Preparation of Sorbitol Fatty Acid Polyesters, Potential Fat Substitutes: Optimization of Reaction Conditions by Response Surface Methodology

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ABSTRACT: Effects of the reaction temperature, reaction time, mole ratio of fatty acid methyl esters (FAME) to sorbitol, and mole ratio of fatty acid sodium soaps (FASS) to sorbitol on yields of sorbitol fatty acid polyester (SFPE) were examined with a response surface methodology. The optimum reaction conditions selected with response surface analysis were as follows: reaction temperature, 144°C; reaction time, 6.65 h; mole ratio of FAME to sorbitol, 10.7:1; and mole ratio of FASS to sorbitol, 0.77:1. Under these reaction conditions, the experimental yield of sorbitol fatty acid polyester (mean value: 92%, range: 89–94%) obtained from seven replications was close to the predicted value (94%) calculated from the polynomial response surface model equation. The response surface methodology approach used in this study was able to predict the reaction conditions necessary for a high yield of sorbitol fatty acid polyester. *JAOCS 73*, 637–643 (1996).

KEY WORDS: Fat substitute, optimum reaction condition, response surface methodology, sorbitol fatty acid polyester.

Recently, carbohydrate fatty acid polyesters (CPE) have received considerable attention as possible fat substitutes due to their unique characteristics. The nondigestibility of CPE provides a low-calorie alternative with possible cholesterol-lowering effects (1). Therefore, many researchers (2–5) have been pursuing an economical method for synthesizing CPE in high yields. Among the CPE, particular attention has been focused on sucrose fatty acid polyesters (SPE). Sorbitol fatty acid polyester (SFPE) also seems to have great potential as a fat substitute. Mattson and Volpenhein (6) reported that both sorbitol hexaoleate and sucrose octaoleate were not hydrolyzed by pancreatic lipase. It was confirmed that CPE were neither digested nor absorbed in rat and human subjects (7,8). Akoh and Swanson (9) reported that sorbitol hexaoleate, synthesized by interesterification, exhibited physical properties that would allow its potential substitution as a fat substitute in food systems without adversely altering the functional properties of the foods.

For the preparation of CPE, some research groups (10–12) used toxic solvents, such as dimethylformamide or dimethyl sulfoxide, to facilitate the reaction between carbohydrates (polyol) and fatty acids. However, the CPE prepared with such solvents were unsuitable for foods due to residual toxicity and undesirable odor. Therefore, another method, known as the "solvent-free synthesis process," which did not produce residual toxicity or odor was developed. Feuge *et al.* (11) proposed a direct interesterification of polyol (sucrose) with fatty acids at 170–187°C and a fatty acid soap for the purpose of forming a homogeneous melt. However, a reaction with molten sucrose and fatty acids at high temperatures is not favored due to the caramelization of sucrose, which results in a significant loss of yield. Rizzi and Taylor (2) also adopted a fatty acid soap as a catalyst for a one-phase reaction in their process and developed their two-stage solvent-free transesterification process for higher SPE yield. Although the two-stage process of Rizzi and Taylor minimized the loss resulting from disproportionation of initially formed partial esters, it still had some drawbacks in that a mole ratio of fatty acid methyl esters (FAME) to sucrose of 16:1 was required. Volpenhein (3) reported a method with a mole ratio of FAME to sucrose of 12:1 at a higher soap/polyol mole ratio (0.75:1) for the synthesis of SPE. However, Chung (13) reported some problems when an actual attempt was made to synthesize CPE without preparing a homogeneous reactant mixture before adding FAME to the reactant mixture. It was pointed out that heating a mixture of polyol, fatty acid soap, and an alkaline catalyst with fatty acid esters at 0–5 mmHg pressure frequently formed excessive foam and eventually caused an overflow of the reaction mixture.

Akoh and Swanson (9) prepared sorbitol hexaoleate by a one-stage solvent-free synthesis procedure. They reported a 96% yield of sorbitol hexaoleate by reacting sorbitol hexaacetate with methyl oleate at 110–115°C for 2.5 h in the presence of 1–2.5% sodium metal catalyst. This process appears to be successful due to its high yield of products with a relatively low reaction temperature in the absence of toxic solvents.

Despite the several processes introduced for CPE preparation, there have been few publications on a methodological approach to find the optimum reaction conditions for a high yield of CPE, especially for sorbitol fatty acid polyester.

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Thus, the present study was done to optimize the reaction conditions for SFPE synthesis. In this study, a response surface methodology (RSM) was employed to optimize reaction conditions for the production of SFPE by controlling four parameters: reaction temperature, reaction time, mole ratio of FAME to sorbitol, and mole ratio of fatty acid sodium soap (FASS) to sorbitol.

EXPERIMENTAL PROCEDURES

Materials. Sorbitol (D-glucitol), methyl oleate, sodium oleate, and potassium carbonate were purchased from Sigma Chemical Co. (St. Louis, MO), Fluka Chemie AG (Buchs, Switzerland), Wako Pure Chemical Ind. (Osaka, Japan), and Tedia Co., Inc. (Fairfield, OH), respectively. All solvents used for analysis and preparation were high-performance liquid chromatography (HPLC)-grade and were purchased from Tedia Co., Inc.

Reaction apparatus. The reaction system for SFPE synthesis is shown in Figure 1. The oil bath temperature and the stirring motor speed were controlled on the digital control panel. An analog vacuum gauge was connected to check the vacuum condition inside the reaction flask.

Synthesis. For the synthesis of SFPE, finely powdered (100 mesh) D-sorbitol (2.73 g, 0.015 mol), potassium carbonate (0.1 g), sodium oleate, and methyl alcohol were mixed and stirred in a reaction flask. The temperature of the reaction flask was gradually increased to *ca.* 80°C and refluxed for 1 h. Methyl alcohol was then evaporated at 10–50 mmHg of pressure while being purged with dry nitrogen gas. As soon as the methyl alcohol was completely removed from the reactants, methyl oleate was placed in the reaction flask. The reaction temperature, reaction time, and the amount of methyl oleate and sodium oleate used were varied according to the experimental design of Table 1. The resulting mixture was then allowed to react under 0.1–10 mmHg of pressure.

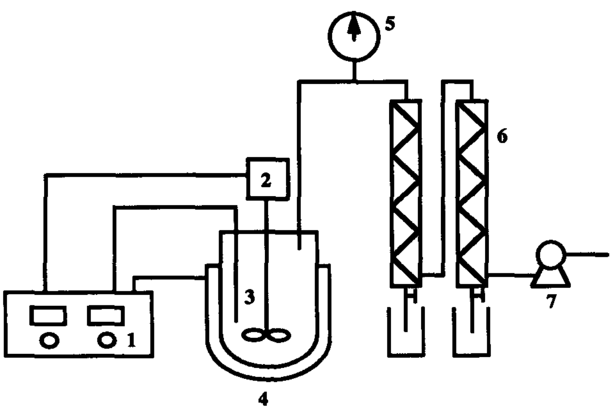

FIG. 1. Sorbitol fatty acid polyester reaction system where 1 = control panel; 2 = stirring motor and tachometer; 3 = temperature sensor; 4 = reaction vessel; 5 = vacuum gauge; 6 = condenser; and 7 = vacuum pump.

TABLE 1
Coded Levels for Independent Variables Used in Developing Experimental Data[a]

Variable	Coded level					Unit
	−2	−1	0	1	2	
Temperature (°C)	110	125	140	155	170	15
Time (h)	2	4	6	8	10	2
Mole ratio of FAME to sorbitol	6:1	8:1	10:1	12:1	14:1	2
Mole ratio of FASS to sorbitol	0.25:1	0.5:1	0.75:1	1:1	1.25:1	0.25

[a] FAME, fatty acid methyl esters; FASS, fatty acid sodium soaps.

Purification. A series of purification processes (95%-methanol washing, decolorization, filtration, and evaporation) was carried out to remove the residual FAME and low-substituted products from the crude reaction products. The 95%-methanol washing process was optimized in the previous study (13) to remove the residual FAME to as low as 0.01% (w/w) and low-substituted products completely in the final product. The amounts of residual FAME were measured by gas chromatography (GC) with methyl heptadecanoate as an internal standard. The presence of low-substituted products in SFPE was checked by HPLC as described in the *Analysis* section of the Experimental Procedures section in this study. The 95%-methanol washing process was assumably affected by three independent variables: washing temperature, ratio (w/w) of washing solution to crude reaction products, and washing time of each repetition. The optimum levels obtained in the previous study for each parameter were as follows: washing temperature, 22°C; ratio (w/w) of washing solution to crude reaction products, 5:1; and washing time of each repetition, 10 min based on nine repetitions. The crude reaction products were washed with 95%-methanol by following the optimized condition. Hexane was then used to take the 95%-methanol-insoluble portions of the reaction products, and active carbon was used to bleach these hexane-taken portions. The bleached sample was filtered, and the filtrate was evaporated while being continuously purged with nitrogen gas. For structure confirmation and/or sensory evaluation of the obtained SFPE, further purification was done by steam distillation, not only for removing the residuals but also for deodorization. The final purified product was weighed, and the yield (moles of SFPE produced/moles of sorbitol reacted) was calculated.

Analysis. The compositions of SFPE were analyzed according to individual ester groups with an HPLC-evaporative light-scattering detector system. The HPLC system consisted of a ACS 350/04 gradient pump and an evaporative light-scattering detector (Applied Chromatography System Ltd., Macclesfield, United Kingdom) with a two-column (Zorbax Reliance 3 silica, 40 mm length × 6 mm i.d.) cartridge. Chromatography was carried out with a gradient elution program, shown in Table 2, to elute all sorbitol fatty acid esters . The flow rate was 3 mL/min. The operating conditions of the evaporative light-scattering detector were as follows: temperature of evaporator, 55°C; attenuation, 8; photomultiplier, 2; time constant, 5; and air inlet pressure, 2 psig. The degree of substitution was estimated by measuring the hydroxyl value of SFPE according to the AOCS method (14).

TABLE 2
Gradient Profile of Mobile Phases in High-Performance Liquid Chromatographic Analysis

Time (min)	Hexane	Methyl *t*-butyl ether	Isopropanol
0.0	99.9	0.0	0.1
0.1	99.9	0.0	0.1
0.2	95.9	4.0	0.1
0.3	95.9	4.0	0.1
3.0	83.9	16.0	0.1
3.1	83.9	16.0	0.1
5.1	74.9	25.0	0.1
5.2	74.9	25.0	0.1
7.0	49.9	50.0	0.1
7.1	49.9	50.0	0.1
9.0	0.0	99.9	0.1
9.1	0.0	99.9	0.1
11.0	0.0	90.0	10.0
11.1	0.0	90.0	10.0
13.0	50.0	49.9	0.1
13.1	50.0	49.9	0.1
15.0	99.9	0.0	0.1
20.0	99.9	0.0	0.1

Structure confirmation. The structure of the SFPE was confirmed by Fourier transform infrared (FTIR) and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. For infrared spectroscopy, 5 mg of SFPE was placed between NaCl plates and analyzed with the Bruker IFS 66 FTIR spectrometer (Bruker GmbH, Rheinstetten, Germany). For ^{1}H NMR spectroscopy, 1 mg of SFPE was dissolved in 1 mL of deuterated chloroform ($CDCl_3$) with 2.5 mg of 3-(trimethylsilyl)propane sulfuric acid sodium salt. A ^{1}H NMR spectrum was obtained with a Bruker AMX 500 NMR spectrometer (Bruker GmbH). However, when analyzing sorbitol, deuterated dimethyl sulfoxide (DMSO) was used instead of $CDCl_3$, and the analysis was conducted under the same conditions as for the SFPE analysis.

Experimental design. A response surface methodology was employed for optimizing reaction conditions to produce a high yield of SFPE (Table 3). The synthesis reaction was assumed to be affected by four independent variables, ξ_i (reaction temperature, ξ_1; reaction time, ξ_2; mole ratio of FAME to sorbitol, ξ_3; and mole ratio of FASS to sorbitol, ξ_4). It was also assumed that one dependent variable (referred to as a response), η (the yield of SFPE produced), which was experimentally measured, defined the system.

$$\eta = f(\xi_1, \xi_2, \xi_3, \xi_4) \qquad [1]$$

Second degree polynomial equations were assumed to approximate the true functions:

$$\eta = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} x_i x_j \qquad [2]$$

where β_0, β_i, β_{ii}, and β_{ij} are regression coefficients, and x_i are the coded independent variables linearly related to ξ_i. The coding of ξ_i into x_i is expressed by the following equation:

$$\xi_\iota = 2(\xi_i - \xi_i^*)/d_i \qquad [3]$$

where ξ_i = actual value in original units; ξ_i^* = mean of high and low levels of ξ_i; and d_i = difference between the low and high levels of ξ_i.

A central composite rotatable design (15) with four variables was used. For the four variables, this design yielded 31 experiments with sixteen (2^4) factorial points, eight extra points (star points) to form a central composite design with $\alpha = 2$, and seven center points for replication. The range and center point of the four variables (Table 1) were chosen based on preliminary trials. Response surfaces were obtained by using the RSREG procedure of the SAS (16) program. Contour plots were generated by assigning constant values to two variables and then solving the fitted equations as a quadratic in the other two, by means of the GCONTOUR procedure of SAS/GRAPH (17).

RESULTS AND DISCUSSION

Synthesis process. A solvent-free transesterification process for the preparation of sorbitol fatty acid polyester was devel-

TABLE 3
Experimental Data for Yield of Sorbitol Fatty Acid Polyester[a]

Run	Variable coded level x_1	x_2	x_3	x_4	Experimental data yield (%, mol/mol)
1	-1	-1	-1	-1	68
2	1	-1	-1	-1	79
3	-1	1	-1	-1	70
4	1	1	-1	-1	83
5	-1	-1	1	-1	69
6	1	-1	1	-1	80
7	-1	1	1	-1	74
8	1	1	1	-1	86
9	-1	-1	-1	1	69
10	1	-1	-1	1	81
11	-1	1	-1	1	75
12	1	1	-1	1	85
13	-1	-1	1	1	70
14	1	-1	1	1	82
15	-1	1	1	1	77
16	1	1	1	1	86
17	-2	0	0	0	55
18	2	0	0	0	87
19	0	-2	0	0	74
20	0	2	0	0	92
21	0	0	-2	0	89
22	0	0	2	0	92
23	0	0	0	-2	74
24	0	0	0	2	82
25	0	0	0	0	89
26	0	0	0	0	94
27	0	0	0	0	89
28	0	0	0	0	93
29	0	0	0	0	90
30	0	0	0	0	93
31	0	0	0	0	88

[a] With different combinations of reaction temperature (x_1), reaction time (x_2), mole ratio of FAME to sorbitol (x_3) and mole ratio of FASS to sorbitol (x_4) used in the central composite, rotatable second-order design for response surface methodology. Abbreviations as in Table 1.

oped by modifying the conventional solvent-free synthesis process (Fig. 2). The process was composed of two stages, the stabilization stage and the main reaction stage designed to minimize foaming and overflowing of the reaction mixture. Stabilization of reactants was achieved through the formation of a homogeneous reaction mixture. The reaction mixture was made by stirring, refluxing, and applying a vacuum to remove methanol from the original mixture. Formation of foam and overflow of reactants were not observed during the modified synthesis reaction process, probably due to the low vacuum of 10–50 mmHg.

Product confirmation. Analyses of SFPE by the HPLC-evaporative light-scattering detector system showed that the prepared SFPE was composed of a single ester group rather than a mixture of individual hexa-, penta-, and tetraesters. An SPE sample obtained from the Akoh and Swanson research group appeared as a single peak on the HPLC chromatogram but eluted slightly later than the SFPE peak (Fig. 3).

The degree of substitution (DS) in the prepared SFPE was estimated indirectly by measuring the hydroxyl value. The hydroxyl values of SFPE prepared in this study were below 10, indicating that the DS was approximately 6. Akoh and Swanson (9) reported a DS of 6 by ^{13}C NMR spectroscopy for the sorbitol polyester prepared by a one-stage solvent-free interesterification of methyl oleate and sorbitol hexaacetate.

FTIR and ^{1}H NMR spectroscopy were also used for structural analyses of SFPE. In the FTIR spectrum of SFPE (Fig. 4), asymmetrical stretching and stretching vibrations of the methyl and methylene groups of the fatty acid chains were observed in the region of 3005–2854 cm^{-1}. However, an absorption band at 1745 cm^{-1} by ester carbonyls in the IR spectrum of SFPE was absent in the IR spectrum of sorbitol (Fig. 5). This indicates that the fatty acid chains present in SFPE are esterified to sorbitol. An absorption band of the hydroxyl group at 3335 cm^{-1} in the IR spectrum of sorbitol (Fig. 5) was not present in the IR spectrum of SFPE (Fig. 4). This indicates that all hydroxyl groups in sorbitol were esterified. Akoh and Swanson (9) reported similar results in that they observed C-H stretching vibrations of methyl and methylene groups of the fatty acid chains at 3000–2840 cm^{-1}, overtone stretching vibrations at 3460 cm^{-1}, and an absorption band at 1740 cm^{-1}, which confirmed the presence of carbonyls.

Figures 6 and 7 show the ^{1}H NMR spectra of SFPE and sorbitol, respectively. The following features were observed: signals of methyl group protons on the omega end of fatty acid chains (0.799–0.826 ppm), methylene group protons of fatty acid chains (1.201–1.226 ppm), and methylene group protons connected to a double-bonded carbon (1.933–1.945 ppm). Signals from the protons of hydroxyl groups were observed at 4.2–4.7 ppm in the spectrum of sorbitol but were not observed in the spectrum of SFPE. The results show that fatty acids were esterified to sorbitol molecules and that hydroxyl groups are not present in SFPE molecules.

Regression coefficients. Regression coefficients and the equations describing response surfaces are shown in Table 4. Regression coefficients showed that x_1 (reaction temperature) and x_2 (reaction time) linearly and quadratically affected ($P < 0.001$) the yield, whereas x_3 (mole ratio of FAME to sorbitol) and x_4 (mole ratio of FASS to sorbitol) had no significant linear relationship with the yield. However, x_4 (mole ratio of FASS to sorbitol) had a quadratic effect ($P < 0.001$) on the responses. There were no significant two-factor interactions.

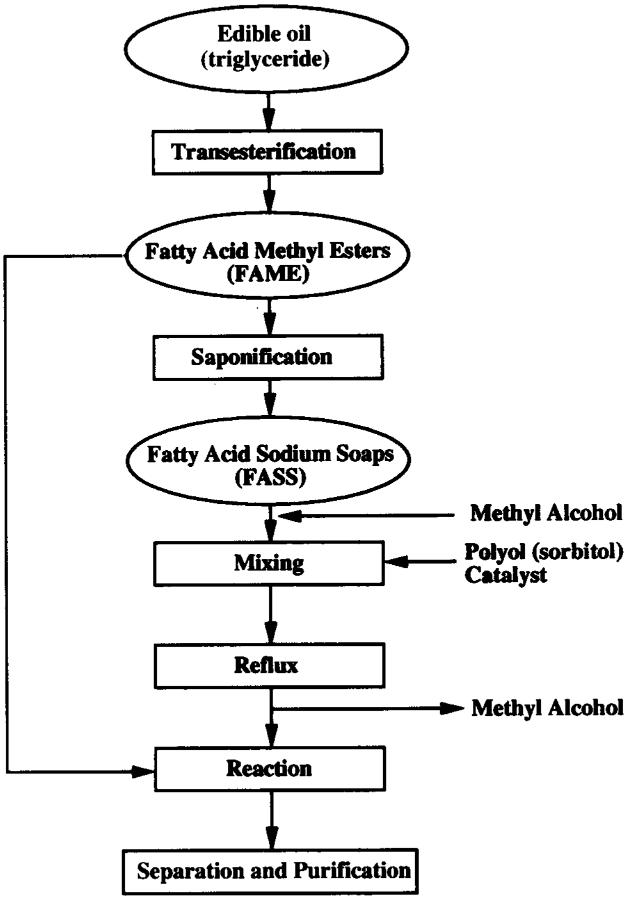

FIG. 2. Sorbitol fatty acid polyester synthesis flow sheet.

Adequacy test of model. The adequacy of this model was tested by the lack-of-fit and the coefficient of determination,

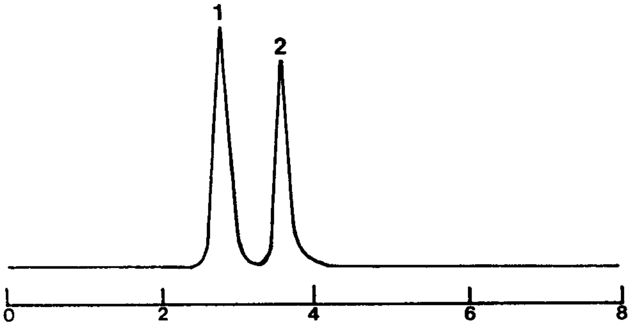

FIG. 3. A typical high-performance liquid chromatography chromatogram of sorbitol fatty acid polyester on two-column (Zorbax Reliance 3 silica) cartridge where 1 = sorbitol fatty acid polyester; 2 = sucrose fatty acid polyesters.

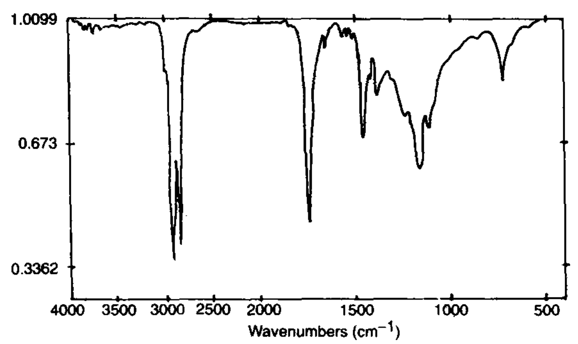

FIG. 4. Infrared spectrum of sorbitol fatty acid polyester (SFPE).

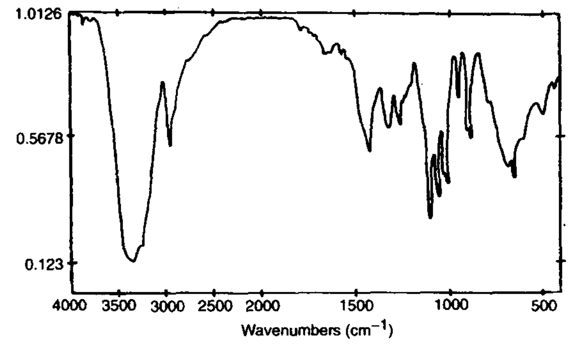

FIG. 5. Infrared spectrum of sorbitol.

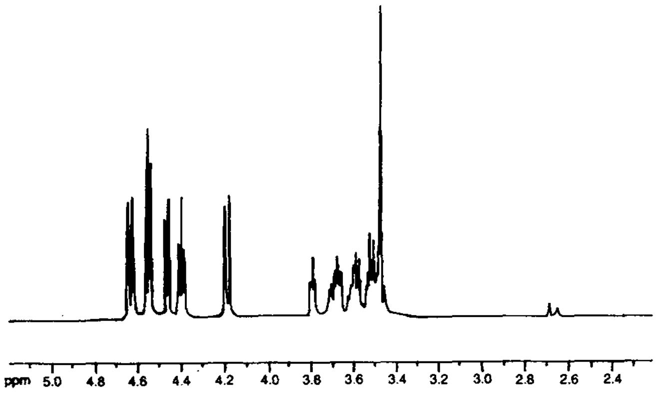

FIG. 7. ^{1}H nuclear magnetic resonance spectrum of sorbitol.

R^2 (Table 5). The lack-of-fit data and the coefficient of determination (R^2) for equation revealed that the model was adequate.

Reaction temperature. Although SFPE synthesis is a typical S_N2-type reaction in which increasing reaction temperatures increase the reaction rates, the reaction temperatures should be carefully controlled to avoid decomposing the reactants as well as the products. Volpenhein (3) suggested 110–180°C, preferably 150°C, as the optimum reaction temperature range for a high yield of SPE. Therefore, it is advisable not to run the reaction above 150°C to avoid the decomposition of sucrose by caramelization. Regarding the stability of the starting materials in the CPE synthesis reaction, sorbitol seems to have a better thermostability than sucrose. This is characteristic of sorbitol because of its chain structure, which offers it a greater stability than the cyclic structure of sucrose. Also, there are no glycosidic bonds present in the sorbitol structure, which are known to break at high reaction temperatures. Akoh and Swanson (9) reported that the optimum range for the reaction temperature was 110–115°C. They were able to synthesize SFPE under such mild reaction conditions because they used sorbitol hexaacetate, which has a good leaving group (acetate group), as a starting material, instead of sorbitol.

In this study, reaction temperatures were varied from 110 to 170°C at a 15°C interval. The response surface analyses

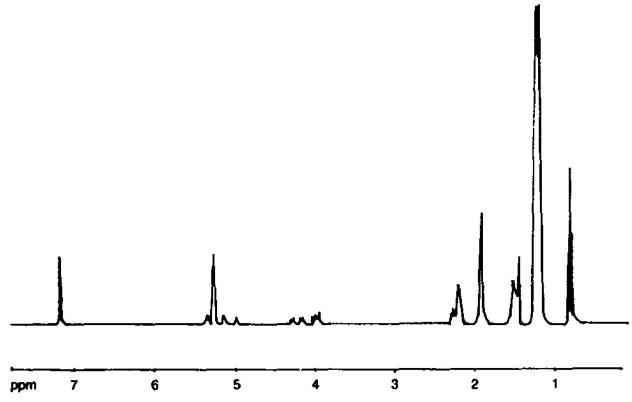

FIG. 6. ^{1}H nuclear magnetic resonance spectrum of sorbitol fatty acid polyester.

TABLE 4
Regression Coefficients and Equations for the Response Surface Model[a]

Coefficients	Yield
β_0	90.857[b]
β_1	6.417[b]
β_2	3.083[b]
β_3	0.833
β_4	1.333
β_{11}	–5.548[b]
β_{21}	–0.125
β_{22}	–2.548[b]
β_{31}	–0.125
β_{32}	0.375
β_{33}	–0.673
β_{41}	–0.250
β_{42}	0.250
β_{43}	–0.250
β_{44}	–3.798[b]

[a] Response $\eta = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1{}^2 + \beta_{21} x_2 x_1 + \beta_{22} x_2{}^2 + \beta_{31} x_3 x_1 + \beta_{32} x_3 x_2 + \beta_{33} x_3{}^2 + \beta_{41} x_4 x_1 + \beta_{42} x_4 x_2 + \beta_{43} x_4 x_3 + \beta_{44} x_4{}^2$, where η = yield of sorbitol fatty acid polyester; x_1 = coded value for reaction temperature, x_2 = coded value for reaction time, x_3 = coded value for mole ratio of FAME to sorbitol, and x_4 = coded value for mole ratio of FASS to sorbitol. Abbreviations as in Table 1.

[b] $P < 0.001$.

TABLE 5
Analysis of Variance for the Fit of Experimental Data to Response Surface Model

Source	Degrees of freedom	Sum of square	Mean square	*F*
Model	14	2542.46	181.60	17.61[a]
Linear	4	1275.67	318.92	30.92[a]
Quadratic	4	1261.04	315.26	30.57[a]
Cross product	6	5.75	0.96	0.09
Residual	16	165.02	10.31	
Lack of fit	10	130.17	13.02	2.241
Pure error	6	34.86	5.81	
R^2	0.94			

[a] $P < 0.01$.

were conducted with the yields of SFPE produced at each reaction temperature interval. Response surface contour plots for the yields of SFPE are presented in Figure 8. Two variables were maintained at their center point values and the responses of the fitted equations were plotted with the other two variables. The level of the reaction temperature had significant effects on the yield (Fig. 8A, B, and C). The yields showed a convex curve with the reaction temperatures; increasing the reaction temperature increased the yield to a certain point and steadily decreased thereafter. The optimum reaction temperature was calculated to be 144°C from the polynomial regression model equation.

Reaction time. To find out the optimum reaction time for the synthesis of SFPE, response surface analyses were done by varying the reaction time from 2 to 10 h as shown in Table 1. Figure 8C, D, and E show that the reaction temperature, as well as the reaction time, significantly affects the yield of SFPE. Contrasting the slopes of each independent variable in Figure 8 indicates that the effect of the reaction time on the yield was less than the effect of the reaction temperature but greater than the effect of the amounts of FAME or FASS. The optimum reaction time was found to be 6.65 h according to the equation for the polynomial regression model. However, the yield of SFPE changed insignificantly as the reaction time increased to the maximum level (10 h).

The mole ratio of FAME to sorbitol. One of the factors that affect the rate of SFPE synthesis is the mole ratio of FAME to sorbitol. In general, it is known that increasing the mole ratio of reactants improves the reaction rate of S_N2-type reactions by increasing the frequency of collisions between the reactant molecules. Rizzi and Taylor (2) patented their two-stage solvent-free synthesis process for SPE with sucrose as a polyol source, which required a mole ratio of FAME to sucrose of 16:1, reaction temperatures between 130 and 150°C and reaction times of 8–9 h. Volpenhein (3) introduced an improved two-stage process for SPE synthesis in which the reaction temperatures were between 130 and 160°C, reaction times between 4 and 12 h, and a mole ratio of FAME to sucrose of 12:1. On the other hand, Akoh and Swanson (9) concluded that it was not necessary to increase the mole ratio when using carbohydrate acetates as starting materials; carbohydrate acetates have good leaving groups and therefore react mole to mole for optimum interesterification. In their one-stage solvent-free synthesis, an 8:1 mole ratio of methyl oleate to sucrose octaacetate and a 6:1 mole ratio of methyl oleate to sorbitol hexaacetate resulted in the greatest yields of sucrose polyoleate (99.8%) and sorbitol polyoleate (96.0%). Nevertheless, it seems necessary to optimize a mole ratio of FAME to sorbitol in a solvent-free process with sorbitol as a starting material because it appears that polyol does not react with FAME stoichiometrically in a soap process.

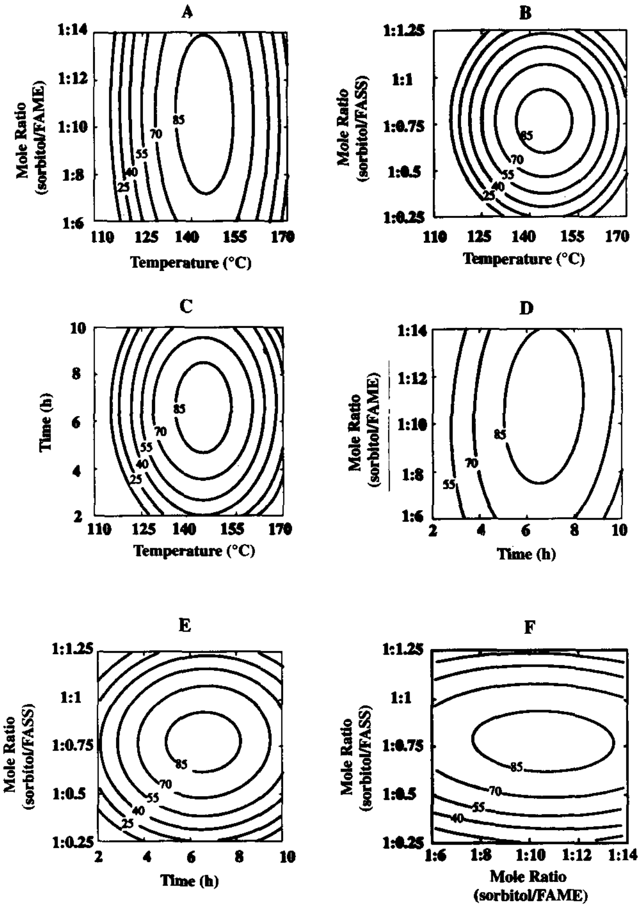

FIG. 8. Response surface contours for yields of sorbitol fatty acid polyester as a function of reaction temperature, reaction time, mole ratio of fatty acid methyl ester (FAME) to sorbitol, and mole ratio of fatty acid sodium salts (FASS) to sorbitol as plotted for two variables with the other two variables fixed at 0 coded levels.

In a solvent-free transesterification process with polyol as a starting material, phase separation might occur between sorbitol and FAME during the reaction when the mole ratio of FAME exceeds a certain level. This phenomenon seems to be caused by the use of a higher mole ratio of FAME to sorbitol at the selected level of FASS, which enhances the reaction between polar (sorbitol) and nonpolar (FAME) reactants. Therefore, it is necessary to optimize either the mole ratio of FAME to sorbitol and/or the mole ratio of FASS to sorbitol to overcome phase separation between the two reactants.

The optimum mole ratio of FAME to sorbitol was studied with a response surface analysis according to the levels indicated in Table 1. The optimum mole ratio of FAME to sorbitol, assumed by the polynomial regression model, was 10.7:1. As shown in the contour plots in Figures 8A, D, and F, increasing the mole ratio of FAME/sorbitol to 14:1 did not increase the yield of SFPE. It appears that yields gradually decreased when FAME was used beyond the estimated optimum mole ratio. It seems that phase separation might occur during the reaction.

The mole ratio of FASS to sorbitol. Feuge *et al.* (11) suggested that solid polyol materials, such as sucrose, could be solubilized and reacted with long-chain methyl esters if fatty acid soaps of comparable chainlength were present. Rizzi and Taylor (2) introduced a solvent-free transesterification process with fatty acid soap as a catalyst to obtain a higher yield of polyol fatty acid polyesters. They claimed to use an alkali metal fatty acid soap from approximately 1–30% in a reaction mixture. Volpenhein (3) reported an improved solvent-free transesterification process for CPE synthesis at higher soap to polyol mole ratios. He claimed that the mole ratio of soap to polyol for a high-yield synthesis of SPE was from about 0.75:1 to about 1:1. Fatty acid sodium soaps were used to form a homogeneous melt in this study so that sorbitol and FAME can react in a one-phase melt during the one-stage solvent-free synthesis reaction. To estimate the precise mole ratio of FASS to sorbitol for an optimum reaction, response surface analyses were conducted according to the levels indicated in Table 1. The optimum mole ratio of FASS to sorbitol was 0.77:1, based on the estimation obtained by the polynomial regression model equation. As shown in the contour plots of Figures 8B, E, and F, it seems that the level of FASS had a significant effect on the yield as did the reaction temperature and reaction time.

Optimum reaction conditions. The optimum reaction conditions selected with the response surface analyses were as follows: reaction temperature, 144°C; reaction time, 6.65 h; mole ratio of FAME to sorbitol, 10.7:1; and mole ratio of FASS to sorbitol, 0.77:1. Under these reaction conditions, the yield of SFPE was estimated to be 94% according to the equation for the response surface model. Adequacy of the model equation was tested experimentally at the optimum reaction conditions, which were previously predicted by the RSM. The experimental values (mean value, 92%; range, 89–94%) obtained from seven replications were close to the predicted value. This suggests that the optimum reaction conditions predicted by the RSM can be successfully applied to obtain a high yield of SFPE.

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