

# Optimization of starch oleate derivatives from native corn and hydrolyzed corn starch by response surface methodology

Amol C. Kshirsagar, Rekha S. Singhal \*

*Food Engineering and Technology Department, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400 019, India*

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## Abstract

Conditions for the preparation of starch oleates of native and hydrolyzed corn starch were compared with the aim of developing a hydrophobic starch as gum arabic substitute for use as a wall material in microencapsulation. Optimization of the reaction parameters for maximization of degree of substitution (DS) of starch oleate was carried out using response surface methodology (RSM). Corn starch and maltodextrins of dextrose equivalent (DE) 12 and 18 were used in the study. A central composite rotatable experimental design (CCRD) was chosen to explain the combined effects of the three parameters, viz., oleic acid concentration, reaction time and reaction temperature to design minimum number of experiments. The optimal levels of the three parameters for corn starch (50 g) were an oleic acid concentration of 1.2 g, a reaction time of 201 min at 160 °C, wherein a maximum DS of 0.021 was obtained. For maltodextrin of 12 DE, 1.53 g oleic acid concentration, a reaction time of 334 min at 150 °C gave a corresponding DS of 0.0353. Similarly, for 18 DE, 1.36 g oleic acid concentration, a reaction time of 300 min at 129 °C gave a DS of 0.053. The optimized samples were compared to gum arabic with respect to emulsifying capacity.

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**Keywords:** Starch oleate derivatives; Corn starch; Hydrolyzed starch; Response surface methodology

## 1. Introduction

Encapsulation by spray drying is one of the best-known and economical methods of providing solutions, emulsions, and dispersions in dry form. The key to optimum encapsulation of these ingredients is dependent on the performance of the encapsulating agents. Among the several encapsulating agents, emulsifying starches and gums, essentially gum arabic, serve as the most common carrier materials (Reineccius, 1989). Gum arabic has now become the traditional standard (Thevenet, 1988). Gum arabic has some inherent shortcomings. Being a tree exudate, its supply and quality is dependent on the climatic conditions. Its cost factor is also not very advantageous. These reasons have prompted many manufactures to look for substitutes for gum arabic

for use as a wall material for encapsulation of sensitive food constituents.

Native starch and starch hydrolysis products are hydrophilic, and has no affinity for hydrophobic substances such as oils. However, modifying the starch with fatty acids can introduce hydrophobic groups. Reports on the reaction of starches with fatty acids are scant. Starch–lipid interactions of linoleic acid (Kapusniak & Siemion, 2005) and stearic acid (Varavinit, Chaokasem, & Shobsngob, 2001) have been reported. We have been working on octadecenyl succinic anhydride for introduction of hydrophobic group in the hydroxyl group of the starch. As a strategy, esterification of starch with oleic acid was also carried out for the preparation of starch oleates. Native starch oleates cannot be used for encapsulation due to their high viscosity, thereby necessitating hydrolysis. Most of the patented information available in this regard indicate modification and its subsequent hydrolysis. Hence our initial attempts were made to check the sequence of modification, i.e., modification followed

\* Corresponding author. Tel.: +91 022 24145616; fax: +91 022 24145614.

E-mail address: [rekha@udct.org](mailto:rekha@udct.org) (R.S. Singhal).

by hydrolysis, or hydrolysis followed by modification. Herein, we report modification followed by hydrolysis. For this purpose, we carried out the modification of native corn starch and maltodextrins of DE of 12 and 18. The starches modified in this way could also act as emulsion stabilizers.

To accomplish esterification, oleic acid was first coated on the surface of starch granules. The coated granules were used for esterification. The synthesis was monitored by measuring the degree of substitution (DS).

The present work reports on the synthesis of starch oleates by esterification of starch with oleic acid. Response surface methodology (RSM) was chosen to explain the combined effects of the three parameters, viz., oleic acid concentration, reaction time and reaction temperature on the DS. Native corn starch and maltodextrins of DE of 12 and 18 were compared with respect to DS during modification.

## 2. Materials and methods

### 2.1. Materials

Corn starch was obtained from Anil starch, Ahmedabad, India. Maltodextrin of 12 DE was obtained from Roquette, France, while that of 18 DE was obtained from Gujarat Ambuja, Baroda. All other reagents used in this work were of analytical grade.

### 2.2. Methods

#### 2.2.1. Effect of processing parameters on esterification of starches

Oleic acid concentration (0.7, 0.9, 1.2, 1.5, 1.7 g) was dissolved in 40 ml of 95% ethanol. Fifty grams of starch (native, 12 DE and 18 DE) was slowly added to obtain a slurry and thoroughly mixed. The granulated starch was heated in an oven at different temperature (77, 95, 120, 145, 162 °C) for various times at (58, 120, 210, 300, 362 min). Oleic acid concentration, reaction temperature and duration of reaction were the processing parameters that were studied with respect to their DS (Table 1). The range of these parameters was selected on the basis of initial experiments.

#### 2.2.2. Determination of DS of oleic acid substitution

Removal of unesterified oleic acid was accomplished by the addition of 100 ml of absolute alcohol to about 15 g of starch oleate with constant stirring for about 10 min. The ethanol supernatant was decanted. The residue was rewashed with 100 ml ethanol and the residual starch dried at 80 °C for 1 h to evaporate the residual ethanol. A sample (5 g) of the resulting clean, dry starch oleate was accurately weighed and dispersed in 50 ml water containing 25 ml of 0.5 M NaOH followed by shaking on magnetic stirrer at room temperature (30 ± 2 °C) for 30 min. Excess NaOH was then titrated

Table 1  
Experimental design of starch, 12 DE and 18 DE Maltodextrin

No.	Coded values and actual values		
	$X_1$	$X_2$	$X_3$
1	−1 (0.9)	−1 (120)	−1 (95)
2	1 (1.5)	−1 (120)	−1 (95)
3	−1 (0.9)	1 (300)	−1 (95)
4	1 (1.5)	1 (300)	−1 (95)
5	−1 (0.9)	−1 (120)	1 (145)
6	1 (1.5)	−1 (120)	1 (145)
7	−1 (0.9)	1 (300)	1 (145)
8	1 (1.5)	1 (300)	1 (145)
9	−1.68 (0.7)	0 (210)	0 (120)
10	1.68 (1.7)	0 (210)	0 (120)
11	0 (1.2)	−1.68 (58.6)	0 (120)
12	0 (1.2)	1.68 (362)	0 (120)
13	0 (1.2)	0 (210)	−1.68 (77)
14	0 (1.2)	0 (210)	1.68 (162)
15	0 (1.2)	0 (210)	0 (120)
16	0 (1.2)	0 (210)	0 (120)
17	0 (1.2)	0 (210)	0 (120)
18	0 (1.2)	0 (210)	0 (120)
19	0 (1.2)	0 (210)	0 (120)
20	0 (1.2)	0 (210)	0 (120)

Actual values are given in parentheses;  $X_1$ ,  $X_2$ , and  $X_3$  are oleic acid, reaction time, and reaction temperature.

to pH 7 with 0.1 N HCl. The DS of oleic acid was calculated according to the equation below (Rutenberg & Solarek, 1984):

$$W = \frac{(\text{Blank} - \text{Sample}) \times M \times N \times 100}{\text{Weight of the sample, g} \times 1000}$$

where  $W$  = % Oleic acid substitution

Blank = Volume of HCl required for blank titration

Sample = Volume of HCl required for sample titration

$N$  = Normality of HCl solution

$M$  = Molecular weight of oleic acid = 282

$$\text{DS} = \frac{162 \times W}{100 \times M - (M - 1) \times W}$$

Hence, for starch oleate  $\text{DS} = 162 \times W / (28200 - 281 \times W)$

### 2.3. Response surface methodology

RSM is an empirical statistical modeling technique employed for multiple regression analysis using quantitative data obtained from designed experiments to solve multivariable equations simultaneously (Rao, Kim, & Rhee, 2000). RSM was performed to optimize oleic acid concentration, time and temperature to obtain maximum DS using central composite design (CCD). A set of 20 experiments was performed with three variables, each variable varied at five levels ( $\alpha = 1.68$ ). For statistical calculations, the relationship between the coded values and actual values are described as the following equation:

$$X_i = \frac{A_i - A_0}{\Delta A}$$

where,  $X_i$  is coded value of variable;  $A_i$  the actual value of variable;  $A_0$  the actual value of the  $A_i$  at the center point; and  $\Delta A$  the step change of variable. The design matrix is shown in Table 1. The DS is taken as response. The experiments were carried out in triplicate. The data were modelled using an equation of the form:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j$$

where,  $Y$  is the predicted response;  $\beta_0$  a constant;  $\beta_i$  the linear coefficient;  $\beta_{ii}$  the squared coefficient and  $\beta_{ij}$  the cross-product coefficient.

The software Design Expert Version 6.0.10 was used to analyze the results. By keeping one variable at its optimum level, three-dimensional plots of two factors verses DS were drawn, and corresponding contour plots was obtained.

#### 2.4. Emulsification activity

This was measured using the method reported by Vishwanathan (1999). 0.025% and 0.05% w/w of the starch oleates were dissolved in 15 ml water. Ten micro-liters of oil phase (heptane and toluene, individually) was then added. The suspension was then homogenized using a shear homogenizer at 5000 rpm for 3 min. The emulsion formed was allowed to settle and the turbidity was measured using a Hach turbidimeter 2001P, Germany. The blank turbidity was also measured without the

oil phase. The values reported here are the differences between the turbidity with and without the oil phase. Gum arabic and native starch was used as a standard for comparison.

### 3. Results and discussion

#### 3.1. Combined effect of three different components on DS

To examine the combined effect of three different components (independent variables) on DS, a central composite factorial design of 1–14 experiments were performed at different combinations, and those from 15–20 were under same conditions (Table 1). The actual MS obtained in experiments and predicted MS produced by the model are given in Table 2. The application of RSM yielded the following regression equation, which is the empirical relation between DS ( $Y$ ) and the independent variables in coded units.

For corn starch

$$Y = -0.059 + 0.055X_1 + 5.53 \times 10^{-5}X_2 + 3.07 \times 10^{-4}X_3 - 0.022X_1^2 + 8.95 \times 10^{-9}X_2^2 + 6.02 \times 10^{-7}X_3^2 + 7.65 \times 10^{-5}X_1X_2 - 8.3 \times 10^{-5}X_1X_3 - 1 \times 10^{-6}X_2X_3$$

For 12 DE maltodextrin

$$Y = -0.022 + 0.052X_1 + 5.52 \times 10^{-5}X_2 - 4.51 \times 10^{-4}X_3 - 0.027X_1^2 - 3.72 \times 10^{-7}X_2^2 + 1.26 \times 10^{-6}X_3^2 + 3.17 \times 10^{-5}X_1X_2 + 1.60 \times 10^{-4}X_1X_3 + 1.03 \times 10^{-6}X_2X_3$$

Table 2

Experimental design and responses for the DS of starch, 12 DE and 18 DE maltodextrin and predicted values of DS

No.	Actual values			Degree of Substitution, DS $\times 10^{-3}$					
	$X_1$	$X_2$	$X_3$	Starch		12 DE		18 DE	
				Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.9	120	95	4.3 $\pm$ 0.72	3.5	1.5 $\pm$ 0.19	1.1	13.0 $\pm$ 0.13	12.1
2	1.5	120	95	5.7 $\pm$ 0.87	4.8	4.4 $\pm$ 1.15	3.9	13.5 $\pm$ 1.47	14.7
3	0.9	300	95	11.3 $\pm$ 1.80	9.4	6.4 $\pm$ 1.79	5.5	16.0 $\pm$ 1.28	17.0
4	1.5	300	95	17.2 $\pm$ 0.78	19.0	11.4 $\pm$ 1.37	11.7	26.0 $\pm$ 1.37	27.1
5	0.9	120	145	19.6 $\pm$ 8.13	16.4	5.5 $\pm$ 1.56	7.0	7.2 $\pm$ 2.56	9.3
6	1.5	120	145	14.8 $\pm$ 9.08	15.2	12.0 $\pm$ 1.08	14.7	19.0 $\pm$ 1.08	21.1
7	0.9	300	145	13.7 $\pm$ 1.54	13.1	18.6 $\pm$ 1.85	20.9	33.0 $\pm$ 2.54	34.9
8	1.5	300	145	20.8 $\pm$ 1.95	20.2	29.8 $\pm$ 1.46	32.0	50.0 $\pm$ 1.86	54.1
9	0.7	210	120	1.8 $\pm$ 1.35	5.0	4.5 $\pm$ 0.35	4.0	16.0 $\pm$ 0.35	15.1
10	1.7	210	120	13.2 $\pm$ 0.16	12.1	17.6 $\pm$ 1.57	15.7	37.0 $\pm$ 0.06	33.5
11	1.2	58.6	120	7.9 $\pm$ 0.19	9.9	0.1 $\pm$ 0.18	0.9	9.0 $\pm$ 1.75	7.8
12	1.2	362	120	19.0 $\pm$ 0.19	19.1	18.6 $\pm$ 1.92	17.3	43.0 $\pm$ 2.32	39.7
13	1.2	210	77.5	9.0 $\pm$ 1.95	9.4	6.2 $\pm$ 1.15	8.0	17.0 $\pm$ 1.25	17.1
14	1.2	210	162	19.7 $\pm$ 0.55	21.3	34.3 $\pm$ 1.95	30.1	42.0 $\pm$ 1.95	37.5
15	1.2	210	120	14.2 $\pm$ 0.87	14.3	16.4 $\pm$ 1.57	16.8	47.0 $\pm$ 1.16	47.0
16	1.2	210	120	14.5 $\pm$ 1.94	14.3	17.3 $\pm$ 1.24	16.8	46.0 $\pm$ 1.24	47.0
17	1.2	210	120	14.8 $\pm$ 1.56	14.3	16.4 $\pm$ 1.56	16.8	48.0 $\pm$ 1.66	47.0
18	1.2	210	120	13.9 $\pm$ 0.66	14.3	17.9 $\pm$ 0.66	16.8	46.0 $\pm$ 0.66	47.0
19	1.2	210	120	14.6 $\pm$ 0.66	14.3	15.9 $\pm$ 0.66	16.8	46.0 $\pm$ 0.66	47.0
20	1.2	210	120	13.9 $\pm$ 1.26	14.3	16.0 $\pm$ 1.86	16.8	48.0 $\pm$ 1.66	47.0

All values are means  $\pm$  SD of three determinations.

Table 3  
ANOVA for quadratic model

Source	SS $\times 10^{-5}$			DF			F-value			P > F		
	Starch	12 DE	18 DE	Starch	12 DE	18 DE	Starch	12 DE	18 DE	Starch	12 DE	18 DE
Model	47	147	458	9	9	9	13.86	30.8	60.3	0.0002	<0.0001	<0.0001
Residual	3.8	5.1	8.4	10	10	10						
Lack of fit	3.7	4.8	7.9	5	5	5	52.10	15.2	16.4	0.003	0.0048	0.040
Pure error	$7.2 \times 10^{-7}$	$3.1 \times 10^{-6}$	$4.8 \times 10^{-6}$	5	5	5						
Total	51	8.9	466	19	19	19						

SS, sum of squares; DF, degree of freedom;  $R^2 = 0.926$ , Adj  $R$ -Squared = 0.859, CV = 14.82% for starch;  $R^2 = 0.965$ , Adj  $R$ -Squared = 0.934, CV = 16.74% for 12 DE;  $R^2 = 0.982$ , Adj  $R$ -Squared = 0.966, CV = 9.33% for 18 DE.

Table 4  
Model fitting results for DS

Model	Coefficient			t-value			P-value		
	Starch	12 DE	18 DE	Starch	12 DE	18 DE	Starch	12 DE	18 DE
Intercept	$-4.3 \times 10^{-2}$	$-2.2 \times 10^{-2}$	$-2.4 \times 10^{-1}$	17.88	18.09	39.63	$2.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$
$X_1$	$3.8 \times 10^{-2}$	$5.2 \times 10^{-2}$	$1.9 \times 10^{-1}$	3.98	5.63	6.95	$2.6 \times 10^{-3}$	$1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$
$X_2$	$5.9 \times 10^{-5}$	$5.5 \times 10^{-5}$	$1.8 \times 10^{-4}$	5.16	8.81	12.06	$4.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$
$X_3$	$2.83 \times 10^{-4}$	$-4.5 \times 10^{-4}$	$2.0 \times 10^{-3}$	6.69	10.64	7.71	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$
$X_1^2$	$-1.85 \times 10^{-2}$	$-2.8 \times 10^{-2}$	$-9.0 \times 10^{-2}$	-3.92	-4.07	-10.48	$2.9 \times 10^{-3}$	$<1.0 \times 10^{-4}$	$<1.0 \times 10^{-4}$
$X_2^2$	$-8.9 \times 10^{-8}$	$-3.7 \times 10^{-7}$	$-1.0 \times 10^{-6}$	0.14	-5.07	-10.71	$8.9 \times 10^{-1}$	$1.5 \times 10^{-2}$	$<1.0 \times 10^{-4}$
$X_3^2$	$-1.1 \times 10^{-6}$	$1.2 \times 10^{-6}$	$-1.1 \times 10^{-5}$	0.75	1.34	-9.09	$4.7 \times 10^{-1}$	$1.7 \times 10^{-2}$	$<1.0 \times 10^{-4}$
$X_1X_2$	$1.7 \times 10^{-5}$	$3.1 \times 10^{-5}$	$6.8 \times 10^{-5}$	2.97	1.06	1.79	$1.4 \times 10^{-2}$	$1.9 \times 10^{-1}$	$1.0 \times 10^{-1}$
$X_1X_3$	$6.8 \times 10^{-5}$	$1.6 \times 10^{-4}$	$3.0 \times 10^{-4}$	-0.90	1.50	2.22	$3.9 \times 10^{-1}$	$1.5 \times 10^{-1}$	$5.0 \times 10^{-2}$
$X_2X_3$	$-5.5 \times 10^{-9}$	$1.0 \times 10^{-6}$	$2.2 \times 10^{-6}$	-3.33	2.93	5.02	$7.7 \times 10^{-3}$	$9.7 \times 10^{-1}$	$5.0 \times 10^{-4}$

For 18 DE maltodextrin

$$Y = -0.239 + 0.185X_1 + 1.75 \times 10^{-4}X_2 + 2.00 \times 10^{-3}X_3 - 0.09X_1^2 - 1.08 \times 10^{-6}X_2^2 - 1.08 \times 10^{-5}X_3^2 + 6.86 \times 10^{-5}X_1X_2 + 3.04 \times 10^{-4}X_1X_3 + 2.26 \times 10^{-6}X_2X_3$$

where  $Y$  is the DS of the modified starch, and  $X_1$ ,  $X_2$  and  $X_3$  are the coded values of the test variables, viz., oleic acid concentration, reaction time and reaction temperature, respectively.

The results of the second order response surface model fitting in the form of ANOVA are given in Table 3. The ANOVA of quadratic regression model demonstrates that the model is significant, as is evident from Fisher's  $F$ -test value being 13.86, 30.8 and 60.3 for corn starch, maltodextrin of 12 DE and maltodextrin of 18 DE, respectively, with a very low probability value [(Pmodel >  $F$ ) = 0.0002] for corn starch and [(Pmodel >  $F$ ) = 0.0001] for maltodextrins of 12 DE and 18 DE. The goodness of the fit of the model was checked by determination coefficient ( $R^2$ ). In these case, the value of determination coefficient for corn starch ( $R^2 = 0.926$ ), maltodextrins of 12 DE ( $R^2 = 0.965$ ) and 18 DE ( $R^2 = 0.982$ ) indicates that only 7.42% of corn starch, 3.47% of 12 DE and 1.81% of 18 DE total variations were not explained by the model. The value of adjusted determination coefficient  $R^2_{adj}$  (0.859 for corn, 0.934 for 12 DE and 0.966 for 18 DE) is also high to advocate for high significances of the model. At same time, a relatively low value of the coefficient of

variation 14.28% for corn starch, 16.74% for 12 DE and 9.33% for 18 DE indicates a better precision and reliability of experiments carried out for 18 DE as compared to 12 DE and corn starch.

The significance of each term was determined by Student's  $t$ -test and  $P$ -values which are listed in Table 4. The larger the magnitude of  $t$ -value and smaller the  $P$ -value, the more significant is the corresponding coefficient. For

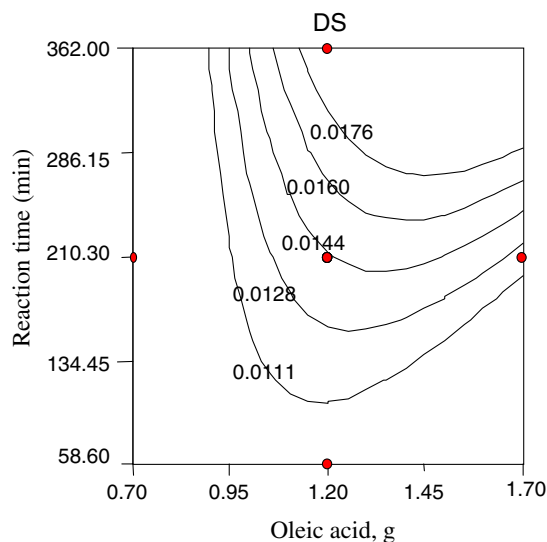


Fig. 1. Contour plots for cornstarch; the effect of oleic acid and reaction time on DS. Other variables are held at zero level.

corn starch the coefficient estimates and the corresponding  $P$ -values suggest that, among the test variables used in the study,  $X_1$  (oleic acid concentration),  $X_2$  (reaction time),  $X_3$  (reaction temperature),  $X_1 \times X_2$  (oleic acid concentration  $\times$  reaction time) and  $X_2 \times X_3$  (reaction time  $\times$  reaction temperature) and  $X_1^2$  (oleic acid concentration)<sup>2</sup> are significant model terms with  $P$ -values of less than 0.05. Reaction temperature ( $P < 0.001$ ) has the largest effect on DS. Other interactions were found to be insignificant. For 12 DE, the liner terms  $X_1$  (oleic acid concentration),  $X_2$  (reaction time),  $X_3$  (reaction temperature), and squares of  $X_1$  (oleic acid concentration) are significant model terms with  $P$ -values of less than 0.05. Oleic acid concentration, reaction time, and reaction temperature and square of oleic acid concentration term with ( $P < 0.0001$ ) have largest effect

on DS. Similarly for 18 DE, the liner terms  $X_1$  (oleic acid concentration),  $X_2$  (reaction time),  $X_3$  (reaction temperature), and their squares are significant model terms with  $P$ -values of less than 0.0001 having largest effect on DS. It is clear that the interactive terms of oleic acid concentration, reaction time and reaction temperature are the least significant ( $P > 0.05$ ).

The 3D responses and 2D contour plots are generally the graphical representations of the regression equation; the 2D contour plots are presented in Figs. 1–9, from which the values of DS for different concentration of variables can be predicted. Each contour curve represents an infinite number of combinations of two variables with the others maintained at zero level. The maximum predicted value is indicated by the surface confined by the smallest ellipse

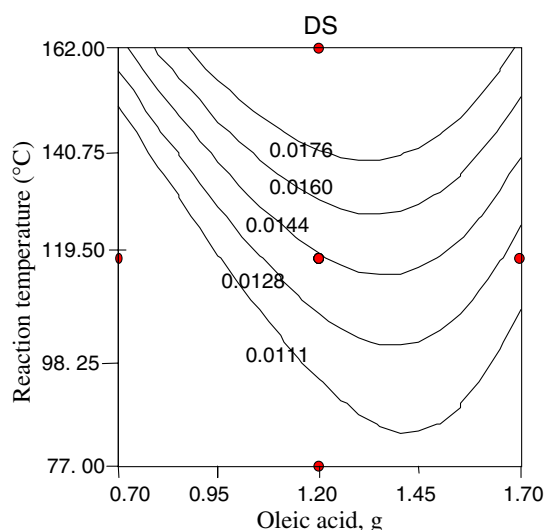


Fig. 2. Contour plots for cornstarch; the effect of oleic acid and reaction temperature on DS. Other variables are held at zero level.

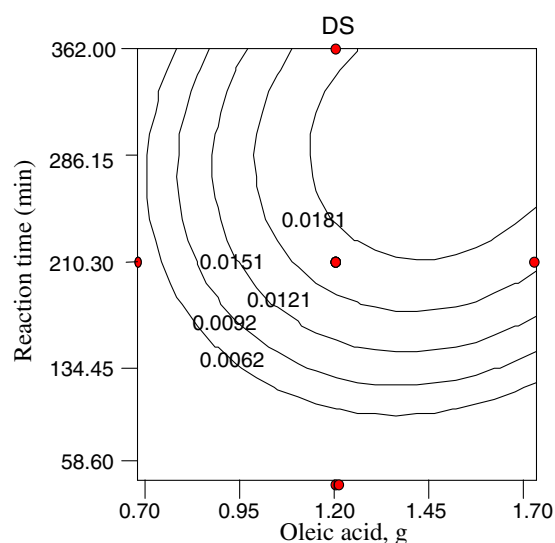


Fig. 4. Contour plots for 12 DE; the effect of oleic acid and reaction time on DS. Other variables are held at zero level.

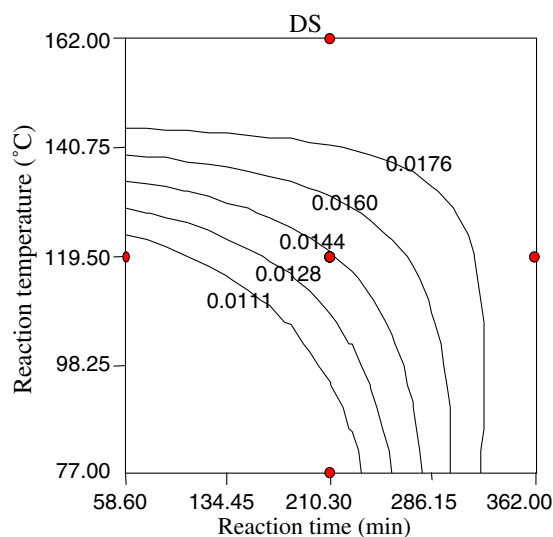


Fig. 3. Contour plots for cornstarch; the effect of reaction time and reaction temperature on DS. Other variables are held at zero level.

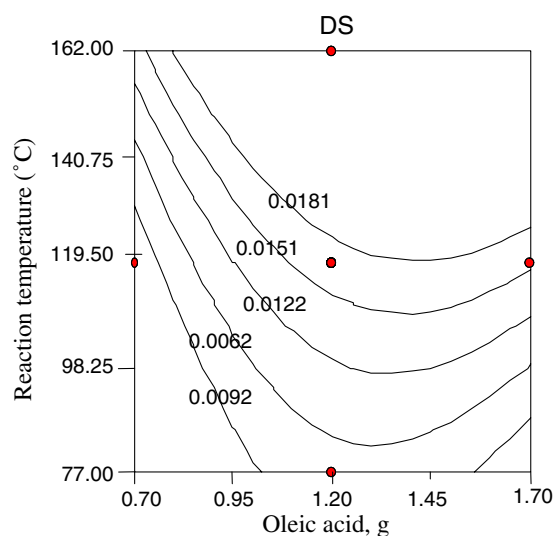


Fig. 5. Contour plots for 12 DE; the effect of oleic acid and reaction temperature on DS. Other variables are held at zero level.

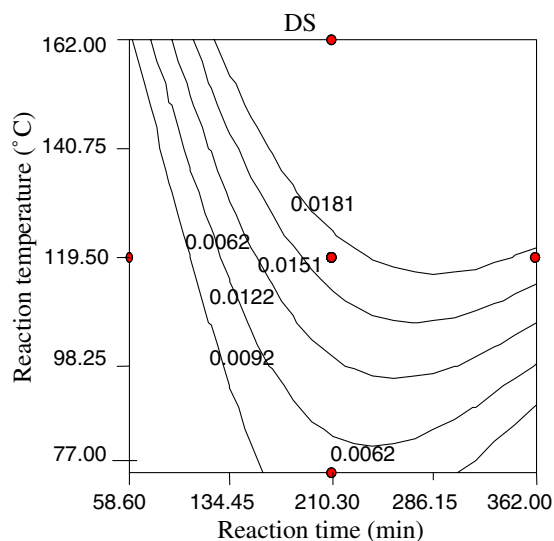


Fig. 6. Contour plots for 12 DE; the effect of reaction time and reaction temperature on DS. Other variables are held at zero level.

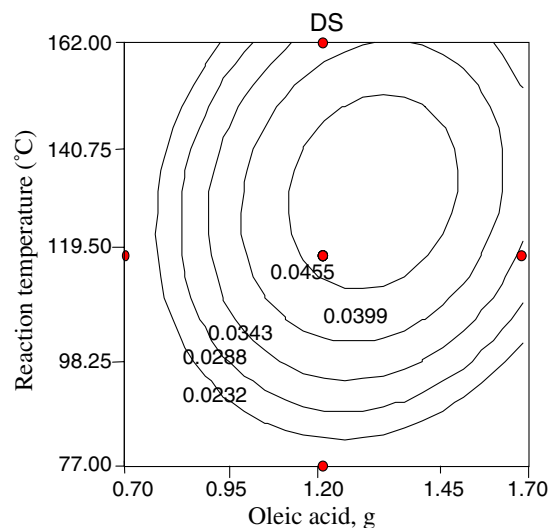


Fig. 8. Contour plots for 18 DE; the effect of oleic acid and reaction temperature on DS. Other variables are held at zero level.

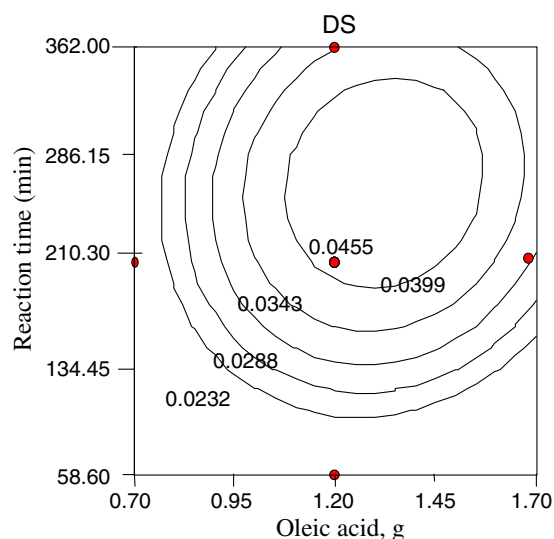


Fig. 7. Contour plots for 18 DE; the effect of oleic acid and reaction time on DS. Other variables are held at zero level.

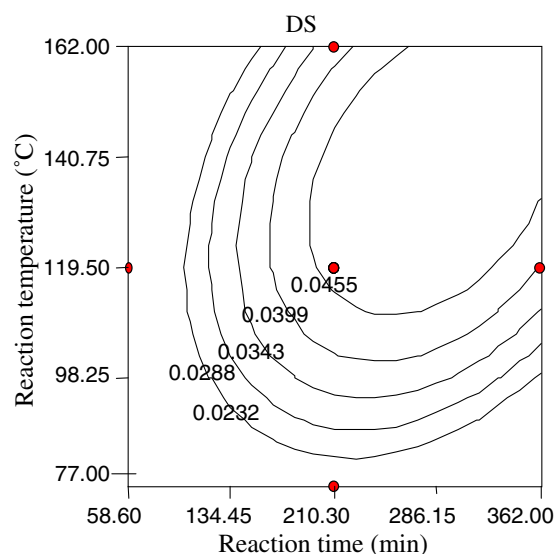


Fig. 9. Contour plots for 18 DE; the effect of reaction time and reaction temperature on DS. Other variables are held at zero level.

in the contour diagram. According to the optimized mathematical model, the optimal level of the three parameters was: oleic acid concentration of 1.2 g, a reaction time of 201 min at 160 °C, when a maximum DS was 0.021 was obtained. For maltodextrin of 12 DE, 1.53 g oleic acid concentration, a reaction time of 334 min at 150 °C gave a corresponding DS of 0.0353. Similarly, for 18 DE, 1.36 g oleic acid concentration, a reaction time of 300 min at 129 °C gave a DS of 0.053. It was clear that the optimal values obtained from response surface plots were almost consistent with those obtained from optimized mathematical equation. In order to verify the predicted result, experiments were performed using the optimized levels of the parameters, and the experimental value was 0.0190 for corn

starch, 0.032 for 12 DE and 0.050 for 18 DE, suggesting that the experimental and predicted values of DS were in good agreement.

### 3.2. Emulsification capacity

After optimization of process parameters, native corn starch and maltodextrins of 12 and 18 DE were evaluated for emulsification capacity as shown in Table 5. The original premise was that increasing the DS would increase the net hydrophobicity of the sample, thereby increasing the interactions between the substrate and the oil phases. This was, however, not the situation encountered with malto-



Table 5  
Emulsification activity<sup>a</sup> of the starch oleates *vis-à-vis* gum Arabic, expressed as turbidity, NTU

Sample		Turbidity, NTU			
		Heptane		Toluene	
		0.025 %	0.05 %	0.025 %	0.05 %
Starch	DS, 0.01	3.6 ± 0.1	5.5 ± 0.0	4.4 ± 0.06	8.2 ± 0.06
	DS, 0.02	5.1 ± 0.15	4.5 ± 0.04	7.9 ± 0.05	6.9 ± 0.0
Maltodextrin, 12 DE	DS, 0.02	5.8 ± 0.00	5.0 ± 0.07	3.4 ± 0.10	5.7 ± 0.13
	DS, 0.03	6.7 ± 0.02	7.3 ± 0.12	15.2 ± 0	17.1 ± 0.06
Maltodextrin, 18 DE	DS, 0.04	3.6 ± 0.0	7.6 ± 0.04	7.3 ± 0	8.1 ± 0.14
	DS, 0.05	3.6 ± 0.13	5.5 ± 0.13	3.6 ± 0.11	7.1 ± 0.08
Gum Arabic	–	5.1 ± 0.16	12.3 ± 0	7.8 ± 0.04	15.9 ± 0
Native starch	–	0	0.3	0	0.5

<sup>a</sup> Results are means ± SD of three determinations.

dextrin of 18 DE, although some correlation was observed with native starch and maltodextrin of 12 DE. The emulsification activities observed for all the samples were dependent on concentration. While the emulsifying activity of native starch oleate was independent of oil concentration, and that of the maltodextrins (12 and 18 DE) increased with an increase in concentration.

The densities of the oil phase seemed to have an effect on emulsion formation. Heptane being less dense (density = 0.683 g/ml) did not give a good emulsion, while toluene having a higher density of 0.863 g/ml gave a better emulsion. This was observed for all the samples. Gum arabic was found to be superior for emulsifying oils, as seen from the turbidity values. These results indicate starch oleates to be useful as extenders of gum arabic for the purposes of emulsification, and possibly microencapsulation.

#### 4. Conclusion

RSM could successfully optimize the reaction conditions for maximizing the DS of starch oleates prepared from native corn starch and maltodextrins of 12 and 18 DE. The maximum DS observed were 0.0190, 0.032 and 0.050 for corn starch, maltodextrin of 12 DE and maltodextrin of 18 DE, respectively. All the starch oleates had an emul-

sifying activity comparable to gum arabic. Further studies to understand the effect of DS on microencapsulation of sensitive food ingredients are in progress.

#### References

- Kapusniak, J., & Siemion, J. (2005). Thermal reactions of starch with long chain unsaturated fatty acids. Part 2. Linoleic acid. *Journal of Food Engineering*, 78, 323–332.
- Rao, J. K., Kim, C. H., & Rhee, S. K. (2000). Statistical optimization of medium for the production of recombinant hirudin from *Saccharomyces cerevisiae* using response surface methodology. *Process Biochemistry*, 35, 639–647.
- Reineccius, G. A. (1989). Flavor encapsulation. *Food Reviews International*, 5(2), 147–176.
- Rutenberg, M. W., & Solarek, D. (1984). Starch derivatives: production and uses. In R. L. Whistler, J. N. BeMiller, & E. F. Paschall (Eds.), *Starch: Chemistry and technology* (pp. 344–349). New York: Academic Press.
- Thevenet, F. (1988). Acacia gums: stabilizers for flavor encapsulation. In S. J. Risch & G.A. Reineccius, Flavor Encapsulation, *ACS Symposium Series*, 370, pp. 37–44.
- Varavinit, S., Chaokasem, N., & Shobsngob, S. (2001). Studies of flavor encapsulation by agents produced from modified sago and tapioca starches. *Starch/Stärke*, 53, 281–287.
- Vishwanathan, A. (1999). Effect of degree of substitution of octenylsuccinates starch on emulsification activity on different oil phases. *Journal of Environmental Polymer Degradation*, 7, 191–195.