

Synthesis of Oleyl Oleate as a Jojoba Oil Analog

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Synthesis of a wax ester analog of jojoba oil was accomplished from oleic acid and oleyl alcohol with a zeolite as catalyst. A full 2³ factorial design at two levels has been used in the synthesis. The variables selected were temperature, reduced pressure and initial catalyst concentration. The most important variable within the range studied was temperature. Reduced pressure had a negative influence, and initial catalyst concentration showed a positive influence on the process. A response equation has been determined for the yield of ester. The properties of the synthesized product are similar to those of natural jojoba oil.

KEY WORDS: Esterification, factorial design, jojoba oil, wax ester, zeolite.

Wax esters are high added-value products often produced by batch processes in multiproduct plants. Interest in developing such new materials increases if their synthetic processes can be optimized for a profitable scale of production.

High-molecular weight esters from long-chain alcohols and long-chain acids are typically referred to as waxes. Jojoba oil and sperm whale oil are compounds that fall within the fine chemicals group. The use of jojoba oil has increased in the last few years because it can be considered as an adequate substitute for sperm whale oil. Jojoba oil applications include cosmetics, pharmaceuticals, food additives and high-pressure lubricants (1).

Jojoba oil is obtained from a semi-desert shrub, *Simmondsia chinensis* (Schneider). It is composed mainly of monoesters of C₂₀ and C₂₂ alcohols and acids, with two double bonds per chain (docosenyl eicosenoate [C₄₂] and eicosenyl eicosenoate [C₄₀]). The main obstacle to large-scale use of jojoba oil is its cost and availability. Commercial jojoba plantations require up to five years to begin initial seed production. High-producing cultivars are only beginning to be available. Jojoba seeds contain about 50% oil (2).

As starting materials for our wax ester, we used the most available unsaturated acid and alcohol in Spain, oleyl alcohol (C₁₈) and oleic acid (C₁₈). We used zeolite of the faujasite type as catalyst, thus avoiding difficulties in catalyst separation and avoiding metal impurities that are prevalent when using Lewis acids as catalyst (3).

A factorial experimental design describes the yield of ester as a function of operating conditions. Influence, interactions and value of any of the variables involved will thus be known in the range considered, thereby reducing research time and costs (4).

In this work, esterification of oleic acid and oleyl alcohol was studied in a batch reactor by using a factorial design to optimize the process and to search for relationships between the yield of ester and the operation variables. The variables studied were reaction temperature, catalyst concentration and reduced pressure. Commercial specifica-

tions for the product made it necessary to work at a molar ratio of acid/alcohol of 1.0 (5).

EXPERIMENTAL PROCEDURES

Equipment. The experiments were carried out in a completely stirred tank reactor (CSTR) of 500 cm³ volume, 10 cm high and 7 cm diameter. This equipment has been described elsewhere (6). Temperature, impeller speed and pressure recorders and controllers were installed.

Materials. Oleic acid (purity > 98%) and oleyl alcohol (purity > 98%) were supplied by Henkel-Iberica (Barcelona, Spain). The Y-Zeolite was prepared by steam calcination at 550°C of partially NH₄⁺-exchanged NaY zeolites (70% of Na⁺ exchanged), followed by exchange of the remaining Na by NH₄⁺, and final calcination at 550°C of the sample. In this way, increasing amounts of Al were removed from the framework.

Analytical method. Reaction products were monitored by gas chromatography/mass spectrometry (GC/MS) and quantitatively determined by capillary-column gas chromatography. The GC/MS data were obtained on a 5992B Hewlett-Packard instrument (Palo Alto, CA). Gas chromatography was performed on a fused-silica capillary column (OV-1, 12-m × 0.31-mm i.d., 0.17-μmm film). A Hewlett-Packard gas chromatograph was equipped for split-splitless injections (30 s). The GC/MS operating conditions were as follows: ionization energy, 70 eV; scan speed, 11,100 amu/s; mass range, 40–400 amu; data treated with a Hewlett-Packard 9825B computer.

The GC column oven temperature was held at 150°C during 1 min, then raised 15°C/min to 275°C and maintained at that temperature until all components had eluted. Quantitative GC analyses were performed on a Hewlett-Packard 5790A instrument with the column and conditions described above in the GC/MS analysis connected to a Hewlett-Packard 3390A integrator. The detector was a flame-ionization detection (FID) type at 270°C, and the injection system was splitless. The carrier gas was helium at a flow rate of 1 mL/min. We also determined the freezing point, saponification value, iodine value and viscosity (7).

The reactants and catalyst were added to the reactor. When the appropriate reduced pressure was reached, the reaction mixture was heated to the desired temperature, stirring was begun and reactants were stirred for 8 h. Analysis of samples removed at 30-min intervals was done by gas chromatography. During each experiment, the following variables were set at determined values: reactor temperature, impeller speed and reduced pressure. Before starting an experiment, the reactor was flushed with nitrogen.

Mechanism of the reaction. The first step in the mechanism observed for the acid-catalyzed esterification involves a fast protonation of the acid, followed in subsequent steps by the nucleophilic attack of the alcohol (8).

Statistical analysis. A full 2³ factorial experimental design (three factors at two levels) was applied in this study. The standard experimental matrix for the factorial

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TABLE 1

2³ Factorial Experiment Matrix and Experimental Results^a

Run number	Run order	T (°C)	C (wt%)	P (mmHg)	Coded values			Y _o (%)
					x _T	x _C	x _P	
1	4	120	0.2	16	-1	-1	-1	39
2	7	180	0.2	16	+1	-1	-1	45
3	5	120	0.6	16	-1	+1	-1	42
4	2	180	0.6	16	+1	+1	-1	47
5	1	120	0.2	710	-1	-1	+1	37
6	6	180	0.2	710	+1	-1	+1	42
7	3	120	0.6	710	-1	+1	+1	40
8	8	180	0.6	710	+1	+1	+1	45

^aAbbreviations: T, reaction temperature (°C); C, initial catalyst concentration (wt%); P, reduced pressure (mmHg); Y_o, estimated response for the experiments (ester yield).

design is shown in Table 1. Columns 3–5 list variables of temperature, catalyst concentration and pressure, respectively, columns 6–8 give the ±1 coded factor levels in the dimensionless coordinates. The levels for each factor, T, C and P, were selected on the basis of results obtained in a preliminary study. The upper limit was chosen as 180°C to avoid secondary oxidation reactions, which could interfere with this esterification process. Temperatures below 120°C did not produce relevant yields of ester. The pressure levels were the atmospheric value (710 mmHg) and the minimum value possible in our experimental installation (16 mmHg). The levels of catalyst concentration were also chosen on the basis of preliminary experiments, in which the amount of catalyst was progressively increased and the yield of ester was monitored *vs.* time. The levels chosen were 0.2 and 0.6 wt% catalyst. The coded values, X_K, are obtained by calculating

$$x_K = \frac{x_k - \bar{x}_k}{d} \quad [1]$$

where x_k = natural value for factor K, \bar{x}_k = the mean of factor K, and d = unit of variation from x_k to \bar{x}_k ; K represents either C (catalyst concentration), P (pressure) or T (temperature).

Experiments were run in random order. In the design, both the reaction time (2 h) and molar ratio acid/alcohol (1.0) were fixed. Error estimation was made by Daniel's method of analysis (9). This method is not offered as a general substitute for the analysis of variance and its use is only advisable for well-known processes. Factorial design of the experiments allowed us to express the amount of ester produced as a polynomial model. Statistical analysis included the main effects and interaction effects for the variables.

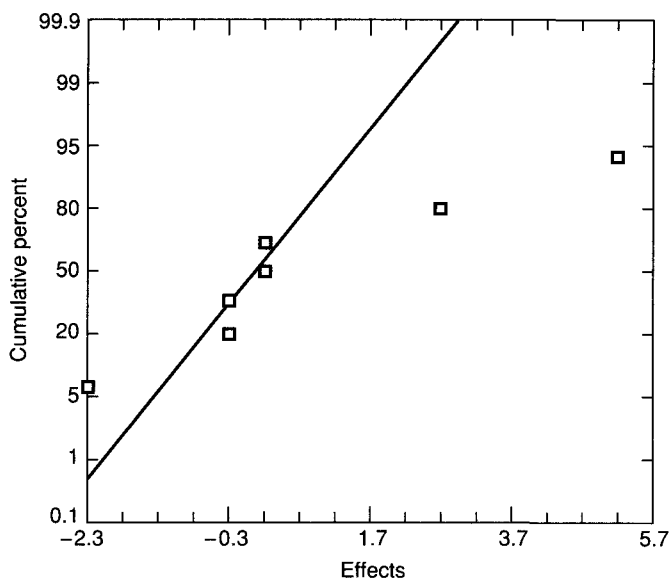
RESULTS AND DISCUSSION

Table 1 shows the yield of ester after 2 h for eight reaction conditions. The analysis of main effects and interactions for the chosen response, ester yield, together with the test of statistical significance, are given in Table 2. From Daniel's method of analysis, the significant main effects were temperature, catalyst concentration and reduced pressure because they deviate from the half normal distribution plot as shown in Figure 1. The best fitting

TABLE 2

Statistical Analysis of Results in Table 1

Main effects and interactions			
T = 5.25	C = 2.75	P = -2.25	
TC = -0.25	TP = -0.25	CP = 0.25	TCP = 0.25
Statistical significance of Daniel's method			
Significant main effects and interactions: T(+), C(+), P(-)			
Response equation			
$Y = a_0 + a_1x_T + a_2x_C - a_3x_P$			

FIG. 1. Half normal plot of a 2³ experiment.

response function for the significant effects is the statistical model:

$$Y = 42.125 + 2.625 x_T + 1.375 x_C - 1.125 x_P \quad [2]$$

being the correlation coefficient (r) = 0.995 and technological model:

$$Y = 27.43 + 0.0875 T + 6.875 C - 0.00324 P \quad [3]$$

where statistical model data are fitted to the coded variables, giving the real influence of each variable in the process, and the industrial model data are fitted to real values of the variables, for use in the industrial process.

Table 3 shows the parameters we chose for comparison of refined jojoba oil and the oleyl oleate product synthesized and purified in this work. The products have similar values.

The influence of the process variables, *i.e.*, reaction temperature, initial catalyst concentration and operation pressure, on the ester yield will now be discussed. The influence of the main factors and interactions will be derived from Equation 1.

TABLE 3

Properties of Jojoba Oil and a Synthetic Analog (oleyl oleate)

	Solidifying temperature (°C)	Saponification value	Iodine value	Viscosity (25°C) cp
Jojoba oil	8	92	82	35.2
Oleyle oleate	6	94	94	29.0

Influence of temperature. Statistical analysis shows that temperature has a positive influence on ester yield. With our zeolite catalyst, the influence of temperature is much lower (0.09% ester yield increase per 1°C of temperature increased) than when Lewis acids are used (0.67% ester yield per 1°C) (10). This is likely due to diffusion control of the reactants into the zeolite cavities. To check this, the influence of the zeolite's crystal size on conversion was studied by employing zeolites with similar physicochemical properties but which have been crystallized within smaller and larger crystal-size particles. Figure 2 shows that higher conversion is obtained with zeolite of smaller crystal size and thus greater specific surface, suggesting that the reaction may be controlled by diffusion of reactants into and out of the micropores of the zeolite (3).

Influence of initial catalyst concentration. The influence of the initial catalyst concentration is statistically significant in the range studied. It seems to have a slight positive influence, probably as a result of the narrow experimental range considered. The lowest initial catalyst concentration shows a small influence on the ester yield, as has also been observed on conventional Lewis catalyst (6).

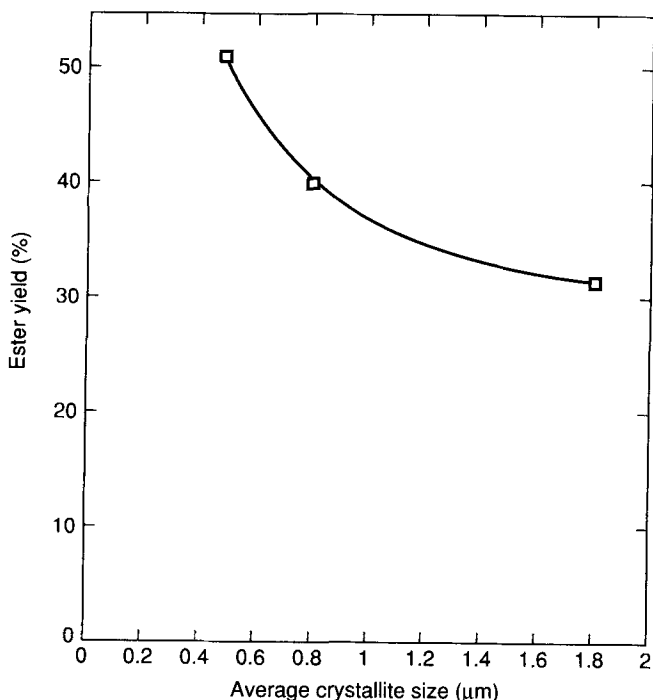


FIG. 2. Influence of average crystallite size on zeolite activity for esterification of oleic acid with oleyl alcohol at 60 min of reaction.

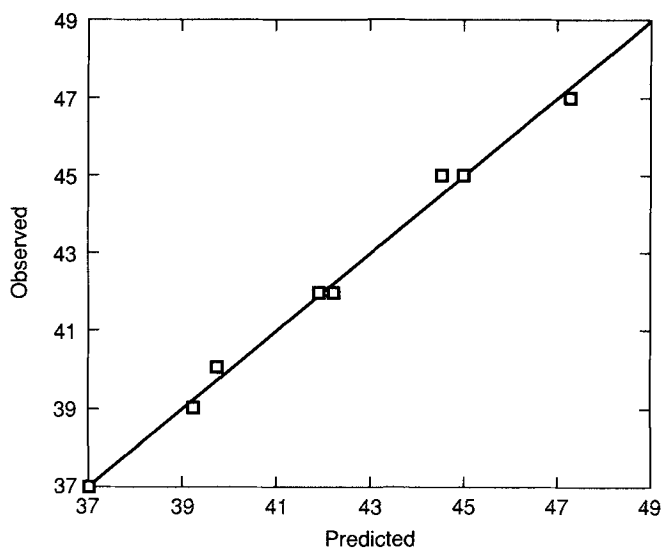


FIG. 3. Predicted ester yield vs. experimental data of ester yield.

Influence of reduced pressure. Reduced pressure has a positive influence on the process. This is to be expected because reduced pressure (16 mmHg) easily eliminates the water produced in the esterification. Therefore, the equilibrium is driven toward ester formation.

With respect to initial catalyst concentration and reduced pressure, the zeolite catalyst functioned similar to Lewis acid catalysts.

Influence of interactions. There were no significant main effect interactions (temperature, initial catalyst concentration and reduced pressure) on ester yield (Fig. 1).

Analysis of response: Yield of ester. In our experiments, the maximum ester yield was achieved at the maximum temperature (180°C), minimum reduced pressure (16 mmHg) and maximum initial catalyst concentration. These can be varied further for optimum economic considerations.

It is not recommended to increase the temperature above the upper limit (180°C) to avoid secondary reactions, which will increase the level of impurities and therefore will increase the purification costs. The mathematical model, obtained from the 2³ design for the prediction of ester yield, gives a good fit of the experimental data to predicted data obtained by the polynomial equation as shown in Figure 3.

From an industrial point of view, an analog of jojoba oil has been synthesized (oleyl oleate). This product has properties similar to that of raw jojoba oil. Oleic acid and oleyl alcohol, obtained from readily available olive oil have been used as raw materials. From an economic point of view, the process developed in this work is attractive for its simplicity and because of low costs (2–4 \$/kg) of the raw materials. The methodology used (factorial design of experiments and statistical analysis of the data) is suitable to aid in the development and optimization of a process for synthesizing wax esters.

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