A Novel Continuous Countercurrent Epoxidation Process[1]

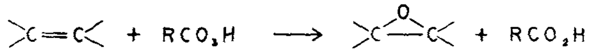
H. K. LATOURETTE, H. M. CASTRANTAS, R. J. GALL, and L. H. DIERDORFF,
Chemical Research and Development Center, Food Machinery and Chemical Corporation,
Princeton, New Jersey[2]

Epoxidation has advanced in 10 years from little more than a laboratory curiosity to a major commercial chemical process. Epoxidized fatty esters, derived from such natural oils as soybean oil and from such synthetic oils as butyl oleate, are major products of epoxidation technology. These find use principally as secondary plasticizers for polyvinyl chloride and copolymers, to which they impart a spectrum of properties including heat and light stability, superior aging, and low-temperature flexibility.

In 1945 Findley and associates (1) reported the first practical synthesis of epoxides from a preformed peracetic acid. The first *in situ* epoxidation (in which hydrogen peroxide and a carboxylic acid are allowed to react, usually in the presence of a strong acid catalyst, to form the peracid *in situ* with the olefin to be epoxidized) was reported by Niederhauser and Koroly (2) in 1949. These authors used formic acid. An *in situ* process, employing acetic acid, was reported by Gall and Greenspan (3) in 1955. Ion-exchange resins were first used in 1955 (4,5) to replace the mineral acids in *in situ* epoxidations. Continuous processes for epoxidation were described in 1958. Barlow and coworkers (6) described a continuous cascade (overflow) process which was operated cocurrently. Bataafsche (7) has a British patent describing a countercurrent cascade process characterized by separation vessels between reactors, from which the aqueous phase may be pumped countercurrently to the flow of the oil phase.

The chemical equations showing the major reactions involved in epoxidation are as follows:

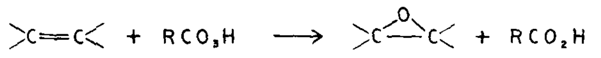
Preformed Technique



$$>C{=}C< \; + \; RCO_3H \longrightarrow \; >C\overset{O}{\text{—}}C< \; + \; RCO_2H \qquad 1$$

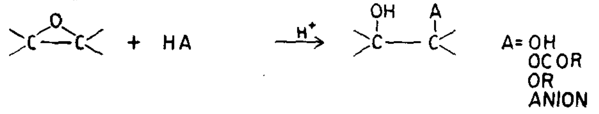
In Situ Technique

$$RCO_2H + H_2O_2 \xrightleftharpoons{H^+} RCO_3H + H_2O \qquad 2$$



$$>C{=}C< \; + \; RCO_3H \longrightarrow \; >C\overset{O}{\text{—}}C< \; + \; RCO_2H \qquad 3$$

By-Product Formation



$$>C\overset{O}{\text{—}}C< \; + \; HA \xrightarrow{H^+} \; >\overset{OH}{\underset{}{C}}\text{—}\overset{A}{C}< \qquad A = OH,\ OCOR,\ OR,\ ANION \qquad 4$$

The economic advantages of the *in situ* epoxidation technique are well known (2,3,4). A smaller quantity of organic acid may be used, resulting in a savings in material cost and an increase in volume productivity. A much greater utilization of active oxygen results since virtually all of the hydrogen peroxide is converted to peracid. A savings in capital and operating costs results since only one operation is involved rather than two.

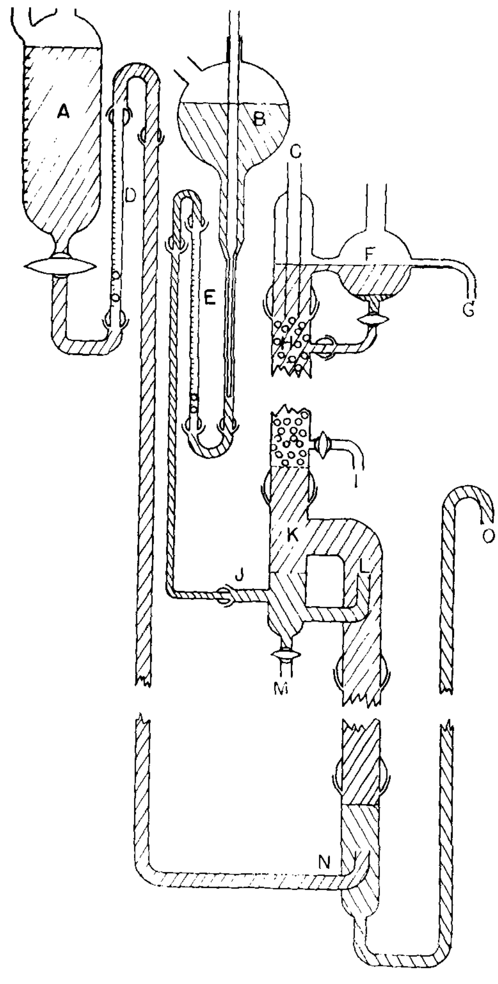


FIG. 1. Epoxidation equipment.

In general, continuous processes are known to be economically superior to batch processes, particularly at large volume. When a continuous process can be run by passing two immiscible phases countercurrently to one another, additional advantages will be realized. The over-all rate of reaction and thus the time-volume productivity is increased since one of the reactants is present in relatively large concentration throughout the reaction. If the product reacts with the medium, side reactions are minimized by reducing the time and manner of contact.

In order to apply *in situ* technique and the countercurrent principle to epoxidation, a process was conceived in which the unsaturated oil to be epoxidized is introduced into the bottom of a packed column where it flows upward as a continuous phase. Into the top of the column is introduced aqueous hydrogen peroxide, which since it is more dense than the oil, proceeds downward as discontinuous droplets through the oil phase. Into the side of the column is introduced a carboxylic acid which contains a catalytic quantity of a mineral acid. The carboxylic acid,

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which dissolves in the oil phase, is extracted from the rising oil phase by the descending aqueous droplets. The hydrogen peroxide then reacts with the carboxylic acid in the aqueous phase to form peracid in the presence of the mineral acid catalyst. The peracid is extracted from the aqueous phase by the oil phase, where it reacts with the olefin to form epoxide and regenerate acetic acid. The acetic acid which is formed is extracted again into the aqueous phase where the cycle repeats itself.

Experimental

Equipment. The reactor consisted of a number of sections of glass tubing, 1.2 in. (30.5 mm.) in diameter and 2 ft. (61 cm.) long. Each section was packed to a height of 1.4 ft. (43 cm.) with 6-mm. Berl saddles. Details of construction are shown in Figure 1.

Between each packed section were reservoirs, K, in which the descending aqueous phase collected before overflowing through L into the next section. The volume of aqueous phase contained in each reservoir was 37 ml. The oil was fed to the bottom of the column from a 2-liter graduated addition funnel, A, through a rotameter, D, into the bottom of the column at N. Acetic acid was passed in from a 1-liter Hershberg dropping funnel, B, through rotameter, E, into reservoir, K, through J. Hydrogen peroxide was introduced directly into C from a 1-liter Hershberg dropping funnel without passing through a rotameter. The overflow reservoir, F, was used to separate any aqueous phase that might overflow from the column before passing through the product line, G. The spent aqueous phase overflowed through O, the height of which was adjusted to maintain the interfacial level between aqueous and oil phases at the top of the lowest column section. During operation of the column, samples of the oil and aqueous phases could be withdrawn from I and M, respectively, for analysis.

The column containing seven packed sections and six interconnecting peracid reservoirs, had an over-all height of 16 ft. (4.88 m.) of which approximately 10 ft. (3.05 m.) were packed. The total volume of fluid contained in this packed column was 3,500 ml. Eighteen-millimeter glass tubing was used to introduce the oil to the column, and 8-mm. tubing for the acetic acid and hydrogen peroxide. The sample removal tubes, I and M, were constructed of 2-mm. capillary tubing. All connections were made with suitable-sized ball joints. The large ball joints used in connecting sections of the main column were sealed with fused Saran, as described by Quin and Greenlee (8). For the acetic-acid addition joints a Teflon sealing compound was used. For all other ball joints a heavy petroleum grease sufficed.

For temperature control each section of the column was wound with nichrome wire, and each was controlled with an individual variac. Cooling was accomplished either by blowing air on the outside of the column or by installing within the column sections spiral glass cooling coils through which tap water could be run as needed. Temperatures were measured by means of thermocouples inserted in thermowells located near the base of each column section and were recorded on a 12-point Brown recorder.

Passivation. As in the case of other epoxidations, the equipment was passivated before use (9,10). Briefly the method used involved thorough rinsing with trichloroethylene; after removing the residual trichloroethylene by evaporation, rinsing with de-ionized water; heating with 45% nitric acid at 45°C. for 45 min.; and rinsing with de-ionized water.

Materials. Soybean oil, alkali-refined; butyl oleate, distilled grade; hydrogen peroxide, 50%, Becco; acetic acid, glacial, ACS grade; formic acid, 90%, ACS grade; phosphoric acid, 85%, ACS grade; and sulfuric acid, 96%, ACS grade.

Procedure. The oil to be epoxidized was introduced to the column through A until the column was completely full. Heat was applied to the column and adjusted until the temperature of the entire column was that desired, usually about 60°. The flow of oil was again started and adjusted by means of a glass stopcock until the flow, as measured by rotameter, D, was at the desired rate. A secondary check on the flow rate of the oil over a period of time was obtained by timing the decrease in volume of oil from graduated addition funnel, A. Introduction of acetic acid[3] and hydrogen peroxide was then started simultaneously at the desired rate. The additions were made from graduated Hershberg dropping funnels in which flow control is maintained by inserting a cylindrical drawn-out glass rod into a cylindrical capillary tube for varying distances, depending on the rate of flow desired. The acetic-acid flow rate was measured by rotameter, E, and checked by timed disappearance of acid from the graduated funnel. If acetic acid was introduced at more than one point, separate funnels and rotameters were used.

Although peroxide was fed through a Hershberg dropping funnel, its flow rate could not be measured by means of rotameter since small gas bubbles collecting on the rotameter floats completely distorted the readings. The peroxide flow was estimated by counting the drop rate and checked as with the other flows by measuring the decrease of volume with time in the graduated funnel. After about 3 hrs. of operation when the aqueous phase had completely filled the reservoirs and was overflowing through the aqueous outlet O, the height of O was adjusted to control the height of the aqueous-oil interface at the desired point, usually the top of the bottom section.

The epoxidized oil product was collected in a graduated receiver at G. The aqueous phase which collected in F was periodically drained out by use of the indicated stopcock.

Careful temperature control was required since at temperatures above about 80° excessive gas evolution occurred.

Sampling and Analyses. Samples of the aqueous solution were taken every 3 hrs. from the base of each peracid reservoir, M, and at the spent acid outlet, O. Oil samples were taken from the base of each column section, H, every 3 hrs. and from a point directly preceding the oil settling basin, F, every hour.

The aqueous samples were collected in bottles kept between 0–10°C. to minimize decomposition losses and equilibrium shifts. The hydrogen peroxide and peracid concentrations were determined, using the method of Greenspan and MacKellar (11).

Oil samples were analyzed for their acid content after standing 24 hrs. to permit suspended aqueous droplets to settle out. The samples were titrated with 0.1 N sodium hydroxide by using a mixed indicator of bromthymol blue and phenolphthalein. The acid

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[3] The word "acetic" is used for convenience and is intended to include acetic and formic acids.

TABLE I

The Continuous Epoxidation of Butyl Oleate Conditions and Results

Residence Time[a] 3.2 Hrs.; Aliphatic Acid, Acetic; Mineral Acid Catalyst, Sulfuric

Run No.	42	43	44	45-A	45-B	45-C	41	14	16	17	18	21
Acid-moles/double bond	0.79	0.92	1.41	0.70	0.70	0.70	0.50	0.51	0.44	0.28	0.58	0.37
Hydrogen peroxide-moles/double bond	1.10	1.10	1.10	1.10	1.10	1.10	2.24	1.09	0.93	1.37	1.22	1.07
Average temperature °C	66	66	68	68	67	68	64	67	66	63	61	58
Points of acid addition	1,3,5	1,3,5	1,3,5	1	1	1	1	1	1	1	1	1
% Epoxy conversion best	54.8	65.3	51.8	60.5	57.5	65.4	83.3	79.3	53.0	42.7	81.0	78.2
% Epoxy conversion average	53.2	64.2	47.5	53.2	56.3	56.2	74.2	53.7	46.3	42.7	65.0	61.8
% Ring opening average	1.2	7.7	31.8	6.5	12.4	18.1	7.9	4.5	3.4	2.5	5.5	3.1
% Unreacted double bond	45.6	28.1	20.7	40.3	31.3	25.7	17.9	41.8	50.3	54.8	29.5	35.1
Moles active oxygen recovered/mole double bond	0.37	0.18	0.13	0.24	0.21	0.18	1.1	......	0.31	......	0.30	......
Moles active oxygen decomposed/mole double bond	0.19	0.20	0.18	0.26	0.17	0.18	0.32	......	0.11	......	0.22	......
% active oxygen decomposed	17	18	16	24	15	16	14	......	12	......	18	......

[a] Run 41, 2.6 hrs.

Residence Time 2.6 Hrs.

Run No.	23	31	32	33	35	36	37	38 A,B,C	26
Acid-moles/double bond	0.54	0.45	0.44	0.72	0.69	0.70	0.70	0.80	0.63
Hydrogen peroxide-moles/double bond	0.79	0.77	1.16	1.04	1.10	1.09	1.08	1.08	1.12
Acid (aliphatic)	HOAc	HCOOH	HCOOH	HCOOH	HOAc	HCOOH	HCOOH	HCOOH	HOAc
Catalyst	H_2SO_4	H_2SO_4	H_2SO_4	H_3PO_4	H_3PO_4	H_3PO_4	H_3PO_4	H_3PO_4	H_2SO_4
Oil solvent	None	None	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane	None
Average temperature °C	51	58	58	62	53	55	77	62	72
Points of acid addition	1	1,3	1,3	1,3,5	1,3,5	1,3,5	1,3,5	1,3,5	1,4
% Epoxy conversion best	26.0	21.2	48.8	51.7	25.8	44.1	56.6	68.3	62.6
% Epoxy conversion average	18.4	21.2	43.3	45.5	25.8	44.0	51.8	50.5	53.5
% Ring opening average	1.8	6.0	7.5	7.8	5.5	6.1	11.6	6.2	19.4
% Unreacted double bond	79.8	72.8	49.2	46.7	68.7	49.9	36.6	43.3	27.1
Moles active oxygen recovered/mole double bond	......	0.44	0.59	0.44	......	0.31	0.28	0.24	0.20
Moles active oxygen decomposed/mole double bond	......	0.06	0.06	0.07	......	0.28	0.17	0.27	0.19
% active oxygen decomposed	......	8	5.2	6.7	......	26	16	25	17

content of aqueous samples was also determined by this method.

The oil samples for oxirane analysis were washed with saturated sodium sulfate until free of acid and hydrogen peroxide, dried over anhydrous calcium sulfate, and filtered. The method of Durbetaki (12) was used for the oxirane determination. The standard American Oil Chemists' Society Method (13) for the iodine number was used. The degree of epoxy ring opening was calculated by difference between the oxirane and iodine values.

Conditions and Results. A number of variables were investigated. These are divided into those which are variable only in discrete steps, such as types of organic acid, and those which are continuously variable, such as temperature. The discrete group of variables investigated were butyl oleate *versus* soybean oil, acetic acid *versus* formic acid, sulfuric acid *versus* phosphoric acid, heptane solvent *versus* nonsolvent, Triton X-45 surfactant *versus* no surfactant in oil phase, Nacconal NRSF surfactant *versus* no surfactant in water phase, 1 *versus* 2 and 3 points of acid addition, 1 *versus* 6 peracid reservoirs, and 8.5 ft. (2.59 meters) *versus* 10.0 ft. (3.05 meters), of packed column length.

The continuously variable group consisted of different molar ratios of organic acid to double bond, and molar ratios of hydrogen peroxide to double bond, a temperature range of 50–90°C., residence times of 0.87–4.2 hours and an interface height from column base of 1.7 ft. (0.5 meter)–2.0 ft. (0.6 meter).

The total time of reaction was always sufficient to have completely replaced the contents of the column several times so that equilibrium was achieved. This varied from perhaps 7 hr. to 24 hr. The conditions applied and results obtained on a number of runs are shown in Table I. Several variables, such as the use of surfactant, were found to be relatively unimportant or susceptible to standardization and are not included in the table.

Discussion

Design of Equipment. In the design of equipment for this continuous epoxidation the interrelationship of several prime factors was important: the rates of the reactions shown in Equations 2 and 3; the partition coefficients and rates of migration of the various molecular species within and between the phases; and removal of heat due to the highly exothermic epoxidation reaction.

The rates of reaction, of course, are dependent on temperature and concentration. The time of reaction must be sufficient to bring the yield of epoxide to the desired point. Since Reaction 2 occurs primarily in the aqueous phase and Reaction 3 in the oil phase, the residence times of both of these phases in the column are important. The residence time of the oil can be completely controlled by varying the rate of addition of the unsaturated oil since the oil forms the continuous phase in the column. However the aqueous phase, dropping through as discontinuous droplets, is not controllable in the same manner. Its residence time is dependent on such factors as the length of the column, the nature of the packing, the viscosity of the oil, and the velocity of the rising oil flow.

The results obtained suggest that the rate-limiting steps are a) the formation of peracid and b) its migration into the oil phase. The former was improved by the installation of peracid reservoirs within the column to increase the time available for the formation of peracid. The latter can be improved by increasing the length of the column, increasing the interfacial area (such as by agitation), or by the use of surfactants. We have found that the use of Berl saddles as packing gave excellent dispersion of the aqueous droplets.

An important feature of the packed column design was the introduction of acetic acid at points on the side of the column rather than at the top with the hydrogen peroxide. This allowed the acetic acid dissolved in the rising oil phase to be extracted by the hydrogen peroxide before the oil left the column, thus reducing the acetic acid requirement for the reaction as well as the amount of acetic acid that must be washed out of the epoxidized product. It was found that if acetic acid was introduced at a number of points along the column, the amount of the total reaction that occurred in any one section could be made more uniform. This assisted in the heat-removal problem.

The problem of heat removal in a nonagitated slow-moving liquid is considerable. Some agitation is achieved in this case by the rising gas bubbles formed from the decomposition of minor amounts of hydrogen peroxide, but this remains a problem on scaling up to larger reactors.

Through the use of the effective thermal conductivity data it has been calculated that the maximum diameter of a jacketed glass column for the epoxidation of soybean oil without solvent is about 3 in. This calculation was made with the assumption that a temperature differential of 25°C. between the center of the column and the wall be maintained. A column larger in diameter could be used for epoxidation of oils with a lower degree of ethylenic unsaturation or lower viscosity or if oil was diluted with a solvent.

Preliminary calculations indicate that the maximum diameter of an agitated column, such as a jacketed rotating disc contactor, would be 24 to 30 in.

For commercial use, modified designs will probably be required. Agitated jacketed columns, shell and tube heat exchangers, and jacketed annular reactors have been considered.

Heat Transfer. The effective thermal conductivity of hot soybean oil was determined in a laboratory calorimeter packed with 12-mm. Berl saddles. Agitation was provided by passing dry nitrogen through a sintered-glass plate located at the base of the packed calorimeter tube. Three thermocouples were used to measure the temperatures at the center of the tube, at the wall, and halfway between. A 31.4% solution (calculated to be the average composition of the aqueous phase in the column) of acetic acid was introduced through a graduated dropping funnel, thence to a wire mesh screen before entering the packed bed; and the resulting temperatures were measured.

The effective thermal conductivity k_e (Btu/hr. ft. °F.) was found to be 0.6 under conditions of zero nitrogen and acetic acid flow rates. A k_e value of 0.8 was obtained at a 158 cc./min. nitrogen flow rate and 4.7 cc./min. acetic-acid flow rate.

Operating Variables. In addition to the design of the reactor, the results obtained vary greatly, depending on the variables. An analysis of the results actually obtained in several runs (Table I) allows us to draw a number of conclusions as to the probable optimum conditions. The desired results of course are the largest possible yield of epoxy product and the least possible ring opening. It should be noted that the difficulties of controlling a laboratory reactor and the large number of variables make the results somewhat imprecise, particularly as to the amount of ring opening, since relatively small differences in temperature can have important effects on the ring opening.

It can be seen from Table I that the optimum conditions depend on the oil to be epoxidized. The oils evaluated were butyl oleate, a mono-ester of a monounsaturated fatty acid, with an iodine number of 74, and soybean oil, a naturally occurring mixture of polyunsaturated triglycerides, with an iodine number of 133. The butyl oleate reacts more rapidly, yet with less total heat evolution, and is therefore much easier to control. The carboxylic acid of choice depends on the nature of the oil. For the fast-reacting butyl oleate, acetic acid with a sulfuric acid catalyst gave good results; with less active soybean oil, formic acid with phosphoric acid catalyst seemed preferable. The use of a solvent seems to give better results, particularly with soybean oil.

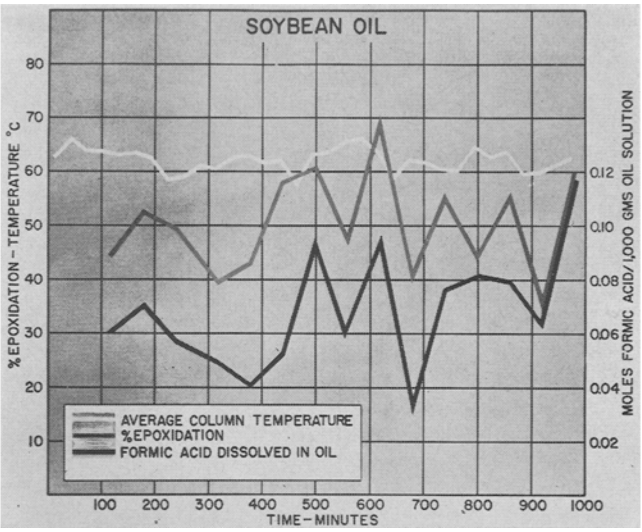

FIG. 2. Correlation of temperature and dissolved acid with percentage epoxidation.

Another variable which depended on the type of oil being epoxidized was the point or points of addition of acetic acid. A single point, 2 ft. from the top of the column, appeared to give the best results with butyl oleate, while several points of addition were preferable with soybean oil in order to spread out the heat load more uniformly.

The residence time of the oil in the column was standardized as much as possible by maintaining the rate of flow of the oils constant throughout the runs. The flow rate of both oils was 16.6 cc./min. By making suitable estimates of the volume occupied by the aqueous droplets and the gas bubbles within the column, the average residence times were estimated to be 3.2 hrs. for butyl oleate and 2.6 hrs. for soybean oil.

The optimum temperature range was the same as that for other *in situ* epoxidations, about 60–70°C.

The concentrations of carboxylic acid and hydrogen peroxide in Table I are expressed as mole fractions of the olefinic unsaturation present. Although a large excess of hydrogen peroxide gave better results, the economic optimum is, of course, one mole of hydrogen peroxide per mole of double bond. With the redesigned column as described below, there is no reason why the use of only slightly more than theoretical hydrogen peroxide should not give good results.

The optimum quantity of carboxylic acid is harder to deduce from the data but appears to vary with the number of points of addition and with the oil used. In general, a concentration between 0.5 and 0.9 moles per mole of double bond appears optimum. However it will be noted, for example, in runs 17 and 21 in Table I, that good results were obtained even when considerably less than 0.5 mole of acetic acid was used. This has been explained (14) on the basis that the rising oil in the column actually extracts some of the acetic acid from the descending aqueous phase, giving an effective concentration in the reaction zone greater than that indicated by the amount added. This concept could logically be extended to lengthening the lower part of the column to extract the aqueous phase with oil so that virtually no acetic acid would need to be added.

Figure 2 shows a profile of a typical epoxidation run, including epoxy yield and average temperature as well as the concentration of formic acid dissolved in the epoxidized product.

In Figure 2 it can be seen that formic acid is more soluble in oil of higher oxirane content. It is postulated that this is due to the greater polar character of the oxirane ring compared to a double bond. If the time lag in the temperature curve is taken into consideration, a rough parallelism can be seen between the temperature, epoxidation, and formic acid curves. Data from Runs 38 A, B, and C were used in preparing Figure 2.

It will be noted that the best conversions obtained were 83% epoxidized butyl oleate and 68% epoxidized soybean oil. If this process is to be practical, much higher conversions must be realized. A number of factors indicate that increasing the length of the column will be necessary to achieve high yields.

Figure 3 relates epoxy conversion to the length of packing in the column by two different methods. The bars represent the average percentage of epoxidation in two series of runs when different length columns were used. The small circles represent the percentage of epoxidation at points at the bottom of each section of the column during a single epoxidation run. A line was then drawn through these circles to include the tops of the bars as nearly as possible. Two extrapolations were made, one an optimistic linear extrapolation and one a pessimistic curve. An inspection of these curves suggests that a column approximately 30 ft. in length should give very high yields of epoxide.

The curve in Figure 3 was taken from Run 42. The average percentage of epoxidation as represented by the smaller bar was taken from Runs 14, 15, and 16. Run 15 is not included in Table I, but the same variables were used as in Run 14. The percentage of epoxidation as represented by the longer bar is an average of Runs 18 and 21.

Conclusion and Summary

A laboratory process has been developed for the continuous countercurrent preparation of epoxidized oils. This consists of introducing continuously, to a packed column, an unsaturated oil, hydrogen peroxide, and acetic acid, and withdrawing the epoxidized product. Operating variables have been investigated and optimum conditions predicted. Obtainment of maximum yields must await construction of a longer column.

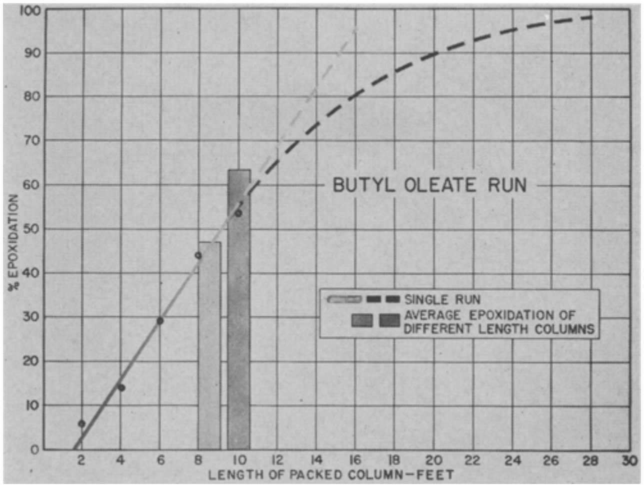

FIG. 3. Percentage epoxidation *versus* column length.

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