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Synthesis of Esters of High Molecular Weight. An Analogue of Jojoba Oil. A Statistical Approach

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The development of an ester, which is the analogue of jojoba oil, which can be used as that product is similar to sperm whale oil and jojoba oil has been made. A process developed in this laboratory for the production of high molecular weight esters uses the esterification of oleic acid and oleyl alcohol to produce oleyl oleate, which can be used as an analogue of jojoba oil. Two full 2^3 factorial designs at two levels have been used in the study of the synthesis of the analogue of natural oil. The variables selected for study were reaction temperature, initial catalyst concentration, initial alcohol–acid molar ratio, and fixed reaction time and pressure. The results may be explained in terms of the known chemistry of the system. All conclusions are restricted to the experimental range studied. The amount of ester formed is enhanced by increasing temperature. Empirical models which use first-order polynomial expressions were found to represent the amount of ester adequately, while the detection of the curvature effect indicates that second-order polynomials will be required for a better satisfactory description. The commercial quality of the synthesized product is very similar to jojoba oil.

The use of jojoba oil has been increased in the last few years, because of jojoba oil's close resemblance chemically and physically to sperm whale oil. Jojoba oil is obtained from an evergreen bush of the Buxaceae family, *Simmodsia chinensis Sheneider*, that grows in semidesert areas and yields a nut that contains 50% oil composed mainly of monoesters of the C_{20} and C_{22} alcohols and acids, with two double bonds per chain (docosenyl eicosenoate (C_{42}) and eicosenyl eicosenoate (C_{40})) (Miwa, 1971).

Commercial planting of the shrub is developing at a growing pace, and large quantities of oil should be available within 10 years.

The number and diversity of uses for which jojoba oil has been proposed are great, such as lubricants for high-speed machinery, numerous pharmaceutical uses, cosmetics, hair oils, etc. (Bhatia and Gulati, 1981).

There are two problems in using jojoba oil. The first is that we cannot get a great amount of this oil, and the second is that it is not economical. For this reason, the purpose of this work is to study the synthesis, characterization, and properties of an analogue of jojoba oil. The problem was to get cheaper raw materials and develop a very easy synthesis process.

As starting products, we used the most available unsaturated acid and alcohol in Spain, oleyl alcohol (C_{18}) and oleic acid (C_{18}). In the synthesis process, we have used the esterification method using an acid catalyst. We have chosen a catalyst that does not react with the double bonds of the molecules, cobalt chloride (Urteaga, 1985).

In this paper, emphasis is placed on the use of factorial design of experiments in order to show that the design and statistical analysis of experiments allow us to obtain a simple but efficient model for industrial control and to reduce the number and cost of experiments. As an illustration of the methodology, the experimental study of the esterification of oleic acid and oleyl alcohol in a batch reactor was undertaken in order to give the phenomenological relation for the amount of ester obtained as a function of initial temperature, catalyst concentration, and alcohol/acid molar ratio. The variables are the most commonly used for modeling esterification reactions.

Experimental Section

Equipment. The experiment was carried out in a continuous stirred tank reactor (CSTR) of dimensions 500-cm^3 semispherical bottom, 7 cm high, and 5 cm diameter. The reactor was equipped with stationary baffles attached along the circumference. A marine-type mixing propeller was employed. The impeller speed was set at 1000 rpm. A temperature recorder and controller and a speed controller were provided.

The reactor that was immersed in a constant-temperature bath was capable of maintaining the reaction temperature to within ±0.1 °C of that desired for the reaction.

Materials Used. The commercial catalyst, cobalt chloride by Merck, of constant activity, was used in our experiment.

Oleic acid, purity of better than 99.0%, was supplied by Merck and oleic alcohol, purity of better than 98.0%, by Henkel Iberica.

Analytical Method. The technique to be used had to be capable of monitoring the reaction components.

These products were determined by gas chromatography/mass spectrometry (GC/MS) and quantitatively by

capillar column gas chromatography.

The GC/MS data were obtained on a 5992B Hewlett-Packard instrument. Gas chromatography was performed on a fused silica capillary column, OV-1 (12-m length, 0.31-mm i.d. 0.17-μm film), Heweltt-Packard. The gas chromatograph was equipped for split–splitless injections (30 s). The operating conditions of the instrument were as follow: ionization energy, 70 eV; scan speed, 1100 amu s^{-1}; mass range, 40–400 amu; data treated with an HP 9825 A computer, connected on line with the GC/MS system. For the separation of the products, the capillary column oven temperature was programmed at 150 °C during 1 min and then raised 15 deg min^{-1} and maintained at 275 °C until all components had eluted.

The quantitative gas chromatography analyses were performed on a 5790 A Hewlett-Packard instrument using the column and conditions described above in the GC/MS analysis. The detector was a FID type and the injection system splitless.

Also, we employed the parameters defining the quality of Jojoba oil, viz., solidifying point, saponification value, iodine value, and viscosity.

The following operation procedure was adhered to: The reactants and catalyst were added to the reactor fitted with a reflux condenser. When the pressure was 0.1 mm Hg, the reaction mixture was heated to the desired temperature. Then the reactants are well mixed for 2 h. The samples following the experimentation at the end of the reaction were then analyzed by gas chromatography.

During the experiment, the following variables remained constant: reactor temperature, impeller speed, and pressure.

Statistical Analysis

Statistical design of experiments as a proven technique continues to show increasing use in chemical process industries. Experimental designs are frequently performed in the study of empirical relationships, in terms of a mathematical model, between one or more measured responses and a number of variables or factors. They have been successfully used since 1935 (Fisher, 1935) in a wide variaty of fields in the research laboratory and industry.

In this paper, statistic type for the study of the synthesis of an ester analogue of jojoba oil was a two full 2^3 factorial design (three factors each at two levels).

The selection of the factors was made by considering the chemistry of the system and the practical use of the model the design generates. The factors were X_T, temperature; X_C, initial catalyst concentration; and X_M, initial alcohol–acid molar ratio. The response, Y, selected was the amount of ester formed.

In the design, both the reaction time and pressure were fixed, although it was envisaged that their effects will be studied later and incorporated in the model. The reaction time was 2 h, and the pressure was 0.1 mmHg.

Table I show the experimental matrix for the two factorials design obtained from the full design presented according to standard order. The first three columns of raw data give the factors on a natural scale and the last three the coded factors, in the dimensionless coordinate.

The coded values, X_T, are obtained by calculating

$$X_T = \frac{x_T - \bar{x}_T}{d} \quad (1)$$

for error estimation was made for four experiments in the central points. The order in which the runs were made was random.

The use of analysis and factorial design of experiments permits us to express the amount of ester formed as a

Table I. 2^3 Factorial Experimentation Matrix

expt	T, °C	C, g	M	X_T	X_C	X_M
			First Design			
1	150	0.10	1.00	+1	+1	+1
2	100	0.10	1.00	−1	+1	+1
3	150	0.05	1.00	+1	−1	+1
4	100	0.05	1.00	−1	−1	+1
5	150	0.10	0.50	+1	+1	−1
6	100	0.10	0.50	−1	+1	−1
7	150	0.05	0.50	+1	−1	−1
8	100	0.05	0.50	−1	−1	−1
9	125	0.075	0.75	0	0	0
10	125	0.075	0.75	0	0	0
11	125	0.075	0.75	0	0	0
12	125	0.075	0.75	0	0	0
			Second Design			
13	150	0.10	1.50	+1	+1	+1
14	100	0.10	1.50	−1	+1	+1
15	150	0.05	1.50	+1	−1	+1
16	100	0.05	1.50	−1	−1	+1
17	150	0.10	1.00	+1	+1	−1
18	100	0.10	1.00	−1	+1	−1
19	150	0.05	1.00	+1	−1	−1
20	100	0.05	1.00	−1	−1	−1
21	125	0.075	1.25	0	0	0
22	125	0.075	1.25	0	0	0
23	125	0.075	1.25	0	0	0
24	125	0.075	1.25	0	0	0

Table II. Experimental Results[a]

expt	expt order	Y_o, %	Y_c, %	e
		First Design		
1	3	70.00	67.04	2.96
2	7	14.00	14.19	−0.19
3	4	60.40	63.36	−2.96
4	5	10.70	10.51	0.19
5	1	34.10	35.39	−1.29
6	8	10.70	12.19	−1.49
7	2	33.00	31.71	1.29
8	11	10.00	8.51	1.49
9	12	44.4		
10	9	43.8		
11	6	46.2		
12	10	45.4		
		Second Design		
13	20	78.10	45.31	2.79
14	16	13.40	17.99	−4.59
15	13	77.00	75.31	1.69
16	19	18.10	17.99	0.11
17	3	70.00	67.44	2.56
18	7	14.00	10.11	−3.89
19	4	60.40	67.44	7.04
20	5	10.70	10.11	0.59
21	15	65.30		
22	17	60.10		
23	14	64.20		
24	18	62.20		

[a] Y_o, observed value; Y_c, calculated value.

polynomial model. If the levels of the factors are equally spaced, then orthogonal polynomials may be used. We can write the response and amount of ester as a function of the factors

$$Y = a_0 + a_1 X_T + a_2 X_C + a_3 X_M + a_{12} X_T X_C + a_{13} X_T X_M + a_{23} X_C X_M + a_{123} X_T X_C X_M \quad (2)$$

Results

The amounts of ester formed are reported in Table II. The influence of the reaction time can be observed in Figure 1. The effect of a factor on the response is simply the difference between the average value of the response
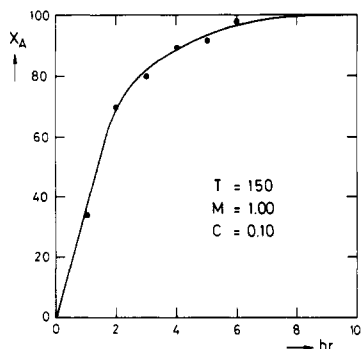
Figure 1. Influence of time on the amount of ester formed.

Table III. 2^3 Factorial: Analysis of Effects and Interactions[a]

rank	identity	ranked est.	confidence range	conclusion
		Curvature: Significant		
1	T	38.03	3.10	S (+)
2	M	16.83	3.10	S (+)
3	TM	14.83	3.10	S (+)
4	C	3.68	3.10	S (+)
5	CM	2.78	3.10	NS
6	TM	1.68	3.10	NS
7	TCM	1.48	3.10	NS
1	T	57.73	6.70	S (+)
2	M	7.88	6.70	S (+)
3	TM	4.48	6.70	NS
4	CM	-4.13	6.70	NS
5	TC	3.03	6.70	NS
6	C	2.33	6.70	NS
7	TCM	-0.13	6.70	NS

[a] S, significant; NS, nonsignificant.

for the four runs at high level and the average value of the response at low level.

From the experimental values, a statistical analysis was undertaken. The main effects and two and three iterations were calculated.

With a confidence level of 99%, the analysis of the experimental results, Table III, shows that temperature and initial molar ratio have a linear effect in both designs. The catalyst and the temperature–molar ratio interaction, a model of the form $Y = a_0 + a_1X_T + a_2X_M + a_3X_C + a_{12}X_{TM}$ for the first design and a model of the form $Y = a_0 + a_1X_T + a_2X_M$ for the second model, were fitted to the data multiple regression analysis.

The best-fitting response function is then conveniently written as follows:

first design

statistical model

$$Y = 30.36 + 19.01X_T + 8.41X_M + 1.84X_C + 7.42X_{TM} \qquad r = 0.997 \quad (3)$$

industrial model

$$Y = 15.74 - 0.13T + 73.50M - 114.60C + 1.19TM \quad (4)$$

second design

statistical model

$$Y = 42.71 + 28.66X_T + 3.94X_M \qquad r = 0.992 \quad (5)$$

industrial model

$$Y = 120.29 + 1.15T + 15.75M \qquad (6)$$

where statistical model data are fitted to the coded vari-

Table IV. Commercial Quality of Analogue of Jojoba Oil

	solidifying pt, °C	saponification value	I value	viscosity (25 °C), cP
jojoba oil	8	92	101	35.2
jojoba oil analogue	6	94	94	29

ables and industrial model data are fitted to real values of variables.

Commercial Quality

The parameters defining the industrial quality of refined jojoba and the product synthesized and purified by us are shown in Table IV.

Discussion

From eq 3 and 5 and Tables III and IV, it is concluded that, in the experimental range, the most significant main effect in both designs is temperature. This effect has a positive influence on the response and amount of ester formed. It signifies that with an increase of temperature the amount of ester increases. In the present results, it is important to note that the amount of ester formed at lower temperature levels is not very significant. This is due, probably, to the high activation energy of the esterification reaction (Urteaga, 1985).

Temperature and alcohol/acid molar ratio have a positive influence on both designs. Meanwhile, the catalyst concentration and the temperature–molar ratio interation have a positive influence only for the first set, so when these factors increase, the amount of ester increases.

The effect of catalyst concentration was statistically insignificant in the second design, probably due at low influence, in the chosen levels, on the reaction.

The statistical analysis indicating curvature effect is then estimated as the difference between the average of the center-point responses and the average of the factorial points, in their response over the range studied. This is due, probably, to the effect of temperature; the reaction rate depends exponentially on temperature. This means that first-order polynomial expressions are inadequate to describe the response surfaces fully and that further experiments are required to combine the design in some way as to obtain improvement of description.

However, the mathematical model used for the prediction of the amount of ester obtained was derived from the 2^3 design, giving a good fit of the experimental data to the polynomial model.

From an industrial point of view, an analogue of jojoba oil was synthesized with a commercial quality very similar at to that of refined jojoba oil, the most available unsaturated acid and alcohol in Spain, oleyl alcohol and oleic acid, obtained from olive oil starting as raw materials.

From an economicial point of view, the synthesis process is considered very attractive based on the low cost of the raw materials (2–4 $/kg) and the simplicity of the synthesis process (the time of the total conversion of the reactants is in the range 6–7 h, depending of the best reactions conditions).

Conclusions

The synthesis process of an analogue of jojoba oil has been studied using a full factorial design.

The response equation for the amount of ester formed has been established. From this equation, it is possible to forecast the conditions of treatment required to obtain a well-defined amount of ester.

In the study of the factors affecting the amount of ester formed, the results show that, within the ranges used for

the factors, the most important factor is temperature.

Even with these advantages, it should be emphasized that factorial design is a tool, a means to an end. It will not replace sound technical judgement or creativity in experimental work.

Nomenclature

a_i = coefficient of the estimated model
CM = catalyst–molar ratio interaction
d = unit of variation of x from $\bar{x}$
e_i = residual of the ith experiment
K = either C, (catalyst), M (molar ratio), or T (temperature)
r = correlation coefficient
x_k = natural variable for element K and $\bar{x}_k$, its mean
x_K = coded variable for element K
Y_{ci} = estimated response for the ith experiment
Y_{oi} = response for the ith experiment
TM = temperature–molar ratio interaction

TC = temperature–catalyst interaction
TMC = temperature–molar ratio–catalyst interaction

Registry No. $CoCl_2$, 7646-79-9; oleic acid, 112-80-1; oleic alcohol, 143-28-2.

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Correlation of Liquid–Liquid Equilibria for Some Water–Organic Liquid Systems in the Region 20–250 °C

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A group-contribution model of the UNIFAC type is used to correlate liquid–liquid equilibria for water–organic liquid systems over a wide temperature range. Good agreement with experiment is obtained using temperature-dependent water–organic interaction parameters. This correlation may be useful for engineering design for processing of fossil fuels.

Mutual solubilities of hydrocarbons and water are of interest in the petroleum and related industries. Hydrocarbon–water systems are sometimes encountered at high temperatures; these systems may also contain a large number of hydrocarbon derivatives such as phenolics. For process design, the compositions of coexisting water and hydrocarbon phases must be known or estimated.

Liquid–liquid equilibria (LLE) may be calculatd from an equation of state or from an excess-Gibbs-energy model. In recent years, equations of state have been used to represent binary water–hydrocarbon equilibria (Tsonopoulos and Wilson, 1983; Kabadi and Danner, 1985; Lüdecke and Prausnitz, 1985; Mollerup and Clark, 1988). However, only limited success was achieved when the same equation of state was used to represent the compositions of both liquid phases over a wide range of temperatures.

Group-contribution models are often used for correlating and estimating fluid-phase equilibria; the best known of these is UNIFAC (Fredenslund et al., 1975). In the original UNIFAC correlation, interaction parameters were fitted primarily to vapor–liquid equilibria (VLE); as a result, predictions of LLE were generally not quantitative. Magnussen and co-workers (1981) later published a set of UNIFAC interaction parameters fitted mostly to LLE data which gave significantly improved predictions of LLE. Further modifications to the UNIFAC model have focused on the combinatorial contribution to the excess Gibbs

energy, and on the temperature dependence of the group-interaction parameters [for a review, see, e.g., Fredenslund and Rasmussen (1985) and Gmehling (1986)]. The most comprehensive and generally applicable group-contribution model currently available is the Modified UNIFAC model of Larsen et al. (1987) intended primarily for predicting VLE and heats of mixing.

UNIFAC predictions are necessarily most reliable for those thermodynamic data for which the interaction parameters are optimized (e.g., VLE, LLE, and heats of mixing) and for the temperature range over which the parameters are correlated. Further, since the UNIFAC model, in principle, applies to a large variety of mixtures, it is often not highly accurate for a limited class of mixtures.

This paper presents a UNIFAC model suitable for LLE of systems containing water and hydrocarbons (and some hydrocarbon derivatives) over a wide range of temperatures. The scope here is much narrower than that of some previous correlations, for example, Larsen's Modified UNIFAC and Magnussen's UNIFAC-LLE. Only a single class of mixtures (water and hydrocarbons) and a single thermodynamic property (LLE) are considered. By sacraficing generality, quantitative predictions are obtained for the systems of interest at normal and advanced temperatures.

We present here interaction parameters for water and seven common organic groups. Interaction parameters between water and organic groups are temperature dependent, while interactions not involving water are temperature independent. Inclusion of additional groups in

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