Laboratory Optimization of Process Variables in Reductive Ozonolysis of Methyl Soyate [1]

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Abstract

The laboratory experiments for reductive ozonolysis of methyl soyate were divided into four statistically designed groups, according to ozonolysis medium (methanol or water) and ozone carrier gas (oxygen or air). Each group comprised 27 separate experiments, each a one-third replicate of a 3^4 factorial. Significant independent variables were determined by a preliminary set of experiments. Besides ozonolysis medium (X) and carrier gas (Y), the following significant independent variables were studied: medium/ester ratio (A), reduction catalyst (B), reduction pressure by hydrogen (C), and reduction temperature (D).

By gas-liquid partition chromatography of the dimethyl acetals of the two products, which included methyl azelaaldehydate (MAZDA) and pelargonic aldehyde (PDA), aldehyde yields were determined for each experiment in the statistical groups.

Analysis of variance of the data (F-test) showed the following main effects and interactions for yield of MAZDA where oxygen carrier gas, water as the ozonolysis medium, and palladium-on-carbon catalyst were used for reduction: Y, YA, YB, YD, AD, BD, and AC. Data fit (regression analysis) provided regression equations. Computer solution of these equations indicated optimum process levels. Based on these optimum levels, the predicted over-all yield of MAZDA is 89% of theoretical.

Introduction

In general, unsaturated fatty esters may be converted to shorter-chain saturated aldehydic esters by reaction with ozone and then reduction of the ozonolysis intermediate (3,7). Either organic solvents, such as methanol, or water (4) may serve as the ozonization medium. Chain length of the aldehydic esters corresponds to that derived through cleavage of the original positions of the unsaturation. Since there is no bond migration during the process, reductive ozonolysis of methyl oleate (I) gives one mole of pelargonaldehyde (II) and one of methyl azelaaldehydate (MAZ) (III) (6). The aldehydes may be converted to their dimethyl acetals and the acetal ester (MAZDA) (IV) separated by distillation.

$$\underset{\text{(I)}}{CH_3(CH_2)_7CH = CH(CH_2)_7COOCH_3} + O_3 \longrightarrow \underset{\text{(Ia)}}{\text{Ozonolysis intermediate}}$$

$$\text{Ia} + H_2 \xrightarrow{Pd/C} \underset{\text{(II)}}{CH_3(CH_2)_7CH = O} + \underset{\text{(III)}}{O = CH(CH_2)_7COOCH_3}$$

$$\text{III} + 2CH_3OH \xrightarrow{BF_3} H_2O + \underset{\text{(IV)}}{(CH_3O)_2CH(CH_2)_7COOCH_3}$$

MAZ is a potentially useful intermediate to make new polymers and resins, for example, by conversion of MAZ to the corresponding 9-aminononanoate and its polymerization to a polyamide (nylon). MAZDA and other ester-acetal derivatives of azelaaldehyde have been shown by Pryde et al. (8) to have potential also as plasticizers for poly(vinyl chloride).

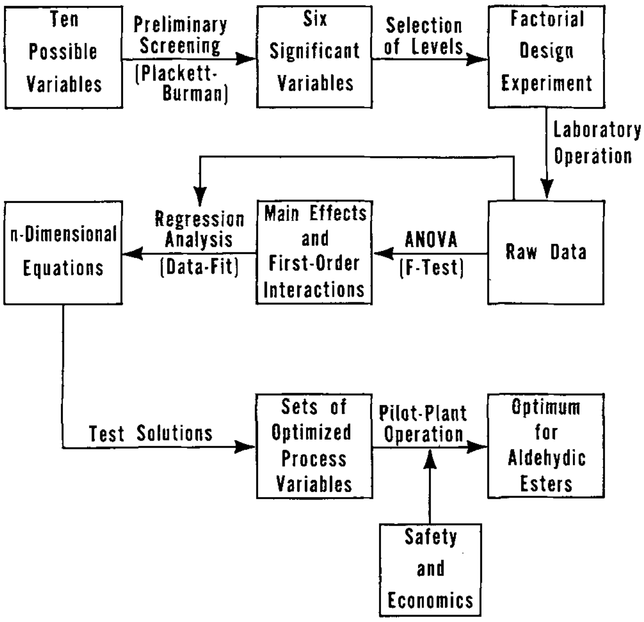

FIG. 1. Factorial experiment outline for the reductive ozonolysis of methyl soyate.

To produce MAZ economically in commercial quantities, a cheap raw material is necessary. Methyl soyate, obtainable by methanolysis of the oil, would appear to be highly suitable. Soybean oil is one of the cheapest unsaturated oils available and has the added advantage that essentially all its unsaturated fatty acids have a double bond in the 9-position. Some other oils have small amounts of unsaturation in other than the 9-position, which would introduce homologous materials that are undesirable for some polymer applications. Soybean oil has some disadvantages, including increased consumption of ozone resulting from multiple unsaturation and the production of more by-products compared with methyl oleate. However, an economic source of methyl oleate is not available at present. Composition of the methyl soyate for this study was 23.9% methyl oleate, 53.5% methyl linoleate, 8.6% methyl linolenate, and 14.0% combined methyl palmitate and stearate. Consequently caproaldehyde, malonaldehyde, and a small amount of propionaldehyde also are products of the reaction, in addition to pelargonaldehyde and methyl azelaaldehydate.

This report presents results of a statistical treatment of laboratory-scale experiments in the reductive ozonolysis of methyl soyate. The statistical treatment had as its objective the optimization of process variables to suppress impurities that could possibly arise during the reaction and to obtain the best MAZ

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TABLE I

Reductive Ozonolysis of Methyl Soyate in Methanol-Oxygen Carrier Gas

Factorial design[a]	GLC Analysis of dimethyl acetals[b]				Yields (% of theory)		
	PDA[c]	MAZDA[d]	Dimethyl azelate	Saturated esters[e]	PDA	MAZDA	Total[f]
X_0Y_0 (0000)	6.9	49.3	5.9	13.7	44.9	78.2	61.0
(0122)	7.3	44.8	8.3	12.5	50.6	75.8	62.4
(0211)	7.6	46.8	8.1	13.1	49.6	74.7	59.2
(1022)	7.0	40.2	5.8	10.0	47.6	66.8	63.0
(1111)	6.4	37.9	4.8	9.6	44.6	64.3	53.7
(1200)	7.7	45.2	4.6	12.2	46.8	67.2	55.5
(2011)	6.1	34.3	6.7	12.4	41.6	57.9	48.4
(2100)	7.2	42.9	7.8	12.8	49.4	71.8	60.1
(2222)	6.2	33.2	5.9	12.0	38.2	49.8	42.5

[a] See Factorial Design and Levels under Experimental Section for explanation.

[b] Column 25 ft of ⅛ in. O.D. Liquid phase 2% UCW-98 carried on 80–100 mesh Diatoport S. A 90C starting temperature, programmed 8.0C/min to 260C hold. Inlet, 270C. Detector, hydrogen flame. Weight percentages given by comparison of corrected peak area to internal standard, methyl myristate. Peak areas observed were corrected by a factor comparing the area with the corresponding known peak area.

[c] Pelargonaldehyde dimethyl acetal.

[d] Methyl azelaaldehydate dimethyl acetal.

[e] Recovered unchanged from *starting methyl* soyate.

[f] Not including aldehydes C_3 and lower, which were lost to the water-wash phases.

yield. Fig. 1 presents on outline of the study. Pilot-plant operation, economics, and plant design will be covered in another report.

Experimental Section

Preliminary Screening

A Placket-Burman design (5), employing 16 experiments, was run on 10 possible process variables in reductive ozonolysis: 1) ester type, 2) ozonolysis medium, 3) medium:ester ratio, 4) total weight of ester, 5) carrier gas, 6) carrier gas rate, 7) catalyst, 8) reduction temperature, 9) reduction pressure (hydrogen), and 10) open bubbling or dispersion-contacting of hydrogen and ozonide. In all, 16 individual preliminary experiments were done. Ozone was bubbled into a solution of methyl soyate through a coarse, fritted disperser, which was scrupulously clean. The reaction was stirred through a magnetic drive. Temperature was maintained constant by a thermostated, external cooling bath. Reduction of the ozonolysis intermediate was performed at once, or the intermediate was stored not more than a few days in a freezing chest.

Six of the 10 variables screened were statistically significant to 90% confidence or greater in effect on total carbonyl (aldehyde). Since a seventh, medium: ester ratio, was significant to 80% confidence, it was included in the experiment. When the ester is specified, as in methyl soyate feed stock, the six possible process variables to consider are ozonolysis medium, carrier gas, medium:ester ratio, catalyst, temperature, and hydrogen pressure of the reduction. These variables are the basis of the factorial design.

Factorial Design and Levels

Designs were set up, beginning with the independent variables, ozonolysis medium (X) and carrier gas (Y). These were coded for identification only as follows: methanol (0), water (1), oxygen (0), and air (1). Four designs were stated as follows: X_0Y_0, X_0Y_1, X_1Y_0, and X_1Y_1. Each design was a one-third replicate of a full 3^4 factorial experiment (that is, 27 experiments in each of the separate designs). Each of the remaining four independent variables was tested at three levels. Again, these were coded for identification by numerals, 0, 1, or 2, according to level. Code numbers following the levels or types are for identification only. The 0/1 (code No. 1) identifies a medium level of zero, that is, the ozonolysis was done neat.

The levels were as follows: medium:ester ratio (weight) at 0.75/1(0), 0/1(1), and 1.5/1(2); catalysts $Pd/BaSO_4$(0), Pd/C(1), and Pd/SiO_2(2); hydrogen pressure at 15 psig (0), 150 psig (1), and 300 psig (2); and reduction temperature at 25C (0), 50C (1), and 75C (2). For example, an experiment designated by the code as X_0Y_1(2121) means that ozonolysis was carried out with methanol as the medium, air as the carrier gas, 1.5/1 parts by weight of methanol to methyl soyate during ozonization and then reduction of the ozonolysis product with Pd/C catalyst at a level of 300 psig hydrogen pressure, and temperature level 50C. Of course, since each design is a one-third replicate, only one-third of all the possible combinations of the design variables were tested experimentally.

Reductive Ozonolysis

Methyl soyate (50.0 g) and ozonolysis medium, if used, were charged to a 125-ml wash bottle, fitted with gas inlet tube with fritted gas disperser. Ozone in air or oxygen was bubbled in at 0.08 ft^3/min (in oxygen 134 mg 0_3/min). Temperature was maintained constant at 50 ± 2C or by use of a medium at 25 ± 2C. Ozonization was continued to approximately 100% to 106% of theory uptake, as measured by reaction of the exit gas with potassium iodide. The ozonolysis intermediate was taken up in 90 g of dry methanol

TABLE II

Reductive Ozonolysis of Methyl Soyate in *Methanol-Air Carrier* Gas

Factorial design	GLC Analysis of dimethyl acetals				Yields (% of theory)		
	PDA	MAZDA	Dimethyl azelate	Saturated esters	PDA	MAZDA	Total
X_0Y_1 (0000)	8.3	46.8	8.7	15.8	51.6	70.9	59.8
(2110)	7.4	41.0	6.4	12.5	51.6	69.5	58.2
(1111)	7.7	44.2	2.9	12.2	48.3	67.6	55.4
(2222)	9.4	40.0	7.0	12.7	60.5	62.7	57.2
(0210)	9.2	53.5	12.4	16.4	52.5	74.4	54.2
(1021)	8.4	50.9	2.4	11.7	54.3	80.2	65.8
(0120)	9.1	45.4	3.5	12.9	60.3	73.4	64.4
(1201)	7.8	45.0	4.0	11.0	56.0	78.5	64.5
(2012)	9.1	48.0	2.6	14.1	51.1	65.1	54.6

TABLE III

Reductive Ozonolysis of Methyl Soyate in Water-Oxygen Carrier Gas

Factorial design	GLC Analysis of dimethyl acetals				Yields (% of theory)		
	PDA	MAZDA	Dimethyl azelate	Saturated esters	PDA	MAZDA	Total
X_1Y_0 (0000)	11.2	50.3	1.2	13.1	77.7	85.1	75.2
(0021)	9.4	48.9	6.4	13.6	65.4	82.9	68.6
(2222)	10.4	51.2	8.6	13.2	64.7	77.8	65.1
(2100)	10.9	50.2	8.5	14.2	63.2	70.8	59.3
(0202)	10.0	51.4	6.9	13.1	64.2	80.4	67.5
(0211)	10.1	49.9	7.9	14.1	64.6	77.8	66.2
(0110)	9.9	50.8	9.3	14.1	61.7	77.3	66.0
(2011)	12.0	41.3	9.3	12.5	83.6	70.0	63.8
(0122)	10.0	53.0	7.4	15.3	67.7	87.5	74.2

if no medium was present; otherwise, the mixture was taken directly to the reduction step. Catalyst was added, and the whole was charged to a stainless steel, 300cc MagneDrive autoclave. Hydrogen pressure was held at 15, 150, or 300 psig. Temperature was controlled automatically to 25, 50, or 75C with a Barber-Colman Company regulator for heating and cooling. Reduction was continued until a negative starch-KI test was obtained.

After the solution of reduced ozonolysis intermediate was filtered and dried over anhydrous magnesium sulfate, excess dry methanol containing a catalytic quantity of BF_3 was added; this mixture was refluxed 15 min and cooled to room temperature. Then 100 ml of benzene was added, and the mixture was washed to neutrality with successive portions of water, 5% $NaHCO_3$, and more water. The washed solution was dried and stripped of benzene by rotary vacuum evaporation. In a typical example, 49.4 g of crude acetals resulted as residue on evaporation. By gas-liquid chromatography (GLC) of this residue, it was determined that total over-all conversion of unsaturation to aldehyde carbonyl and then to the acetals was 55.5% of theory. MAZDA yield was 67.2% of the theoretical. Distillation of the crude acetal product yielded a fraction of methyl azelaaldehydate dimethyl acetal (MAZDA), bp 104–112C (1.8 mm), which contained 85.1% by weight MAZDA by GLC [lit (6), bp 95–103C (0.35 mm)]. The infrared spectrum of the purified product was identical to that of an authentic sample. Typical results from the factorial experiments are shown in Tables I-IV. For brevity each table contains only a one-ninth replicate. (The one-third replicates described were actually carried out in the laboratory.)

Catalysts

The catalysts used were 10% palladium on charcoal (Matheson-Coleman-Bell Company), 5% palladium on barium sulfate (2), and 5% palladium on silica gel. Palladium on silica was prepared as follows. Five grams of $PdCl_2$ was dissolved in 50 cc of water made slightly acidic with HCl and heated to 60C. The solution was added to an aqueous dispersion of 50 g of pure chromatography-grade Silica Gel H, size 10–40 μ (E. Merk A.g., Darmstadt, Germany). The dispersion was maintained and heated to 60C. After stirring for 5 min, the $PdCl_2$ was treated by adding 10% of NaOH to pH 8. The precipitate of palladium oxide was adsorbed as formed onto the silica gel.

This whole mixture was filtered, and the reddish-brown, moist precipitate was washed, redispersed in water, and then reduced at 35 psi H_2 for 1½ hr until hydrogen uptake was complete. The catalyst was then filtered and dried under vacuum at 80C. In the reduction step, the catalyst was always new. It was added in a methyl acetate slurry in quantity equivalent to 0.1% Pd, based on the starting 50-g charge of methyl soyate. After reduction the catalyst was removed by filtration.

Methyl Soyate

Methyl soyate was prepared from Archer-Daniels-Midland Company Superb soybean oil, saponification number 189.3 (mg KOH/g) and iodine number 132 (g I_2/100 g). To prepare the methyl soyate, 15 gal (115 lb) of soybean oil, 65 lb of methanol, and 0.12 lb of potassium hydroxide were mixed and heated with agitation for 3.5 hr. The mixture was allowed to separate, and the methanolic glycerol layer was discarded. The crude methyl soyate was washed three times with equal volumes of water to remove soaps and methanol, dried, and then distilled. A 10-gal fraction of water-white methyl soyate boiling at 170–180C (0.15–0.3 mm) was taken as the sole raw material source for the factorial experiment. *Anal*: iodine number = 131.5 g I_2/100 g; saponification number = 190.5 mg KOH/g; and composition by GLC: 23.9% methyl oleate, 53.5% methyl linoleate, 8.0% methyl linolenate, 9.3% methyl palmitate, and 4.7% methyl stearate.

Results and Discussion

Tabulations taken from experimental results of the one-third statistical replicate run by the 3^4 factorial design are shown in Tables I-IV. To save space, each table contains only the one-ninth statistical replicate rather than one-third of the full 3^4 factorial.

TABLE IV

Reductive Ozonolysis of Methyl Soyate in Water-Air Carrier Gas

Factorial design	GLC Analysis of dimethyl acetals				Yields (% of theory)		
	PDA	MAZDA	Dimethyl azelate	Saturated esters	PDA	MAZDA	Total
X_1Y_1 (0000)	9.2	50.7	3.3	15.4	54.0	72.5	60.4
(2012)	9.5	40.3	3.2	13.8	58.9	60.8	52.6
(2102)	8.9	45.1	12.3	15.1	56.9	70.2	57.0
(0120)	10.5	53.2	3.2	11.5	72.8	89.9	76.3
(2222)	11.2	54.1	6.7	14.9	68.2	80.4	65.1
(0221)	11.3	45.5	9.4	11.9	79.2	77.6	70.7
(2001)	9.0	41.9	8.6	14.6	57.2	64.8	59.0
(2121)	11.7	33.8	10.3	12.7	74.5	52.4	52.7
(2211)	12.6	45.2	7.3	11.1	84.9	74.2	70.6

Consequently, some data on maximum yields, listed below, do not appear in the tables.

Maximum MAZDA yields compared to the theoretical after 100% ozone uptake, which was observed in all cases, were the following:

X_0Y_0 (0110), 85.8%
X_0Y_1 (0112), 80.0%
X_1Y_0 (0012), 89.8%
X_1Y_1 (0120), 89.9%
XY_1 (1122), 86.7% (no solvent)

The experimental error estimate is calculated at the 95% confidence level to be ±3 percentage points.

From the yields listed, above it appears that with water as an ozonolysis medium (X_1), which provides a safe, pumpable dispersion of the ozonide, at least as great a MAZDA yield may be expected as when the medium is methanol (X_0). Therefore, for the procedure to optimize the independent variables for maximum MAZDA, water was selected as the ozonization medium, which is Level 1 of the statistical design. Selection of oxygen (ozonator recycle gas) rather than air as the carrier gas specified an arbitrary level of 0. Since two of the six variables were specified by selection, these two are omitted from optimization. Remaining then are medium:ester ratio (A), catalyst (B), hydrogen pressure (C), and reduction temperature (D) for optimization. But the catalyst is also restricted (because of commercial availability) to palladium on carbon, which fixes variable B at Level 1. So, finally, variables A, C, and D remain to analyze and optimize.

Standard statistical techniques were employed (1). The analysis of variance or MAZDA yield to 90% or greater confidence limit shows the following significant main effects (single letter) and the following first-order interactions (double letters): Y, YA, YB, YD, AD, BD, and AC. AC interaction was somewhat less than 90% confidence limit, but was included in the regression study for better data fit. Since variables A, C, and D appear, they will likely occur in the regression expression for MAZDA yield (M). Analysis of variance for total conversion to aldehydic materials (CON) yields the following main effects and first-order interactions: X, Y, YA, YB, YD, AD, BC, and BD. It will be noted that although analysis of variance shows MAZDA yield to be independent of ozonolysis medium (X), total conversion is not independent of the medium, and an optimum medium may indeed exist for any given set of conditions which constitute a "system." As with the MAZDA yield, total conversion for the system, water-oxygen carrier—Pd/C catalyst, is determined by the significant independent variables A, C, and D.

The process of data fit (regression analysis) will give an equation for each desired dependent variable for each system selected. For the particular system described herein, MAZDA yield, PDA yield (PD), and total conversion to aldehydes are stated in percentage of theory by regression equations. In these equations substitutions for A, C, and D are made directly in the units employed in the study, namely, a ratio (including 0), psig, and °C.

$$M = 91.06 + 12.96A - 1.217D + 0.03311AC - 8.47A^2 + 0.01319D^2$$

$$PD = 50.22 + 30.47A - 0.07557C - 14.01A^2 + 0.0002425C^2 + 0.0007238D^2$$

$$CON = 61.53 + 20.60A - 0.4593D - 10.99A^2 + 0.00004871C^2 + 0.006107D^2$$

Note that X, Y, and B do not appear in these equations since they have been fixed.

In optimizing, the equations are repeatedly solved, and the sets of values are found of independent variables A, C, and D associated with each of the several maxima for M, PD, and CON. With an IBM 1620/1311 computing system, machine solution resulted in thousands of sets of these independent variables that satisfied the regression equation for M, which was of primary interest. The sets for maximum yields of M were selected by the same machine. The process is termed "optimization." By this process it was found that optimum levels of M for the system, water-oxygen carrier-Pd/C catalyst, are as follows:

Medium:ester ratio (A) = 1.3/1
Hydrogen pressure (C) = 300 psig
Reduction temperature (D) = 75C

Solving the regression equation for M by substitution of these optimum levels of A, C, and D gives the maximum MAZDA yield (M) predicted for the system. Solution of the remaining equations (based on optimum MAZDA levels) for PD and CON predicts what levels of pelargonic aldehyde coproduct (PD) and over-all conversion to aldehydes (CON) will result when the conditions of optimum MAZDA yield are employed. The predictions are: M = 89.4% (maximum), PD = 69.4%, CON = 74.0%.

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