B \times C - 0.63 \times A^2 - 0.74 \times B^2 - 0.14 \times C^2 \quad \text{(1)}$$

Where A: Molar ratio of unsaturated fatty acid to Formic acid, B: molar ratio of unsaturated fatty acid to hydrogen peroxide, C: Temperature.

The predicted values for the conversion of OOC yield calculated using Eq. (1) was shown in Table 1. The deviation % was very low indicates the optimum conditions for predicted values are similar to experimental values. The adequacy of the model was analyzed using analysis of variances and results were shown in Table 2. It is more evidence that the regression model was significant (p-value <0.0001) indicates that model equation described the response value. The F-value of this model was 168.63 implies the

model was highly significant. The lack of fit F-value was 0.38 implies the lack of fit was not significant.

Table 1 Prediction of response factor for various experimental parameter

Molar ratio a	Molar ratio b	Temperature (°C)	Reaction time (h)	Experimental value	Predicted value	Std. dev.
0.75	1.5	46.70	6	8.2	8.14	0.006

aMolar ratio of unsaturated fatty acid to Formic acid; bMolar ratio of unsaturated fatty acid to Formic acid

The precision of the model was evaluated in Table 3. The multiple regression coefficient (R^2) indicates that reasonable precision of the model fitted. The R^2 value is always between 0 and 1. This value implies the aptness of the model. R^2 value should be close to 1 for good statistical model. The regression value for maximum oxirane oxygen content was 0.9935 (close to 1) indicates a good correlation between the experimental and predicted response.

Table 2 ANOVA for response surface quadratic model

Source	Sum of Squares	Df	Mean Square	F - Value	p-value Prob. > F	
Model	36.53	9	4.06	168.63	< 0.0001	significant
A-Formic acid	8.56	1	8.56	355.42	< 0.0001	
B-H2O2	7.23	1	7.23	300.34	< 0.0001	
C-temperature	2.99	1	2.99	124.25	< 0.0001	
AB	4.65	1	4.65	193.23	< 0.0001	
AC	0.55	1	0.55	22.9	0.0007	
BC	0.1	1	0.1	4.21	0.0674	
A2	5.78	1	5.78	240.31	< 0.0001	
B2	7.88	1	7.88	327.51	< 0.0001	
C2	0.28	1	0.28	11.5	0.0069	
Residual	0.24	10	0.024			
Lack of Fit	0.066	5	0.013	0.38	0.8469	not significant
Pure Error	0.18	5	0.035			
Cor Total	36.77	19				

Table 3 Statistical data for response surface quadratic model

Statistical Terms	Results
Std. Dev.	0.16
Mean	6.72
C.V. %	2.31
PRESS	0.8
R-Squared	0.9935
Adj. R-Squared	0.9876
Pred. R-Squared	0.9783
Adeq. Precision	41.076

The response surface plots representing the effect of molar ratio of unsaturated to formic acid also to hydrogen peroxide, temperature and their interaction on oxirane oxygen content were shown in Fig 2-4. As gradually increase in temperature, the OOC yield increase in linear form, while the excess of the molar ratio of unsaturated fatty acid to formic acid from 0.75 showed no significant effect on OOC yield which was shown in Fig 2. It has shown there was no significant effect on OOC content with temperature variation which was shown in Fig 3. The molar ratio of unsaturated fatty acid to hydrogen peroxide depicted curvilinear surface which indicates that the excess of molar ratio unsaturated fatty acid to hydrogen peroxide from 1.5 showed didn't significantly increases. The molar ratio of unsaturated fatty acid to hydrogen peroxide and also to formic acid has significant effects on OOC yield which was shown in Figure 4. It was indicated that the molar ratio of unsaturated fatty acid to formic acid 0.75 and molar ratio of unsaturated fatty acid to hydrogen peroxide 1.5 showed the maximum yield of OOC.

3.1.2 Validation of the quadratic model

The predicted response from the quadratic model was increased linearly indicating the experimental values were achieved within the range of predicted values which was shown in Fig 5. The model showed that the maximum conversion of oxirane oxygen content (7.75 %) of epoxy fatty acid by using the optimum conditions such as the molar ratio of unsaturated fatty acid to formic acid was 0.75 and molar ratio of unsaturated fatty acid to hydrogen peroxide was 1.5 and reaction temperature was 42.5 °C for 6 hr. To validate the suggested optimum parameter for maximum yield of OOC was examined by performing the experiments with aforesaid mention reaction conditions. Resulting, the oxirane oxygen content was 7.66% which was nearly equal to the predicted value.

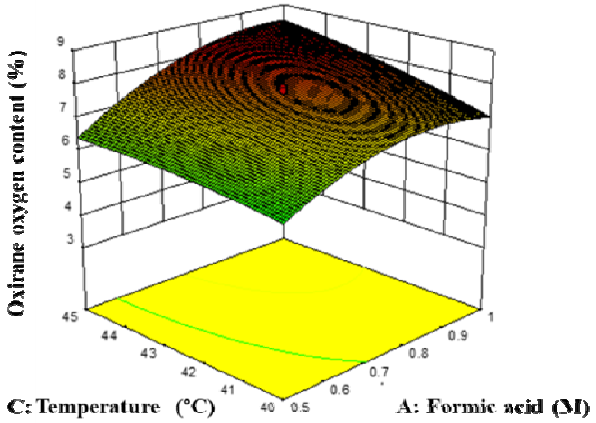

Fig.2 3D Response surface plot of molar ratio of unsaturated fatty acid to formic acid and temperature as a yield of OOC

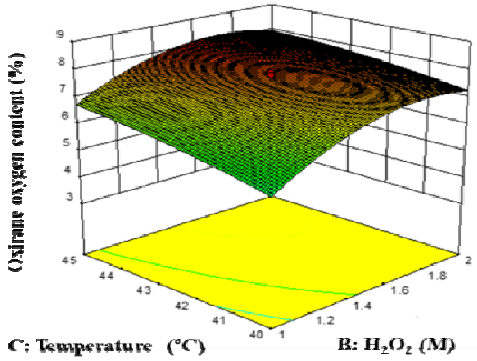

Fig.3 3D Response surface plot of molar ratio of unsaturated fatty acid to hydrogen peroxide and temperature as a yield of OOC

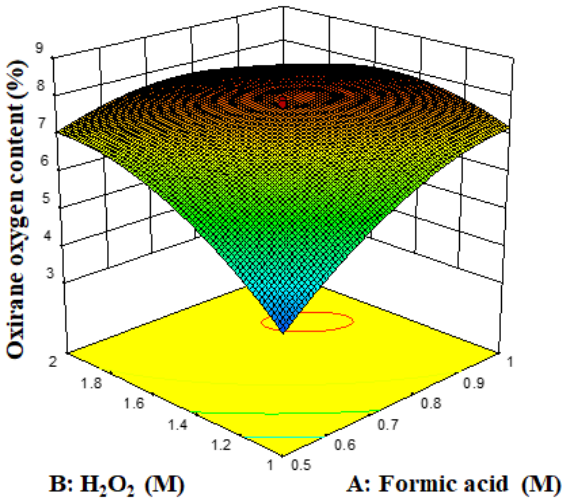

Fig.4 3D Response surface plot of molar ratio of unsaturated fatty acid to formic acid and molar ratio of unsaturated fatty acid to hydrogen peroxide as a yield of OOC

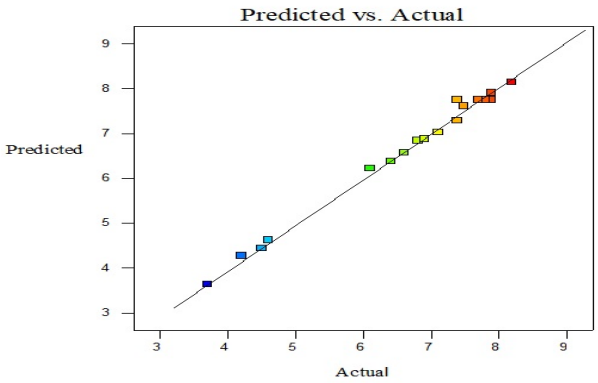

Fig 5. Graphical comparison between the response of predicted values and experimental values

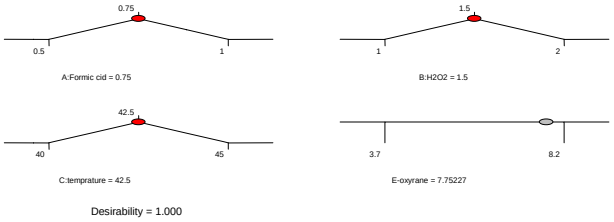

Fig 6. Verification of experimental values under optimum reaction conditions

4. CONCLUSIONS

In this present study, We have emphasized that Camelina oil based epoxy fatty acid have a great potential and may be considered as precursor of bio-lubricant base stock. The reaction conditions of epoxidation were optimized with Response Surface Methodology. The experimental parameters such as molar ratio of unsaturated fatty acid to formic acid and hydrogen peroxide, reaction temperature, were optimized for the maximum yield % of Oxirane oxygen content (OOC). The effect of molar ratio of unsaturated fatty acid to formic was found to be the most significant. The optimized condition for epoxidation of Camelina oil derived fatty acid was found to be 1:0.75 of molar ratio of unsaturated fatty acid to formic acid, 1:1.5 of molar ratio of unsaturated fatty acid to hydrogen peroxide, reaction temperature 46.7 °C resulting maximum 8.11 % yield of OOC corresponding to >88% conversion of double bond to OOC. The Quadratic polynomial models showed that that the predicted value was within the same range of experimental value which was further validated by performing with additional experiments at optimized condition.

5. ACKNOWLEDGEMENTS

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