Development of a Continuous Process for Enol Esters of Fatty Acids

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ABSTRACT AND SUMMARY

A continuous process for the production of isopropenyl stearate from stearic acid and propyne was developed. The reaction proceeds at elevated pressures and temperatures (~550 psig and 400 F, respectively) in about 10 min. A slower, second reaction produces stearic anhydride from the isopropenyl stearate. A recovery section was devised, wherein the liquid product stream is chilled, recovered as flakes, and extracted with a solvent, e.g. Skelly B. Reaction studies were scaled-up from 10 to 40 lb feed/hr using triple pressed stearic acid and MAPP® gas (AIRCO, Inc., Montvale, NJ), a commercially available gas containing a nominal 1/3 propyne, 1/3 propadiene, and 1/3 stabilizing, saturated hydrocarbons. The acid and propyne are reacted in the presence of zinc stearate in a continuous stirred tank reactor (CSTR). The reaction is "finished" in a short tubular reactor. Data are presented on the effect of pressure, temperature, catalyst level, dwell in the reactors, and solvent ratio during extraction. The product is about 92% isopropenyl ester, contaminated with unconverted stearic acid and by-product stearic anhydride.

INTRODUCTION

Isopropenyl stearate (IPS) is a highly reactive chemical intermediate, useful for acylating a variety of chemical compounds. The acylation releases only acetone as a by-product, resulting in a "cleaner" process than alternative acylations.

Rothman et al. synthesized IPS in 1962 (1) and Rothman and coworkers demonstrated that IPS can be used to acylate many classes of compounds under relatively mild and clean reaction conditions (2,3).

Two separate pathways are available for the preparation of IPS. IPS had been produced by the interchange of stearic acid with isopropenyl acetate (1), and by the direct addition of propyne to stearic acid catalyzed by zinc stearate (4).

The kinetics of the interchange reaction was studied by Kozempel et al. (5). The kinetics study was used as the basis for the design of a bench scale semicontinuous recovery process. A cost estimate was made on the entire process. The results of this cost estimate were discouraging, while a preliminary cost estimate based on a paper process of the addition reaction was favorable. Therefore, all research was concentrated on the addition reaction.

The purpose of this study was to (a) identify process variables and specify optimal levels, (b) characterize the products attainable, and (c) describe and demonstrate a technically feasible process.

The study was conducted in four phases. The first was batch and the other three were continuous. In the first phase the reaction was studied in a batch reactor with 95% stearic acid and propyne. In the second phase, designated continuous-bench scale, the batch reactor was utilized as a continuous stirred tank reactor (CSTR). In all continuous stages, MAPP® (AIRCO, Inc., Montvale, NJ) gas[1] was substituted for propyne, and triple pressed stearic acid for 95% stearic acid. The third phase, designated continuous-pilot plant, was the design and operation of an integrated continuous pilot plant process including reaction and recovery. The fourth phase was scale-up of the continuous pilot plant reaction system. A new, larger CSTR was designed and built for phases three and four.

EXPERIMENTAL PROCEDURES

Analytical

Products were analyzed for IPS, stearic acid (HSt), and stearic anhydride (St_2O) by the method of Calhoun and DellaMonica (6). Results were "normalized" so that the sum of the constituents would total 100%. At lower concentrations of St_2O in continuous-pilot plant, the error in St_2O analyses was too great. In those cases, the analysis described by Kozempel and Craig (7) was used. The fatty acid composition of feed and products was determined by the gas liquid chromatography (GLC) method of Luddy et al. (8). MAPP gas composition was determined by the method of Yoshimine et al. (9) on an F&M 720 gas chromatograph.

Materials

Commercially available zinc stearate ($ZnSt_2$), produced from triple pressed stearic acid, was used throughout the study. Fatty acid with a nominal content of 95% stearic acid was used in the batch phase of the study, whereas triple pressed stearic acid was used in the three continuous phases. Representative analyses of the triple pressed acid and catalyst are listed in Table I. The oleic acid used was Emersol 213, low titer.

Propyne, stated 96% purity, was purchased from AIRCO Chemical and Plastics and was used in the batch studies. MAPP gas, a stabilized form of propyne used for welding and brazing, was used in the three continuous phases of the study.

Equipment and Procedures

Batch: The batch reactor was a Parr 1-liter hydrogenation unit, modified by enclosing it in a steam jacket, in lieu of electrical heating. Circulating thermal fluid was later substituted for the steam. Thermocouples and a pressure transducer were attached to the unit.

Reactions were conducted by melting a charge of HSt and $ZnSt_2$ in the closed reactor, flushing with nitrogen, and adding a measured amount of liquid propyne by forcing it

TABLE I

Fatty Acid Distribution of Feed Acid and Catalyst[a]

Stearic acid		Zinc stearate	
Methyl ester	Wt %	Methyl ester	Wt %
$C_{14:0}$	6.1	$C_{14:0}$	7.0
$C_{16:1}$	1.3	$C_{16:0}$	37.1
$C_{16:0}$	44.2	$C_{18:0}$	52.2
$C_{18:0}$	43.1	$C_{18:1}$	tr

[a] Determined by gas liquid chromatography.

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[1] Use of a company or product name does not imply approval or recommendation to the exclusion of others which may also be suitable.

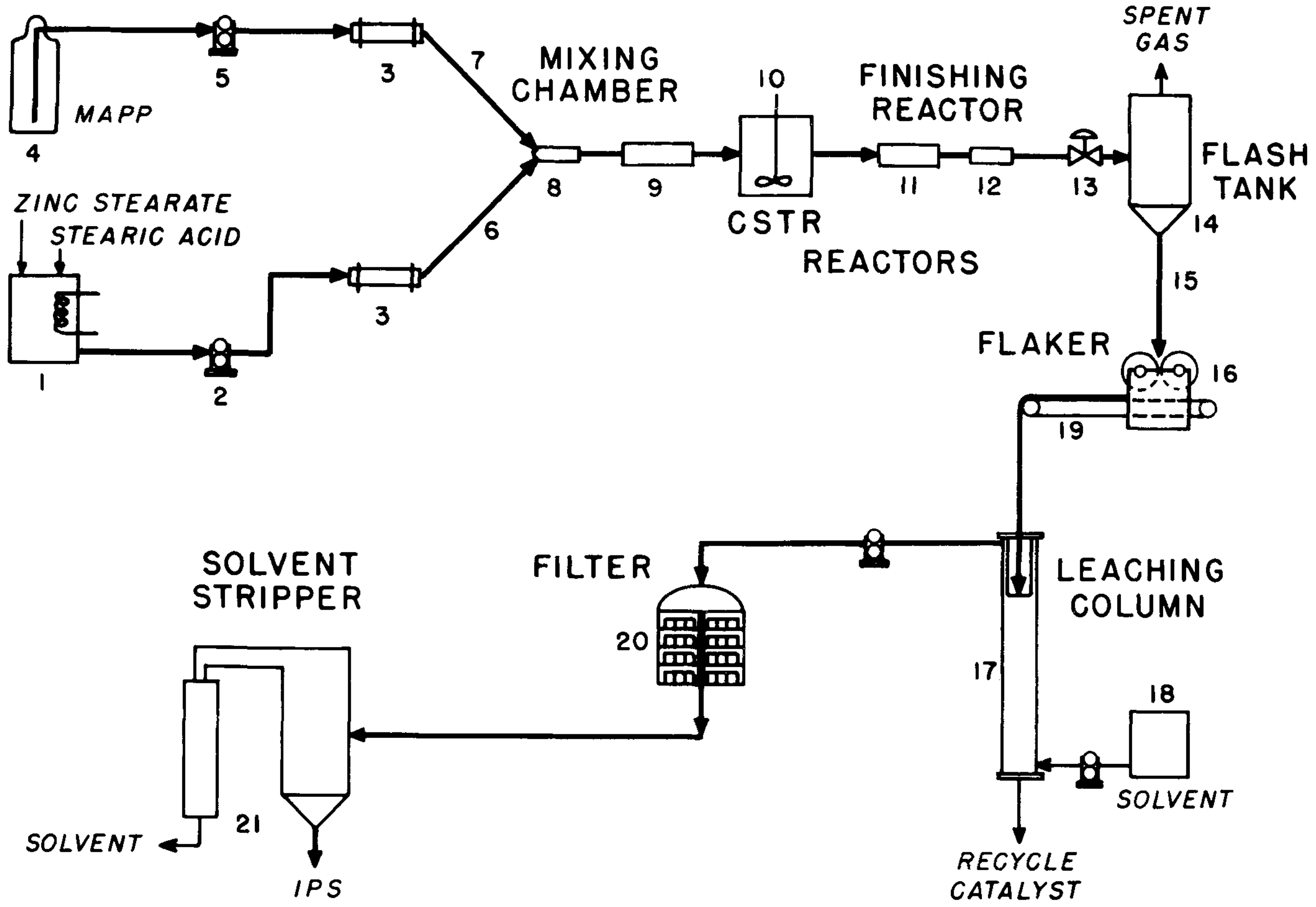

FIG. 1. Layout of continuous reaction pilot plant.

in with nitrogen. The melt filled about 25% of the reactor's volume, and the propyne charges gave a propyne:acid ratio of ca. 2.4:1. Total pressure in the reactor was greater than that exerted by the propyne and was controlled by introducing additional nitrogen.

Continuous-bench scale: The first continuous reactor used was a modification of the batch reactor to a CSTR. The reaction mixture was fed and product withdrawn continuously, maintaining a headspace in the reaction vessel. Dwell time was adjusted by cutting the exit tube to different heights, thus determining the level of removal, and by controlling flow rates. Liquid depth was not determinable, albeit it varied inversely with exit tube length. Thus, residence time could only be treated relatively, within a series of flow rates. Residence time distribution was determined by pumping oleic acid through the system, effecting a step change by switching abruptly to stearic acid, and analyzing the effluent by GLC.

Preliminary recovery studies were made in a small semicontinuous leaching apparatus in which a weighed amount of product was back flushed with solvent (Skellysolve B or petroleum ether) at a known flow rate. The supernatant was filtered by gravity. The filtrate was evaporated to dryness and the weight of the extracted product in the filtrate determined.

Continuous-pilot plant: Figure 1 is a schematic of the continuous integrated pilot plant. Explosion-proof construction was used throughout the process. The components in the reaction zone, [#8] through [#14], as well as the heat exchanger [#3], were enclosed in a barricade for safety.

(a) *Feed:* The HSt and $ZnSt_2$ were comelted and agitated in a glass-lined kettle [#1]. A double pipe heat exchanger (not indicated) was used to convey the liquid to the kettle [#1] to the suction side of a gear pump [#2]. For startup, oleic acid was heated in a tank arranged in parallel, and piped to the suction side of the same gear pump [#2] as the $HSt/ZnSt_2$ line. Hot oleic acid was pumped through the system to warm heat sinks. Immediately following the gear pump [#2] was a double pipe heat exchanger which went from the pump [#2] to the shell and tube heat exchanger [#3] in the barricade.

The shell and tube heat exchanger [#3] had thermal fluid on the shell. The feed streams went through the tubes. (Both gas feed [#7] and liquid feed [#6] streams passed through the same heat exchanger shell [#3] but in separate tubes.)

MAPP [#4] was supplied in cylinders fitted with siphon tubes to permit feeding as a liquid to a diaphragm pump [#5]. The MAPP was pumped to the common shell and tube heat exchanger [#3] in the barricade. The overall heat transfer coefficient was calculated from the combined data obtained during continuous pilot plant and scaleup and correlated as a linear function of flow rate (Figure 2). The equation (r=0.99) for the overall heat transfer coefficient for the MAPP heat exchanger between 2 and 12 lb/hr in BTU/hr ft^2 F was determined as:

$$U = -0.5773 + 1.59\ G$$

(b) *Reaction zone:* The reaction was carried out in a system consisting of a mixing chamber, plug flow reactor, continuous stirred tank reactor (CSTR), and a finishing plug flow reactor in two segments. The CSTR was designed by Heiland (10). It was operated full at all times, as flow enters at the bottom and exits at the top. This eliminated the problem encountered earlier with the modified batch

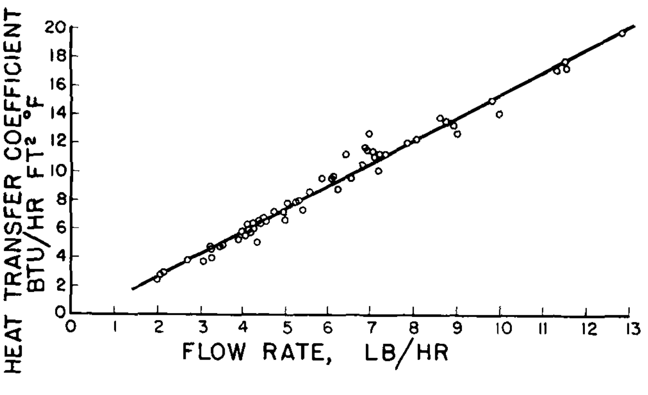

FIG. 2. Overall heat transfer coefficient for MAPP heat exchanger vs flow rate.

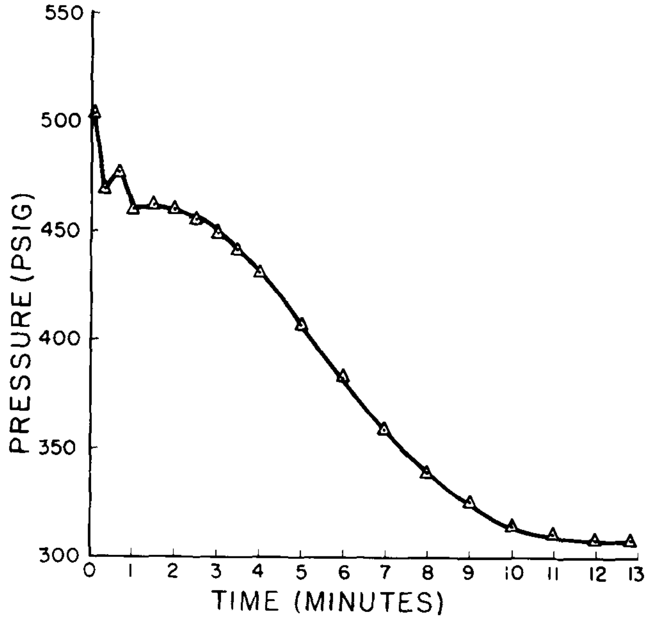

FIG. 3. Example of batch reaction, characterized as headspace pressure, as a function of time.

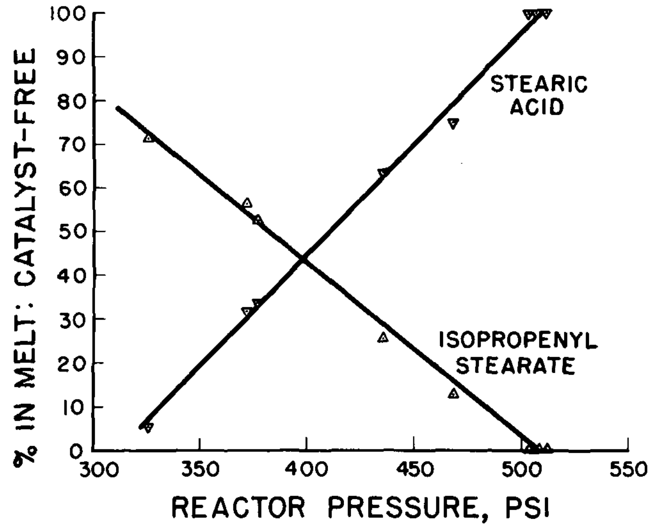

FIG. 4. Correlation of the formation of isopropenyl stearate and the disappearance of stearic acid vs. reaction headspace pressure.

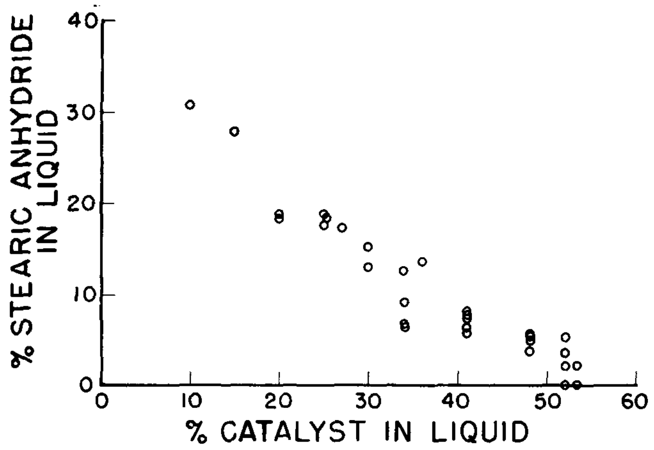

FIG. 5. By-product stearic anhydride formed vs. fraction of zinc stearate catalyst in reactant mass.

reactor, which had an unmeasurable void volume. The volume of the new reactor was twice that of the modified batch reactor. Later, the reactor volume was doubled to provide scaleup data.

Residence time distribution in the continuous pilot plant reactor and in the scaleup were determined as follows. The reactor was filled with oleic acid, and stearic acid was pumped through the bypass. At a given time, the flow was diverted through the reactor, its effluent sampled, and analyzed by GLC for oleic and stearic content.

It was assumed that reaction began in the mixing chamber, wherein the MAPP gas and liquid streams (HSt and $ZnSt_2$) were intimately mixed. The heated tubular section between the mixing chamber and CSTR presumably acted as a plug flow reactor and was designated PFR-1 [#9]. The bulk of the reaction took place in the CSTR [#10]. The two tubular sections after the CSTR were plug flow finishing reactors and were designated PFR-2 [#11] and PFR-3 [#12]. A pressure control valve [#13] immediately following PFR-3 was used to control the pressure in the reactor. A steam jacketed line was introduced between the mixing chamber and PFR-1, to bypass the CSTR during start-up and shutdown. It reentered the process stream between PFR-2 and PFR-3.

The volume of the CSTR was 122 in.^{3}. The total volume of the reaction zone from the inlet of the mixing chamber [#8] to the control valve [#13] was 145.7 in.^{3}. The volume of the reactor from the outlet of the CSTR to the control valve [#11 and #12] was 14.2 in.^{3}.

(c) *Quench:* The spent MAPP was removed from the product mixture in the flash chamber [#14]. The liquid from the flash chamber was at about 280 F with apparently no dissolved gas.

The gases were vented overhead and a liquid seal was maintained at the bottom drain [#15] to prevent spent gases leaking into the room. A sight glass was included before the bottom drain, to permit remote manual control of the liquid level.

IPS reacts slowly with HSt to form St_2O. The reaction was quenched (nominally) by rapidly solidifying the product on a double drum flaker [#16]. This resulted in the formation of an apparently amorphous solid. The drum clearance was .044 in. Cooling water for the drums was circulated at 52 F and 2.9 gal/min. The product was scraped from the drums with doctor blades.

(d) *Recovery:* The recovery system consisted of three unit operations: leaching, filtration, and evaporation. The leaching column simulated one stage of an extractor. Reaction product was fed to the top of the column [#17] via a dry chemical feeder [#19] and solvent [#18] was pumped in the bottom. The supernatant was clarified in a Sparkler filter [#20].

The solvent and product feed rates to the column were

TABLE II

Results of Residence Time Distribution Studies

Reactor system	Back mix, %	Plug flow, %
Continuous-bench	84.9	6.2
Continuous-pilot plant	69.3	35.1
Scale-up	73.9	28.1

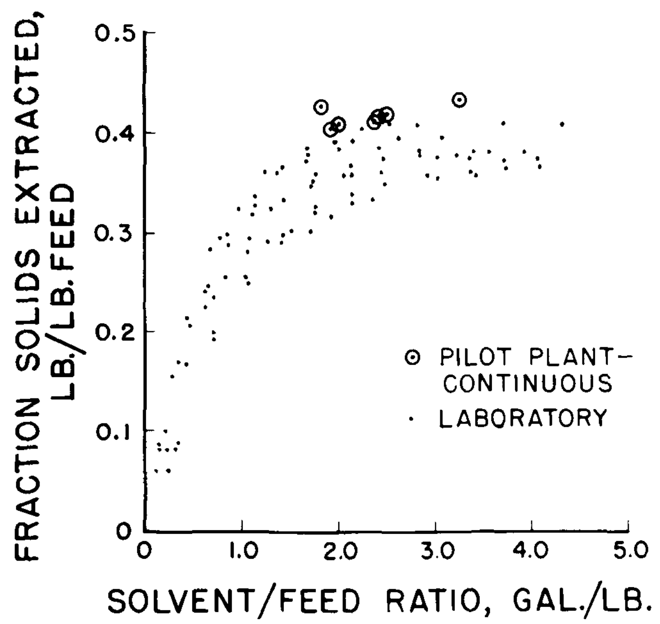

FIG. 6. Feed fraction leached as a function of amount of solvent used.

accurately known. The concentration of the dissolved product in the supernatant at steady state was determined by gravimetrically determining the solids content of the filtrate.

Two pass leaching was approximated by recycling the filtrate to the column while continuously feeding fresh product to the column.

The solvent was removed in a solvent stripper [#21].

RESULTS

Batch

Approximately 270 experimental reactions were made in the batch reactor. Most of the results obtained were confirmed or refined in the continuous operations. Therefore, only the information unique to the batch studies will be presented.

Figure 3 exemplifies a typical, successful reaction. The initial pressure is determined by the total effect of liquid propyne and nitrogen. Within the first minute, liquid propyne apparently is dissolved, is heated, and then is vaporized. The reaction begins, and gradually depletes the propyne, reducing pressure in the reactor. While the small pressure peak at 45 sec is difficult to explain, it is reproducible in this system and was observed more than 100 times. As seen in Figure 3, equilibrium can be recognized by a cessation in pressure drop.

Figure 4 shows the measured depletion of HSt along with the simultaneous formation of IPS (Figure 3). Pressure drop in the reactor was linearly related both to the formation of IPS and to the depletion of HSt. Therefore, the progress of the batch reaction could be followed.

St_2O was formed as a by-product, by the interaction of IPS and HSt. It is undesirable, both because it cannot be tolerated in the recycle (HSt and $ZnSt_2$) stream, and because it represents a net increase in propyne consumption per unit of IPS in the product by reacting with IPS already formed. Figure 5 depicts the effect of $ZnSt_2$ level on St_2O in the product in a series of batch reactions. The study indicates that a $ZnSt_2$ level of 52+% (weight basis) should yield a minimal level of St_2O. For this reason, 52% catalyst level was used in development of the process.

Continuous-Bench Scale

Approximately 450 experimental runs were made in the first continuous reactor. These defined the product, the optimal operating region, and the variables which required precise study. All important variables were studied in continuous pilot plant near the optimum. For that reason, no reaction results for this phase of the study will be presented except to note that the residence time was about 10 min.

The results of the residence time distribution study were plotted as the internal age distribution function and analyzed by the method of Levenspiel (11). The results are summarized in Table II.

Preliminary investigation of recovery of IPS from the reactor effluent was made in the laboratory studies. A plot of recovery vs. solvent:solids ratio is shown in Figure 6. This plot shows that a maximum asymptote is reached at a ratio of about 2 gal/lb.

Continuous-Pilot Plant

Fifty-two experimental runs were made in the continuous pilot plant reactor system which was later integrated with the recovery system. The compositions of representative products are listed in Table III. Figure 7 shows a plot of conversion as a function of the propyne: HSt molar ratio. Note that no consistent increase in conversion was found above a ratio of ca. 0.9. Also, below that point, conversion was greater than stoichiometric. It appears that propadiene (allene), under these experimental conditions, enters into the reaction either directly or by first isomerizing to propyne.

Beginning in the region believed to be optimal, a set of small experimental factorial designs was conducted to clarify and quantify the effect of the controlled variables.

Table IV presents the levels of pressure and propyne concentration tested and their effect on yield. Error variance in these and subsequent tables was estimated from replicates. Variation in the propyne fraction was inad-

TABLE III

Representative Analyses of Products from the Continuous Pilot Plant Process

Product components	Wt %	Method of analysis	Fatty acid distribution of products[a]	Wt %
Isopropenyl stearate	92	IR	$C_{14:0}$	6.3
Stearic acid + stearic anhydride	8	IR	$C_{16:0}$	43.4
Stearic anhydride	4	morpholine test	$C_{18:0}$	42.1
			$C_{18:1}$	3.9

[a] Determined as methyl esters using gas liquid chromatography.

vertent and a result of variable gas supply (see subsequent discussion). Reaction temperature and $ZnSt_2$ content were 410-417 F and 52%, respectively.

No significant difference was found between the two pressure levels. A highly significant difference was found between 12 and 21% propyne in the gas and a probable significant difference between 21 and 30%.

Since no significant difference was found between the two pressure levels of 550 and 660 psi, a lower pressure was incorporated in a new design, combining the data from the two previous higher levels as +1 level. Propyne concentration was studied at 12% and 30%. This design and its effect on yield are shown in Table IV. The effect of both pressure and concentration were highly significant at these levels.

Another design was set up, using the two higher pressure levels of 550 and 660 psi, which were apparently on a plateau with respect to the direct effect on pressure, combined as the +1 level. The other variables studied were $ZnSt_2$ concentration in the feed and reaction temperature. Results are shown in Table V. Propyne:HSt molar ratios were held at or above stoichiometric levels.

The temperature and pressure levels showed no significance whereas the catalyst level did show a significant difference. Hence, optimum reaction conditions are 52% catalyst, 550 psi, 415 F ± 5 F, MAPP containing 30% (or more) propyne and a molar ratio of propyne to HSt of 0.9. A nominal residence time of 9-9.5 min in the reaction zone was found to be satisfactory.

The results of the residence time distribution study are plotted in Figure 8 and are summarized in Table II. Table II lists the results of residence time distribution studies as the fraction of back mix and plug flow in continuous-pilot plant and scale-up. With normalized data, the amount of back mix and plug flow in continuous-pilot plant was calculated as 66.4% and 33.6%, respectively. With a total residence time of 9.5 min, this corresponds to 6.3 min of back mixing and 3.2 min of plug flow in the entire reaction system (mixing chamber to control valve).

TABLE IV

Experimental Designs 1, 2 and 3 and Results—Pressure and Propyne Concentration

	Design 1		Design 2		Design 3	
	-	+	-	+	-	+
A = pressure (psig)	550	660	550	660	440	550(660)
B = propyne concentration in MAPP, %	12	21	21	30	12	30

Results

	Design 1		Design 2		Design 3	
	Effect (% IPS)	Significance	Effect (% IPS)	Significance)	(% IPS)	Significance
A	.92	NS	.33	NS	8.13	p<.01
B	5.57	p<.01	4.08	.05<p<.10	11.59	p<.01
AB	-.57	NS	-.13	NS	-1.53	NS

Recovery was first studied on a continuous basis during this phase of the study. The reactor and recovery units were integrated into a continuous process.

The solvent ratio was varied as shown in Table VI. All the data points lie on the asymptote, Figure 6. (Lower solvent ratios could not be studied due to the physical limitations of the process equipment.) The data show slightly higher recoveries than found in the laboratory studies.

The higher recoveries in the pilot plant are probably due to continuous processing. The product from the flaker is a metastable, amorphous solid. The St_2O very slowly (days to weeks) changes back to HSt. The amorphous structure changes simultaneously. The former structure is readily amenable to leaching, whereas the latter structure is not.

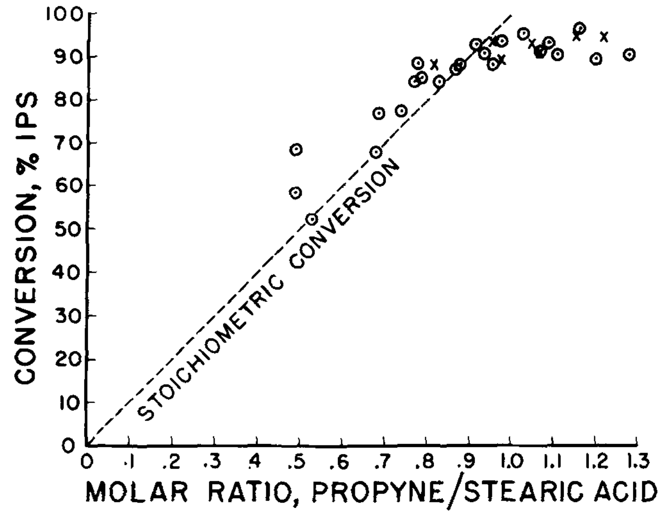

FIG. 7. Conversion measured as % IPS vs. the molar ratio of propyne/stearic acid.

It was observed that leaching aged samples resulted in a very poor performance by the column both in the clarity and ease of filtration of the supernatant and in the amount of product recovered. Therefore, it was important to recover the IPS from $ZnSt_2$ continuously to avoid these changes.

When two pass leaching was approximated as described previously, the concentration in the filtrate was roughly twice the concentration obtained with one pass, as shown in Table VI. Multiple (2) pass leaching should be feasible which would reduce the solvent requirements by 1/2. It would also reduce the load on the evaporator.

TABLE V

Experimental Design 4 and Results—Temperature, Pressure, and Catalyst Level

	Design	
	-	+
A = catalyst, % (w.b.)	46	52
B = temperature, °F	418	432
C = pressure, psig	550	660

Results

	Effect (% IPS)	Significance
A	7.75	p<.05
B	1.75	NS
C	3.25	NS
AB	-2.75	NS
AC	.75	NS
BC	2.75	NS

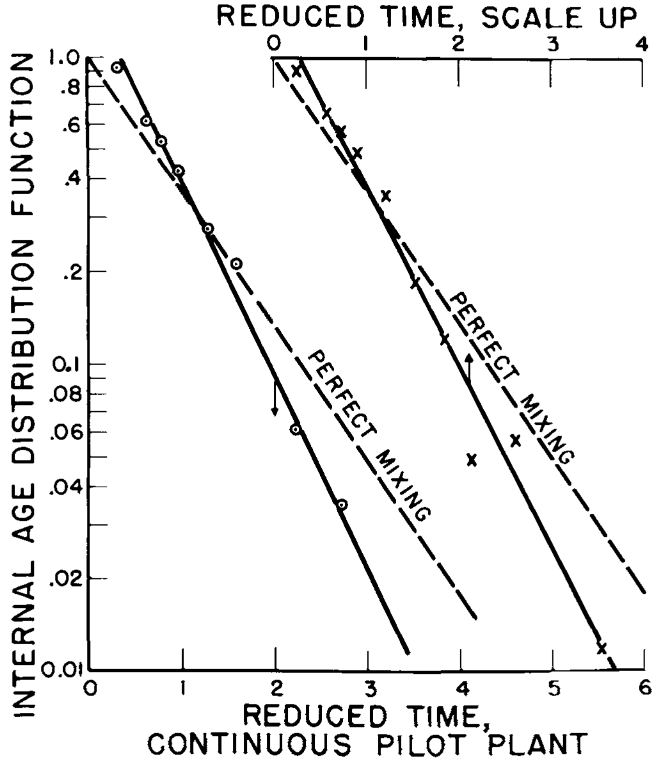

FIG. 8. Residence time distribution for continuous pilot plant and scale-up plotted as internal age distribution function vs. reduced time.

Scale-up

Scale-up from continuous-pilot plant was made on the basis of equal nominal residence times in the CSTR–8.5-9.0 min. This was accomplished by doubling the flow rate of the liquid feed (from 20 to 40 lb/hr) and doubling the volume of the CSTR from 122 in.^{3} to 244 in.^{3}. No other change was made in the system. Residence time distribution data are plotted in Figure 8. The area under the "I curve" characterizes the amount of material younger than a given age. The normalized data are presented in Table II. At scale-up the back mixing residence time was 6.5 min, ca. the same as in continuous-pilot plant. However, the plug flow residence time was 2.4 min compared to 3.2 min in continuous pilot plant (See Table VII). This corresponds to nominal dwell times in the finishing reactors of 0.5 and 0.9 min, respectively.

Several runs were made at these conditions and the conversion was lower than in continuous-pilot plant. A series of runs was made in which the dwell time in the finishing reactors was increased by varying the flow rate. The results, plotted in Figure 9, show that the conversion in the scale-up phase was equal to the conversion in the continuous pilot plant phase when the nominal residence time in the finishing reactor was about 0.6 min. According to data from the residence time distribution study, this corresponds to increasing the plug flow residence time from 2.4 to 2.9 min and back mixing from 6.3 to 7.5 min (Table VII). Hence, the overall residence time must be 9-9.5 min with a nominal dwell in the finishing reactor about 0.6 min, plug flow residence time of 2.9 min, and back mixing residence time of 6.3 min.

Operating the system above the dwell time limits thus established (scale-up modified), and at the optimal reaction parameters previously determined, scale-up was successful.

DISCUSSION

Rothman and Serota (4) have shown that HSt reacts with propyne in the presence of $ZnSt_2$ to produce IPS. A by-product of this reaction is St_2O. It was found that heating IPS with HSt in the presence of $ZnSt_2$ results in the formation of St_2O. These two facts suggest that the reaction can be modeled as a two-step reaction as shown in equation I.

$$\begin{gathered}\mathrm{HSt + propyne} \xrightarrow[\mathrm{ZnSt_2}]{k_1} \mathrm{IPS} \\ \mathrm{IPS + HSt} \xrightarrow[\mathrm{ZnSt_2}]{k_2} \mathrm{St_2O + Acetone} \\ k_1 >> k_2\end{gathered} \qquad \text{(I)}$$

TABLE VI

Leaching Effectiveness for One and Two Passes at Various Solvent/Solids Ratios

Solvent/solids ratio gal/lb	% leached	Product conc. % IPS	One pass, filtrate % solids	Two pass, filtrate % solids
2.40	41.6[a]	85.1	2.83	5.34
2.37	41.1[a]	91.5	3.10	7.2
2.50	41.9	91.9	---	---
1.98	40.9	92.2	3.69	---
3.27	43.4	88.9	2.41	---
1.82	42.7	93.7	4.53	---
1.92	40.3	94.6	3.74	---

[a] First pass only.

TABLE VII

Comparison of Dwell Times in Scale-Up

Scale or phase	Time, minutes					Conversion % IPS[b]
	Total	Back mix	Plug flow	Finishing reactors	CSTR[a]	
Continuous-pilot plant	9.5	6.3	3.2	0.9	8.6	92
Scale-up	8.9	6.5	2.4	0.5	8.4	87
Scale-up; modified	10.4	7.5	2.9	0.6	9.8	92

[a] CSTR = continuous stirred tank reactor.

[b] IPS = isopropenyl stearate.

The reaction is exothermic. In exothermic reactions, equilibrium conversion theoretically increases with a decrease in temperature. The reaction temperature was reduced 10 and 20 F in the continuous pilot plant. The conversion was reduced in both cases. Evidently, in this system, reaction thermodynamics are not controlling.

During start-up, temperature and flow steady state conditions were established while pressure was held below 150 psig. At this pressure, there was apparently no reaction. When the pressure was increased, the reaction proceeded, and temperature rose about 15 F. This new steady state level was used as a measure of the heat of reaction for this exothermic reaction.

To calculate the heat of reaction, the CSTR was considered adiabatic, with the heating fluid acting as insulation. (Actually the heating fluid showed a slight rise in temperature in some runs after the reaction began, indicating a net heat flow, in the CSTR, from the reacting mass to the heating fluid.) The heat of reaction was calculated as 9.9 Kcal/gm mol HSt ± 4.3 @ the 95% confidence interval. This is based on the reaction described by equation I with complete conversion of HSt to IPS.

Propyne under the conditions of temperature and pressure used in the reactor would be dangerous. However, MAPP, which is a nominal mixture of 1/3 propyne and 1/3 propadiene, stabilized with propane, propene, and butane was used. MAPP is relatively inexpensive and safe. However, equilibrium conversion is a function of the propyne concentration in MAPP. Although MAPP is stated to have very little variation in the propyne/propadiene concentration, considerable difficulty was encountered in the continuous pilot plant. GLC analyses on various tanks of MAPP are reported in Table VIII. Large variations were found during continuous pilot plant studies. Although the propyne concentration was less than 1/3 during this phase, the level returned to about 1/3 during scale-up.

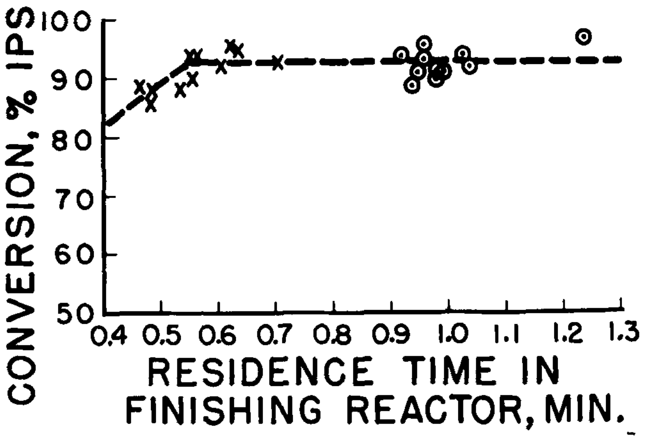

FIG. 9. Minimum residence time required in finishing reactor measured as conversion vs. IPS concentration.

Table IX lists representative steady state temperatures and pressures for the process.

The isopropenyl ester, synthesized from triple pressed acid and catalyst, is a colorless liquid which solidifies at about 62-64 F, depending on the fatty acid distribution of the raw materials. The product from the continuous process is pale yellow, Gardner color ≈6.5. Additional physical property data are presented by Kozempel (12).

Laboratory decolorizing studies were made on IPS, recovered from continuous bench scale, initially having a Gardner color of 8.75. Solutions of 25% IPS in petroleum ether (1 lb IPS/4 lb solution) were pumped through 3/8 in. ID columns packed with granular carbon. When Nuchar WV-G carbon, 12*40 mesh (Westvaco), and a residence time of 12 min were used, the Gardner color of the effluent stream was 1.25 after a cumulative exposure of 6.9 lb IPS

TABLE VIII

	GLC[a] Analyses of MAPP during Continuous-Bench			GLC Analyses of MAPP Purchased during Continuous Pilot-Plant						
Component	Weight %			Weight %						
Propane	4.6	3.6	1.8	31.9	30.0	27.2	25.8	37.2	28.9	3.3
Propylene	31.2	26.1	28.5	32.4	11.5	47.9	16.0	13.8	15.4	17.3
Butane	7.5	40.9	38.9	16.9	22.5	5.5	5.9	6.0	15.9	47.6
Propadiene	29.4			7.7	15.4	9.6	24.5	21.8	18.0	
Propyne	27.4	29.4	30.8	11.9	20.6	9.9	28.6	25.3	21.7	31.8

[a] GLC = gas liquid chromatography.

TABLE IX

Reaction Zone Temperature and Pressure, Continuous-Pilot Plant

Location	Temperature No reaction	Temperature Reaction		Pressure, psig
$HSt/ZnSt_2$ inlet to double pipe heat exchanger	325	325	Out of mixing chamber	560
MAPP liquid into shell and tube heat exchanger	92	93	CSTR	550
$HSt/ZnSt_2$ out of shell and tube heat exchanger	375	375	Flash chamber	25
MAPP gas out of shell and tube heat exchanger	365	371		
Reaction stream out of mixing chamber	382	386		
Reaction stream out of PFR-1[a]	403	403		
Reaction stream in CSTR[b]	401	416		
Reaction stream into PFR-2	377	372		
Reaction stream out of PFR-2	389	399		
Product stream out of flash chamber	-	280		
Heating fluid into PFR-3	403	402		
Heating fluid into CSTR	401	400		
Heating fluid out of CSTR	400	399		
Heating fluid into mixing chamber	394	398		

[a] PFR = plug flow reactor.

[b] CSTR = continuous stirred tank reactor.

per pound of carbon. Using Nuchar WV-L, 8*30 mesh, the Gardner color of the effluent was 2.5 after 6.1 lb of IPS had been processed per pound carbon. With either packing, the early effluent was colorless.

A catalyst recycle line is obviously required, but was not studied during this project. It is important to note that the catalyst stream shown in the flow sheet contains about 20% absorbed IPS. The recycle catalyst cannot be added to the liquid feed tank (#1, Figure 1). If this were done, the IPS would react with the fresh HSt to give St_2O.

One potential recycle process would be to set up a third feed line for the catalyst. The recycle feed kettle would be blanketed with MAPP gas to force any HSt present to convert to IPS instead of St_2O. This catalyst stream would first be mixed with the MAPP in a mixing chamber and this stream would be mixed with fresh HSt.

An economic evaluation of the continuous process is being prepared.

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