Pilot Run, Plant Design and Cost Analysis for Reductive Ozonolysis of Methyl Soyate[1]

P.E. THROCKMORTON, Ashland Oil, Inc., Research and Development Laboratories,
Columbus, Ohio 43216, and **E.H. PRYDE**,[2] Northern Regional Research
Laboratory,[3] Peoria, Illinois 61604

ABSTRACT

Preparation of methyl azelaaldehydate dimethyl acetal (MAzDA) from methyl soyate was investigated on a pilot scale via the sequence ozonization, hydrogenation, acetalization and fractional distillation. A water-methyl soyate emulsion for the ozonization step was preferred to methanolic solution or neat methyl soyate for reasons of cost and safety. Ozonization of the water-methyl soyate emulsion (1.63:1 ratio) in a six-plate sieve tower produced 1271 lb aqueous peroxidic emulsion during 12 days of continuous operation. Because a continuous hydrogenation facility was not available, reduction was done in 200 lb batches. Since batch hydrogenation of the peroxidic emulsion in this quantity was difficult to control and optimum conditions were difficult to maintain, maximum yield of the product was only 56%. The average yield for seven batches was 48.3%. However laboratory hydrogenation under optimum conditions of periodic samples taken from the sieve tower discharge indicated an overall yield of 74.5% (average of eight monitor samples). A plant designed to produce 10 million lb annually should be capable of producing MAzDA at a total manufacturing cost of 39 cents/lb or a net manufacturing cost of 27 cents/lb with byproduct credit conservatively estimated. Methyl soyate ozonolysis products are not sensitive to detonation, and their exothermic decomposition is greatly moderated by the presence of water.

INTRODUCTION

Laboratory optimization of process variables by statistically designed experiments for the reductive ozonolysis of methyl soyate to methyl azelaaldehydate dimethyl acetal (MAzDA) was described in a previous report (1). An overall MAzDA yield of 89% was predicted if the ozonization was conducted in the presence of water at a water-ester ratio of ca. 1.3:1 and if the reduction was carried out with hydrogen over palladium on charcoal at 300 psig of hydrogen and 75 C. The water-ester ratio is not critical over a range of ca. 1.0:1 to 1.7:1 provided a water-in-oil emulsion is maintained. For example, an 88% yield is predicted at a water-ester ratio of 1.7:1 when the regression equation for MAzDA yield is employed (1). An attempt was made to apply these conditions to pilot plant operation to provide data for plant design and cost analysis. The main problem anticipated was development of a continuous ozonization procedure for the water-in-oil emulsion. MAzDA is of interest as an intermediate for the synthesis of nylon-9 (2) and of low temperature plasticizer-stabilizers (3).

EXPERIMENTAL PROCEDURES

Materials

Methyl soyate was prepared as previously described (1) from alkali-refined soybean oil. The distilled methyl soyate had the following composition as measured by gas liquid chromatography (GLC): oleate, 23.9%; linoleate, 53.5%; linolenate, 8.6%; saturated C_{16}-C_{18} esters, 14.0%.

Pilot Plant Operations

Ozonolysis and stripping were carried out continuously in a reactor consisting of 4 in. ID glass pipe fitted with six stainless steel (type 316) sieve trays. The ozonization section was jacketed with 6 in. OD glass pipe to provide annular space for cooling water (Fig. 1). The ozone-oxygen mixture was introduced at tray 4. Nitrogen was introduced at the bottom of the reactor to strip the peroxidic mixture of unreacted ozone and oxygen. A scheme for the ozonization step is provided in Figure 2.

The ozonator (Welsbach Model No. CL34-D19L) was operated at an oxygen pressure of 12 psig at source and 7.5-8 psig in the ozonator chamber, with cooling water at no more than 27 C. The oxygen flow was 3.8-4.4 cf/hr with no provision for oxygen recycle. The nitrogen flow was 10-15 cf/hr. Distilled methyl soyate and water were simultaneously introduced into the tower at the respective average rates of·2.07 lb/hr and 3.38 lb/hr to give an average water-ester ratio of 1.63:1. The liquid level on each tray was maintained at 1.25 in. Temperatures at the top two trays were 51 C; temperatures at the lower trays were 27-35 C.

The ozonization was monitored periodically by sampling the reactor discharge stream and hydrogenating 100 g samples in the laboratory at optimum conditions of 300 psig hydrogen and 75 C. At a water-ester ratio of 1.63:1, the overall yield of MAzDA is predicted to be 88.8% (1). Sample yields of MAzDA increased as the reaction proceeded from 67.5% at 118 hr to 86.2% at 198 hr, 30 min and 96.7% at 210 hr. At 240 hr, 30 min the yield measured 72.2%. The average yield of monitored samples was 74.5%. The amount of water present during hydrogenation had no effect on yield.

Ozonization was carried out for 275 continuous hours out of 288 hr (12 calendar days). The product, an aqueous peroxidic emulsion, was stored at -10 C in seven batches of 140-200 lb each for not more than 48 hr and preferably less than 16 hr. The material balance for the ozonization step over the period operated is shown in Table I. The net loss includes water and the more volatile aldehydes (propionaldehyde and caproaldehyde) that were volatilized or entrained and lost through the vent at the top of the reactor.

Each of the seven peroxidic emulsion lots was hydrogenated in a pilot plant, 30 gal, stainless steel (type 316) autoclave with 0.1% (based on peroxidic emulsion) of 10% Pd on charcoal. Even in the presence of water, this strongly exothermic hydrogenation was difficult to control as a batch system on the pilot scale (140-200 lb), and temperatures approached 100 C, which was above the recommended optimum 75 C (1). Operation at ca. 200 psig, which was below the recommended optimum 300 psig, was necessary to ameliorate the exotherm. As a result, the overall yield of MAzDA from any one of these pilot lots was not greater than 56% of theory.

Storage in glass of the peroxidic emulsion did not affect yields significantly at 0-25 C for periods of less than 16 hr

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[2] To whom correspondence should be addressed.

[3] ARS, USDA.

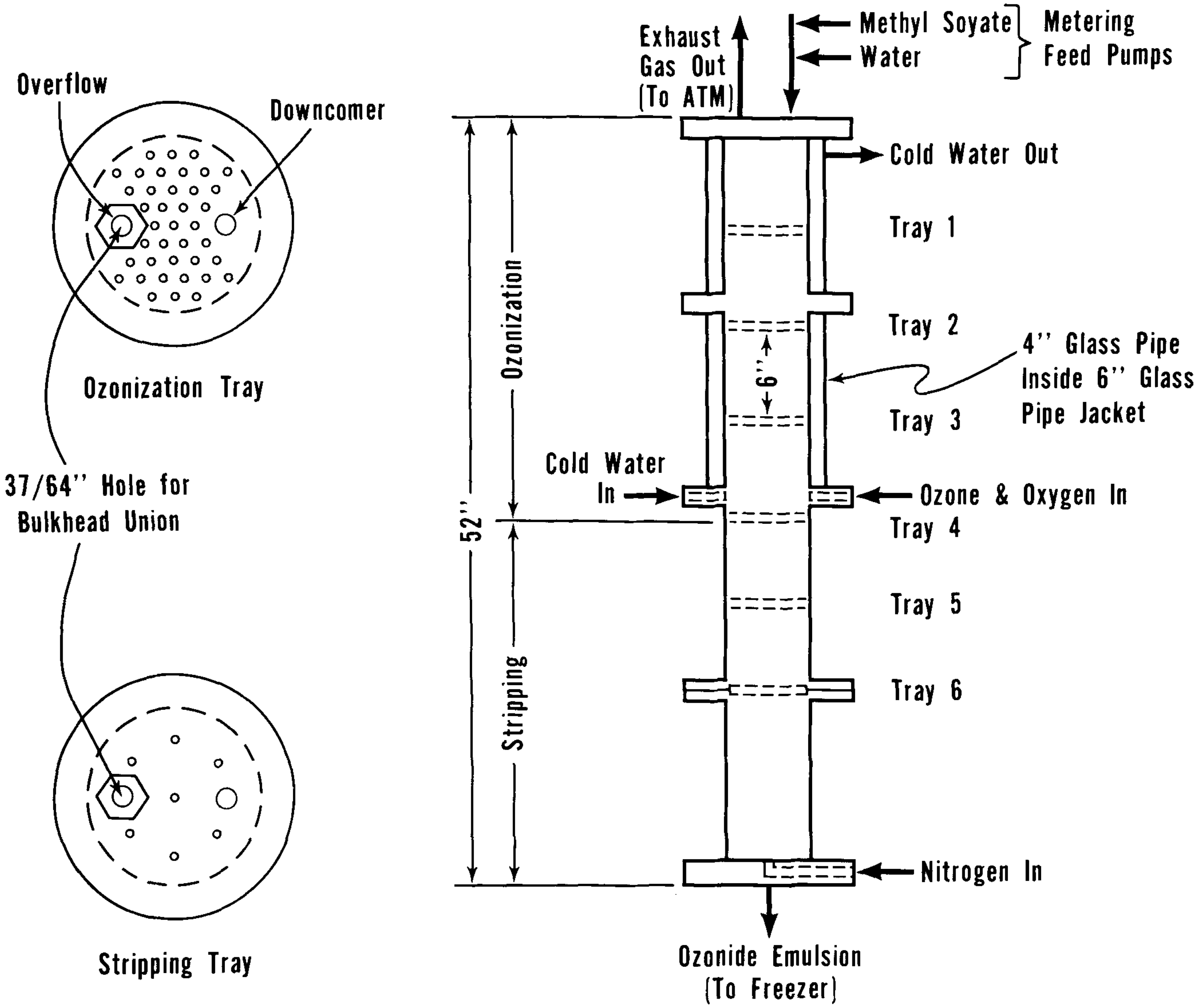

FIG. 1. Continuous ozonization reactor and sieve X-ray detail.

but lowered yields at longer times. Contact with stainless steel, as in the sieve trays, did not reduce yield. Overozonization, up to 130% of theory, did not increase acidity, which was maximum at 100% ozonization. (If methanol replaced water, overozonization steadily increased acidity beyond 100% ozonization.) The catalyst was recovered by rapid filtration and reused for each of the hydrogenation batches. Makeup amounting to 10% of recovered catalyst was added.

TABLE I

Material Balance for Ozonization Step

Material	Average, lb/hr	Total, lb
Charge		
Methyl soyate	2.07	569.5
Water	3.38	930
Ozone	0.48	131.8
Total	5.93	1631.3
Discharge		
Aqueous peroxidic product	4.63	1271.3
Net loss	1.30	360.0

TABLE II

Process, Distillation and Overall Yields

Product[a]	Process yield, mol %	Distillation recovery, mol %	Overall yield, mol %
MAzDA	90	85	76.5
PDA	70	95	66.5
CDA	40	95	38.0

[a]MAzDA = methyl azelaaldehydate dimethyl acetal; PDA = pelargonaldehyde dimethyl acetal; CDA = caproaldehyde dimethyl acetal.

The crude aldehyde mixture was dried by azeotropic distillation from benzene solution and converted to dimethyl acetals in excess methanol with 2.5% concentrated sulfuric acid as catalyst. The solution was washed with water and neutralized with a 10% solution of sodium bicarbonate. After the solvent was removed by distillation, the crude mixture of dimethyl acetals weighed 530 lb and had the following composition by gas liquid chromatography: MAzDA, 40.1%; pelargonaldehyde dimethyl acetal (PDA), 9.6%; caproaldehyde dimethyl acetal (CDA), 7.4%; dimethyl azelate (DMA), 9.3% and C_{16}-C_{18} saturated esters (SE), 22.3%.

Distillation of 570 lb of the crude dimethyl acetals through a batch still, having a 50 gal internal working capacity and heated with Dowtherm and equipped with a steam-boosted liquid lift, produced 22.8 lb of a fraction boiling 85-98 C at 28-10 mm containing 54.4% CDA in other acetals and their enol ethers; 33.5 lb of a fraction boiling 96-100 C at 7-4 mm containing 62.5% PDA in other acetals and their enol ethers; and 155.6 lb of combined

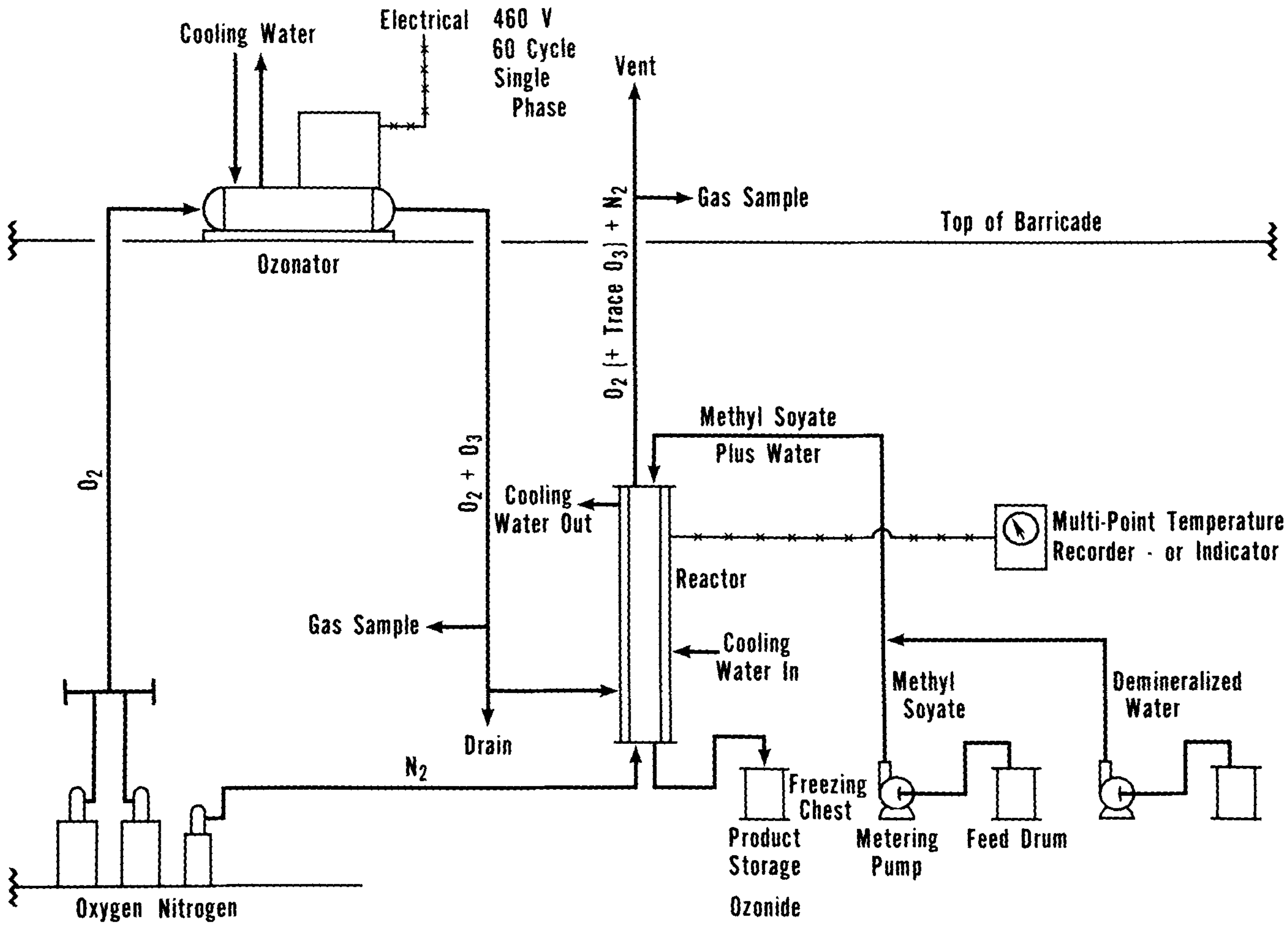

FIG. 2. Continuous ozonolysis pilot plant.

fractions boiling 124-139 C at 6 mm containing 80.9% MAzDA and other acetals, dimethyl azelate and saturated esters. A number of intermediate fractions, 100 lb of higher boiling material (139-152 C at 6-5 mm) and 92 lb of undistilled material also resulted from this distillation.

Ozonization Product Stability

Preliminary tests were carried out by heating the peroxidic material in an open aluminum cup and by thermogravimetric analysis (TGA). The least stable product was soybean oil ozonized without a solvent, i.e., neat; it flashed off the cup at temperatures above 60 C, and TGA indicated total and rapid decomposition starting at 120 C. More stable was the product obtained by ozonizing methyl soyate in methanol; it decomposed slowly and did not flash in the cup. TGA indicated gradual decomposition from 100 to 150 C but rapid above 150 C. The most stable ozonization product was that obtained in the presence of water; TGA recorded slow, gradual decomposition beginning at ca. 100 C, but somewhat less than one-third of its original weight still remained at 300 C.

Further tests were carried out at Thiokol Corp. for JANAF (Joint Army-Navy-Air Force) thermal stability and for impact and detonation sensitivity. The tests were carried out on methyl soyate ozonized neat and on the mixture produced from the neat ozonization product with 75% of its weight of water.

In the JANAF thermal stability test, the sample temperature is continuously compared to the heating medium, heated at a constant rate. Methyl soyate ozonized neat exhibited a gradually increasing exotherm beginning at 50 C. At a bath temperature of 80 C, the sample temperature was 160 C, and thereafter the temperature differential exceeded the recorder capacity. Sample temperature then dropped to 134 C as the bath temperature rose to 125 C, at which point a second but small exotherm occurred. Water-diluted ozonolysis products caused a slight, gently rising exotherm beginning at 94 C that peaked at 138 C, at which point the bath temperature was 130 C. Sample temperature then subsided to bath temperature as the latter reached 157 C.

Neither ozonolysis product was sensitive to impact with a 2 kg weight or to initiation by a standard no. 8 blasting

TABLE III

Mass Flow of Selected Streams

Material	Flow,[a] lb/hr
In	
Methyl soyate	2200
Water (ozonolysis medium)	2860
Oxygen (to ozonator)	9480
Ozone	550
Make-up oxygen	617
Hydrogen	46
Make-up hydrogen	23
Benzene	221
Methanol	1650
Out[b]	
MAzDA	1324
PDA	248
CDA	225
Saturated fatty esters	379
Distillation bottoms	252

[a] Flow on the basis of 24 hr/day, 315 days/year.

[b] For abbreviations, see footnote a in Table II.

[c] Includes 69 lb/hr dimethyl azelate as impurity.

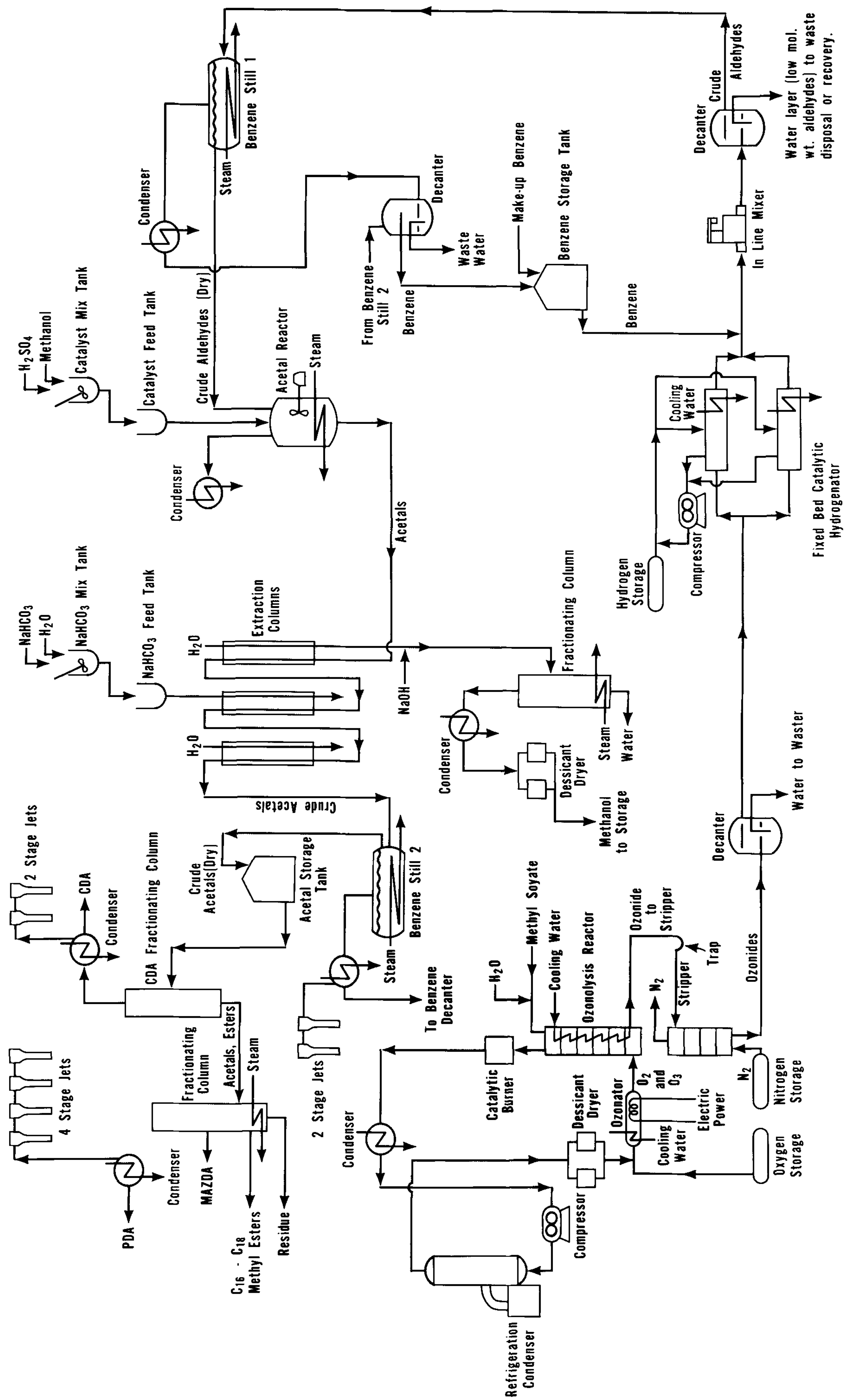

FIG. 3. Production of aldehydic esters by ozonization and reduction. CDA, PDA and MAzDA are the respective dimethyl acetals of caproaldehyde, pelargonaldehyde and methyl azelaaldehydate.

cap measured by volume increase of the lead container in the Trauzl block test.

The test for detonation velocity was carried out in duplicate and only with methyl soyate ozonized neat. One pound samples failed to propagate a detonation when initiated by 150-g tetryl charges at ambient temperature and pressure. Detonation velocity was measured by constant-current resistance wire and by pressure probe methods.

RESULTS AND DISCUSSION

Before pilot scale experiments were attempted, the possible hazards associated with various ozonization products were assessed. Preliminary tests indicated the following order of stability for methyl soyate ozonization products formed in various media: aqueous peroxidic emulsion (H_2O/ester ratio of 1.4:1)≫methanolic peroxidic solution≫peroxidic product formed with solvent absent. In tests conducted at the Thiokol Corp., neither the neat nor the diluted ozonization product was an explosion hazard. Although the neat ozonization product exhibited strongly exothermic decomposition at elevated temperatures, the exotherm was moderated considerably by water.

When present in the ratios indicated, water forms a water-in-oil emulsion with methyl soyate (4). Ozonization of such an emulsion produces an aqueous peroxidic emulsion having characteristics that differ from those of ozonization products formed in oil-in-water emulsions (4,5). Others have noted the ameliorating effect that water has on byproduct ester formation during oxidative ozonolysis (6,7).

These results suggested that pilot scale reactions could be carried out safely but that a continuous process would be desirable to avoid accumulation of large stocks of ozonolysis products. Furthermore the ozonization medium should be water since the aqueous peroxidic emulsion formed was most stable and since it was shown previously (1) to give a predicted yield of 89%.

Pilot Plant Yields

Continuous ozonolysis proceeded smoothly in the sieve-tray column for 12 consecutive days. The aqueous peroxidic emulsion was collected in seven batches, each of which was hydrogenated in a batch reactor. Because of equipment limitations and an unexpectedly strong heat of reaction at the batch size of 140-200 lb, optimum conditions could not be maintained during hydrogenation. As a result the overall yield of MAzDA was 48.3%, much lower than the predicted yield of 89%. For a large plant, continuous hydrogenation over a fixed bed catalyst would appear to be essential; feasibility is indicated by lack of poisoning effects during catalyst reuse in pilot batch hydrogenations.

Although yield was disappointing in the overall pilot plant operations, potential yields indicated by laboratory hydrogenation of several stream samples approached the higher yields predicted. The results of the laboratory hydrogenation proved the efficacy of the pilot scale continuous ozonization. Laboratory hydrogenations were controlled more easily than the pilot hydrogenation in the autoclave; thus, by combining pilot ozonization and laboratory hydrogenation, optimum conditions for hydrogenation—300 psig hydrogen and 75 C—could be tested. Averaging the results from laboratory hydrogenation of all the stream samples taken from the pilot continuous ozonization tower (Fig. 1) produced the following values (mole per cent of theoretical): overall conversion: 62.0%; MAzDA: 74.5%; PDA: 60.4%; and CDA: 25.1%.

TABLE IV

Cost Detail for MAzDA[a] by
Reductive Ozonolysis of Unsaturated Esters
(Finished Product: 10 x 10^6 lb/year MAzDA;
Production Facilities Investment: $3,206,000)

Item	$/Year	$/lb of MAzDA
Raw material costs		
Raw materials		
Methyl soyate @ $0.127/lb	2,112,000	0.2112
Benzene	1,177	0.0001
Sulfuric acid	5,663	0.0006
Sodium hydroxide	21,600	0.0021
Methanol	343,900	0.0344
Sodium bicarbonate	24,060	0.0024
Catalyst	3,000	0.0003
Subtotal raw materials	2,511,400	0.2511
Utility costs		
Electric power @ $0.01/kw-hr[b]	164,250	0.0164
Cooling water	124,600	0.0125
Process water	4,800	0.0005
Steam, medium pressure	13,120	0.0013
Steam, water, electric and miscellaneous	44,000	0.0044
Instrument air	3,840	0.0004
Nitrogen	63,460	0.0063
Hydrogen	177,120	0.0177
Oxygen	120,110	0.0120
Subtotal utilities	715,300	0.0715
Operating expenses		
Direct supervision	8,000	0.0008
Direct process labor[c]	72,000	0.0072
Maintenance labor[d]	80,000	0.0080
Maintenance materials	80,150	0.0080
Operating supplies	480	0.0001
Subtotal operating expenses	240,630	0.0241
Total variable cost	3,467,330	0.3467
Plant fixed costs		
Payroll overhead	1,200	0.0001
General plant overhead	4,800	0.0005
Insurance rate	96,180	0.0096
Depreciation	320,600	0.0320
Subtotal plant fixed cost	422,780	0.0422
Total processing cost	1,378,710	0.1379
Total manufacturing cost	3,890,110	0.3890
Corporate expenses		
General and administration	100,000	0.0100
Research and development	74,760	0.0075
Selling expense	74,760	0.0075
Subtotal corporate expense	249,520	0.0250
Product cost	4,140,000	0.414
Working capital	651,400	
Total investment	3,857,000	

[a] MAzDA = methylazelaaldehydate dimethyl acetal.

[b] Includes process electric load (3.65 kw-hr/lb O_3 or 2010 kw-hr/hr) and plant lighting (20 kw-hr/hr).

[c] At $9.00/hr total for two workers per shift, including 15% overhead charge.

[d] At 2.5% of facilities investment.

TABLE V

Byproduct Credits

Byproduct[a]	Amount produced, lb/lb of MAzDA[a]	Value, $/lb	Value, $/lb of MAzDA
PDA	0.1873	0.20	0.0375
CDA	0.1699	0.20	0.0340
Saturated fatty esters	0.2863	0.15	0.0429
Total	0.6435		0.114

[a] For abbreviations, see footnote a in Table II.

TABLE VI

Selling Price and Profit

Item	Profit markup, %		
	10	20	30
Unit profit, $/lb	0.04	0.08	0.12
Selling price, $/lb	0.46	0.50	0.54
Gross profit, $	414,000	828,000	1,242,000
Gross return on investment, %/year	10.73	21.46	32.19
Net profit, $	215,000	431,000	646,000
Net return on investment, %	5.58	11.16	16.74
Payout, year	5.98	4.26	3.31

Plant Design

A commercial plant for production of 10 million lb of MAzDA annually was designed with the data supplied by laboratory hydrogenation of the pilot ozonization products (Fig. 3), since the pilot hydrogenations were not representative. The yields on which the design was based include an overall yield of 76.5% for MAzDA (Table II). Key features of the design include continuous ozonization of an aqueous methyl soyate emulsion in a sieve-tray tower, hydrogenation of the aqueous peroxidic emulsion over a fixed catalyst bed, acetal formation and then fractionation to separate products. With an input of 2200 lb/hr of methyl soyate, an output of 1324 lb/hr of MAzDA (95% purity) would be expected (Table III). An additional 1104 lb/hr of byproducts would also be expected. In connection with the oxygen recycle, the usual catalytic burner has been provided to remove volatile organic compounds, which, if not removed, might cause an explosion in the ozonator.

Cost Analysis

Cost details for an annual production of 10 million lb of MAzDA are presented in Table IV. The investment in production facilities is $3,206,000, including the necessary bank of ozonators, oxygen recycle system and installation, estimated at $1,035,000. For example, output of 20 ozonator units each producing 27.5 lb/hr, would be required to supply 550 lb ozone per hour. This ozone requirement could be reduced from 550 to 301 lb/hr if the only unsaturated fatty ester present was methyl oleate. Nevertheless methyl soyate was chosen as the basic starting material because of the availability and relatively low cost of soybean oil and because all the unsaturated fatty esters present have unsaturation in the 9,10 position. Use of soybean esters assured the absence of homologous materials in the product, a desirable circumstance in our investigations with nylon-9 (2).

The total manufacturing cost of $0.389 and product cost of $0.414/lb of MAzDA do not reflect any byproduct credit. The marketable byproducts amount to 0.6435 lb/lb of MAzDA (Table V) and should have values estimated conservatively at $0.15-0.20/lb. The byproduct credit reduces the manufacturing cost by ca. 30%: total manufacturing cost: $0.389/lb MAzDA; byproduct credit: $0.114/lb MAzDA; and net manufacturing cost: $0.275/lb MAzDA.

At a selling price of ca. $0.45 to ca. $0.54/lb of MAzDA, the net return on investment should range from 5 to 15% even with no byproduct credit (Table VI).

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