

# Estolide Production with Modified Clay Catalysts and Process Conditions

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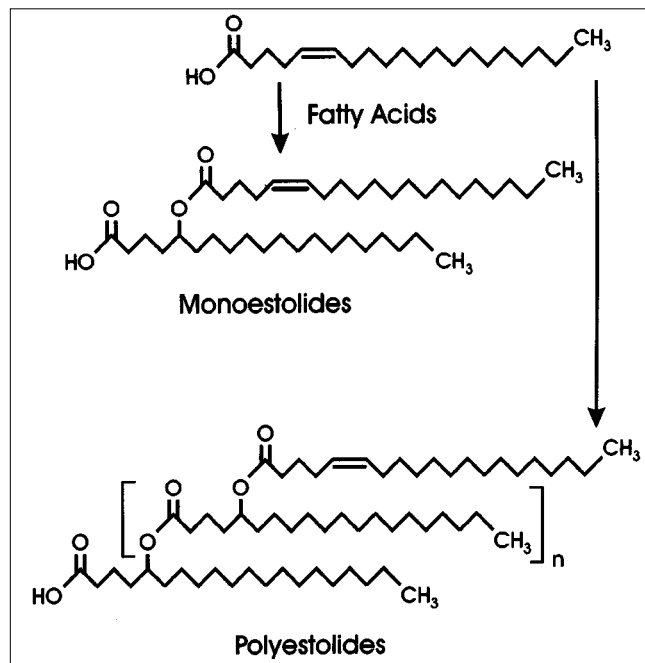
**ABSTRACT:** The 20% yields of estolides prepared from oleic acid and meadowfoam oil fatty acids are improved when the montmorillonite clay catalysts are modified to increase their activity. Changes we explored included acidifying the clay, treating to increase the surface area of clay to introduce new active sites, and decreasing the ionic character of the clay surface to enhance adsorption of the fatty acids. We also evaluated the use of higher levels of clay in the reactions. Clays treated with  $\text{Fe}^{3+}$  salts increase the estolide yield from 21 to 27%, a 28% increase. Clay catalysts were also treated with surface-active reagents. The most active were cationic surfactants, and montmorillonite clays treated with cetyltrimethylammonium chloride increased the estolide yield to 30%. Estolide yields could not be improved beyond 30% by increasing the amount of clay. However, nitrogen sparging increases the efficiency of stirring and increased the estolide yield to 35% estolide. *JAOCs* 74, 249–254 (1997).

**KEY WORDS:** Cation exchanged clays, estolide, meadowfoam oil fatty acids, montmorillonite clays, nitrogen sparging, oleic acid, oleic homopolymer, surface-active agents.

Estolides are unique oligomeric fatty acids that contain a secondary ester linkage on the backbone of one of the fatty acid chains (Scheme 1). Estolides are known to exist in nature (1) and can also be prepared from homopolymerization of hydroxy fatty acids (2–5) or unsaturated fatty acids (6–8). Estolides have high viscosity indices, good oxidative stability, and are biodegradable (9). Monoestolides are formed when the carboxylic acid group of one fatty acid is attached to the unsaturated carbon of another fatty acid (7) through an ester bond. Polyestolides are formed (8) when three, four, or more fatty acids are successively added to existing estolide units (Scheme 1).

Estolides can be produced commercially in facilities capable of dimer acid production by minor modifications to existing dimer acid reaction conditions. The dimer acid industry uses sheet silicates as catalysts for the dimerization process and has a system for obtaining, handling, and disposing of the spent clay. In light of the dimer acid industry's potential

ability to produce estolides, initial efforts in our laboratory have been to synthesize estolides from monounsaturated fatty acids with clay catalysts in a batch reactor. Yields were improved from 10% (6) to 20% (7), and later to 30% (10) with no significant polyestolide, hydroxy fatty acid, and dimer acid formation. Literature reports indicated that additional activation of the clay by cation ion-exchange would enhance the reactivity of the clay with organic functional groups (11–15). Studies have also shown that small amounts of surface-active agents on clay surfaces significantly increase the ability of the clay to trap organic pollutants (16,17). Surfactants then should also make the surface of the clay more attractive to fatty acids. In light of these findings, we set out to improve the conversion of fatty acids into estolides by enhancing the activity of montmorillonite clay catalysts and by improving stirring efficiency.



SCHEME 1

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## EXPERIMENTAL PROCEDURES

**Materials.** Meadowfoam oil was obtained from the Oregon Meadowfoam Growers Association (Salem, OR) and was split to the fatty acids by Witco Corporation, Humko Chemical Division (Memphis, TN). Commercial oleic acid, montmorillonite K-10, dodecyl benzene sulfonic acid sodium salt, and cetyltrimethylammonium chloride were purchased from Aldrich Chemical Company (Milwaukee, WI). Silica gel (particle size 60 Å) was purchased from Mallinckrodt Inc. (Paris, KY). The solvents used for chromatography or extractions were high-performance liquid chromatography (HPLC) or equivalent grade. Boron trifluoride/methanol complex (14% wt/vol) was purchased from Alltech Associates, Inc. (Deerfield, IL).

**Methods.** All experiments were conducted first with oleic acid and then were repeated with meadowfoam fatty acids. The yields in percentage estolide by weight were measured by HPLC of the final reaction mixture (7).

We prepared three modified clays by contacting montmorillonite K-10 clay with a 1.0 molar solution of sulfuric acid, with a 0.25 molar solution of a specific salt, or with a  $1 \times 10^{-5}$  molar surfactant solution for two hours. The treated clay was then washed twice with deionized water, filtered, and dried in a vacuum oven overnight at 70°C, and stored in a desiccator until used. The pH of a suspension of 5.0 g clay in 30 mL water was measured with a Beckman pH 40 (Fullerton, CA) pH meter.

In experiments where water was vented from the batch reactor, reactions were conducted in 1-L and 4-L high-pressure bombs with mechanical stirrers and ports for venting and sampling. The reactors were loaded with fatty acids (100 parts), then clay (8 parts), and finally with distilled water (10 parts), by mass. The mixture was stirred thoroughly prior to sealing the reactor under an initial pressure of 0.4 MPa nitrogen. This pressure prevents the water from vaporizing out of the reaction mixture until the desired removal time, at which time the vent valve was opened until the pressure dropped to atmospheric. The reactor was then flushed with nitrogen three times before it was again sealed under 0.4 MPa nitrogen.

Reactions at atmospheric pressure were conducted in a glass reactor, which was fitted with a mechanical stirrer, a nitrogen inlet tube, and a sampling port (Fig. 1). Reaction temperature in either the glass or steel reactors was set with a controller operating in a proportional integral derivative (PID) mode. In the glass reactor, loss of reactants in the form of aerosols was overcome by using a trap that contained glass beads (Fig. 1). After venting of excess water vapor, the addition of a small amount of substrate fatty acids to the trap prevented loss of reactants that left the reactor in the form of aerosols. Periodically, the flow of nitrogen was interrupted, and the accumulated reactant was allowed to return into the reactor. Analysis of the material that was caught in the trap showed the same composition as the starting material.

A 50-W high-intensity ultrasonic processor (Sonics & Ma-

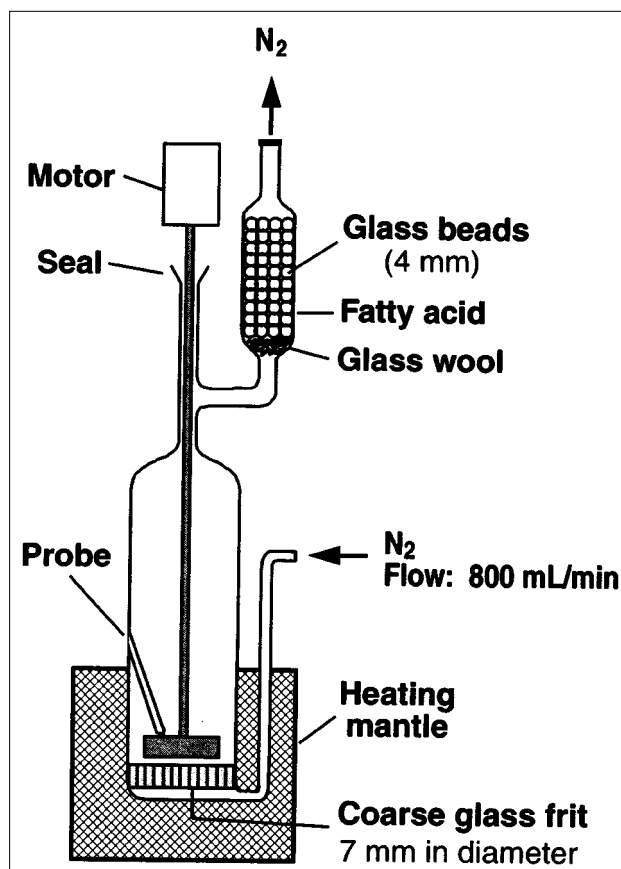


FIG. 1. Glass reactor for nitrogen sparging.

terials, Inc., Danbury, CT) was used in experiments where vibrations from a probe were the source of agitation. These reactions were conducted in 25-mL test tubes. The reaction mixture was blanketed with nitrogen. Upon completion, the reaction mixture was cooled to room temperature, and the contents were washed from the reactor with hexane. The clay was removed by filtration through a Büchner funnel lined with Whatman #54 filter paper (Maidstone, England). The filtrate was dried over  $MgSO_4$  and filtered through a Büchner funnel with a medium-porosity glass frit. Hexane was removed *in vacuo*. The bulk of the unreacted fatty acids were removed by distillation at 180°C and 40 Pa in an Aldrich Kugelrohr distillation apparatus.

Further separation of estolide and unreacted fatty acids (monomer) was achieved by distillation in a wiped-film molecular distillation apparatus, UIC KD1 (Joliet, IL). Two successive distillations were necessary. The monomer was distilled at 175°C under 13.3 Pa, and then the estolide was distilled at 225°C under 13.3 Pa from higher-boiling fractions.

Gas chromatography (GC) analyses were conducted with a Hewlett-Packard 5890 instrument (Palo Alto, CA), fitted with a 15 m  $\times$  0.25 mm DB1 column from J&W Scientific Co. (Folsom, CA). The oven temperature program was from 200 to 390°C at 4°C/min with a 12.5 min hold at 390°C. Methyl

esters were prepared either with  $\text{BF}_3$  in methanol or with diazomethane.

HPLC analyses were performed with a Spectra-Physics 8100 instrument (San Jose, CA) and a Whatman Partisil PXS 10/25 polar silica column (Clifton, NJ), a column flow rate of 0.8 mL/min, and a Varex ELSD II evaporative laser light-scattering detector (Rockville, MD). The detector nebulizing gas was nitrogen; the drift tube was heated to 75°C with an exhaust temperature of 54°C and had a nitrogen flow rate of 55 mL/min. The mobile phase was a mixture of 50% dichloromethane and 50% dichloromethane/methanol/acetic acid (98:2:0.25. vol/vol/vol).

The ELSD response is not necessarily linear with concentration (18,19). Therefore, a calibration curve was used to equate HPLC results to actual estolide percentage by weight from a known mixture of estolide and fatty acids. Pure estolide samples for the calibration curve were prepared by column chromatography, performed on a 40 cm  $\times$  2.5 cm glass column packed with silica gel. Monomers were eluted with 100% hexane, and estolides were eluted with a solvent mixture of 70% hexane, 29% ethyl acetate, and 1% acetic acid (vol/vol/vol). The purities of the fractions were determined by thin-layer chromatography (TLC) on silica gel-coated plates (Whatman) and a solvent system of hexane, diethyl ether, and acetic acid (70:29:1). Figure 2 shows two typical chromatograms of completed reaction mixtures, with the positions of hydroxy fatty acids and dimer acids (Fig. 2A), polyestolides, monoestolides, and unreacted fatty acids (monomer) (Fig. 2B). The reaction mixtures mentioned in this paper contained monoestolides, unreacted fatty acids, and in some cases polyestolides at 0.5% level.

## RESULTS AND DISCUSSION

The estolide reaction is catalyzed by acidic sites on the clay. The clays that work best in these types of reactions are montmorillonite clays (7). They possess a combination of cation exchange, intercalation, and swelling properties that make them unique. The acid-type clays are treated with mineral acids by suppliers to perform at their maximum efficiency. It is known that there is a maximum in the curve of acid treatment and catalytic activity (20,21). Acid treatment increases the surface area and the acidity of the clay. However, if acid treatment is taken beyond a point, the excessive loss of layer ions will cause irreparable disruption in the crystal structure of the clay and will lead to the collapse of the layers. This collapse drastically reduces the surface area and the catalytic activity of the clay (20,21). The commercial acid-treated clay has a pH of 3.51, which can be lowered further by washing with mineral acids. In the batch reactors, the estolide yield did not change when the pH of the clay decreased from 3.51 to 2.50, but it decreased significantly when the pH was lowered to 1.51. The yields were 20, 20, and 6%, respectively. As mentioned earlier, there is a possibility of leaching too many layer cations from the clay during acid treatment, which then leads to collapse of the clay, loss of significant surface area

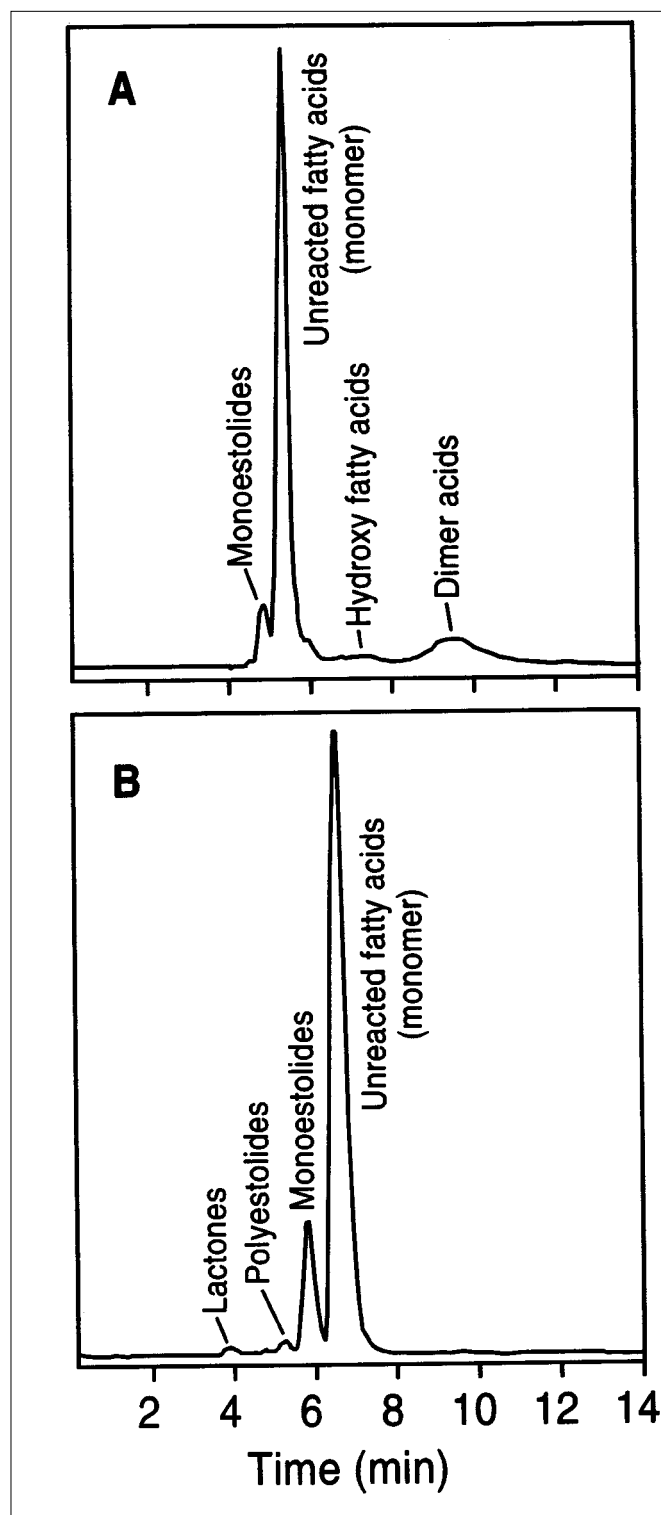


FIG. 2. High-performance liquid chromatography chromatograms of reaction mixtures.

and acid sites, and results in a decrease in the yield of product (20,21).

The most important property of montmorillonites for catalyst design is their ability to expand beyond a single molecular layer of intercalant. The extent of interlayer swelling de-

depends on the nature of the swelling agent, the exchange cation, the layer charge, and the location of the layer charge. In a variety of reactions, hydrated cations are more acidic in clay interlayers than in homogeneous aqueous solution (21). The enhanced Brønsted acidity under intercalated conditions has been attributed partly to the polarizing influence of the cation on the water molecule in the spatially restricted interlayers (21). In the formation of estolides (7,10), the intercalated water may add to the double bonds on the fatty acids, forming hydroxy fatty acids, which are then readily esterified. However, because water also hydrolyses estolides, the removal of free water as the reaction proceeds is imperative for satisfactory yields (10).

The effect of swelling has also been demonstrated in organic reactions where acetone or benzene was used as swelling solvent. Benzene does not swell the interlayers of montmorillonite, and the clays showed no catalytic activity in addition reactions. On the other hand, acetone swells the interlayers from 7.7 to about 15 Å, and clays that are swelled with acetone increase the addition reaction yields 1.5 to 2.3 times above yields obtained under homogeneous reaction conditions (21). The geometry of the approach of the fatty acids is not well known. Even this much swelling may still hinder the movement of especially large molecules, such as meadowfoam oil fatty acids. Acetone-swelled clay was tried in the estolide reactions, and the estolide yield increased about 5%.

Montmorillonite clays are characterized by a three-layered structure that is composed of a central alumina sheet between two silica sheets. There is an overall negative charge that is balanced by mobile, hydrated alkali cations between the layers (20,21). The alkali and alkaline earth interlayer cations ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) can be exchanged by more acidic cations ( $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ) or protons (11–15,20,21). Experimental clays were prepared by treating montmorillonite K-10 clay with salt solutions of  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ . When the clay is washed with solutions of these more acidic cations, the less acidic interlayer cations, such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ , were replaced, making the clay more acidic. The most successful experiment was with clays activated with  $\text{Fe}^{3+}$  ions. In a batch reactor, estolide yields increased from 21% with a commercial montmorillonite clay catalyst (untreated clay, Fig. 3) to 27% with the  $\text{Fe}^{3+}$  catalyst, a 28% improvement in yield. Clay exchanged with  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Al}^{3+}$  ions gave lower yields of estolides.

Previously, in a high-pressure reactor, the optimal amount of clay was determined to be 8 parts to 100 parts of fatty acid. Estolide yields did not change when the amount of clay was above this value (Fig. 4). Because the inside of the reactor could not be viewed, there was no way to know if larger amounts of clay led to more aggregation and less available surface area, which could reduce estolide yields. Reactions conducted in the glass reactor (Fig. 1) gave similar results to experiments conducted in the high-pressure reactor, and there were no visible aggregates of clay. Studies are continuing to clarify this situation.

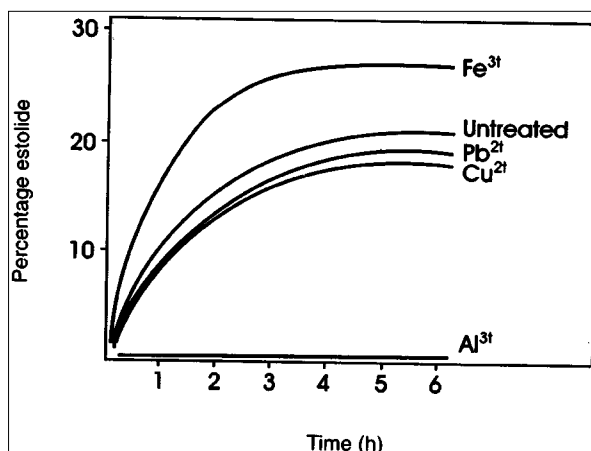


FIG. 3. Estolide yields with clay catalysts that are treated with metal salts.

Introduction of fresh catalyst to an ongoing experiment would be expected to improve the yields if the active sites on the clay become blocked during the reaction. In the experiment whose path is shown in Figure 5, 8 parts clay and 10 parts water to 100 parts fatty acid were heated in the glass reactor for a period of 24 h to ensure that the estolide yield was not changing. At this point, the reaction mixture was cooled, and a fresh batch of 8 parts of clay and 10 parts of water was added. The reaction was brought back to temperature and continued for another 24 h. The final yield of estolide did not change. It is probable that the water added with the fresh batch of clay initially hydrolyzed some of the estolide already formed, resulting in a temporary decrease in the yield. The estolide yield increased again to the previous level as the water left the reaction media through vaporization. As the surface of the fresh clay became saturated, the yield returned to its previous level, leading to the net result of no significant increase in the estolide yield. Cascading reactor systems can

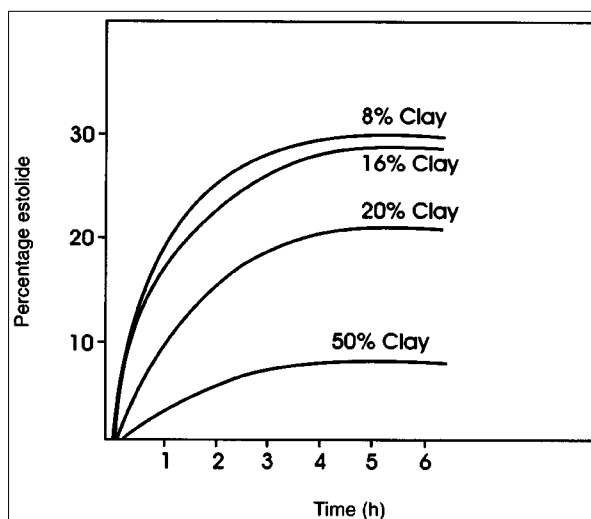


FIG. 4. The significance of the amount of clay.

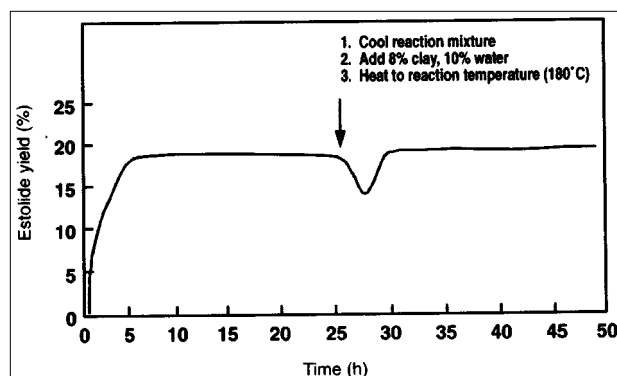


FIG. 5. The effect of the addition of fresh clay to the reaction mixture.

be used to provide a fresh surface for unreacted fatty acids to be converted into estolides. In these reactor systems, the reaction mixture is removed from the first reactor, and after the catalyst is filtered, the reaction mixture is pumped either back into the first reactor or into a second reactor with a fresh batch of catalyst. For the reactions in this paper, we have used the same reactor for subsequent reactions. The estolide yield increased 7%. These experiments indicate that the equilibrium conditions on the clay have to be further studied.

At concentrations below their critical micelle concentration (CMC), surfactants are adsorbed on the surface of the clay, making it more hydrophobic. The clay surface becomes more receptive to organic molecules. Previous studies (16,17) also showed that montmorillonite clays were more responsive to this treatment than bentonite or kaolin, and that cationic surfactants were more effective than anionic or nonionic surfactants. To prevent the formation of micelles that would trap fatty acids in solution, we treated clays with surfactant solutions prepared below their CMC. Yields of estolides were significantly higher in reactions where clays were treated with surface-active agents. Estolide yield increased 30% with cetyltrimethylammonium chloride (CTAC), a cationic surfactant, but only 17.5% with dodecylbenzenesulfonic acid sodium salt, an anionic surfactant (Table 1).

In addition to having an active catalyst, it is also important to provide maximum contact between the catalyst and the reactants. Therefore, studies were continued to improve mixing of the fatty acids and clay catalysts. In a batch reactor, mixing has to start as soon as fatty acids, water, and clay are in contact with each other. Otherwise, the clay and water separate from the fatty acids and form a sticky glob at the bottom

TABLE 1  
Surface-Active Agent-Treated Clay Catalysts

Clay	Estolide yield (%)
Untreated montmorillonite K-10	20
Treated <sup>a</sup> with DBS <sup>b</sup>	23.5
Treated with CTAC <sup>c</sup>	26

<sup>a</sup>Clay was treated with  $1 \times 10^{-5}$  M solution of surface-active agent.

<sup>b</sup>Dodecylbenzenesulfonic acid sodium salt.

<sup>c</sup>Cetyltrimethylammonium chloride.

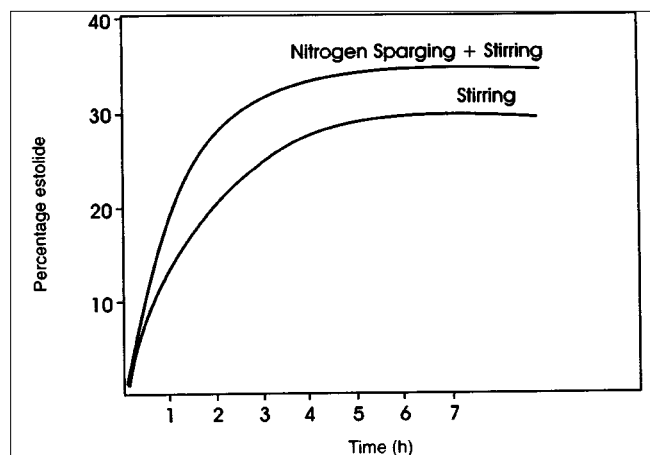


FIG. 6. The difference in estolide yields with nitrogen sparging.

of the vessel that is difficult to stir into suspension. Our current procedures use nitrogen sparging to prevent separation during the charging of the reactor and to keep agglomeration of the catalyst to a minimum. In the glass reactor (Fig. 1), a medium-porosity glass frit at the bottom introduces nitrogen into the reaction mixture as fine bubbles. Combined with mechanical stirring, this system is efficient in keeping the clay suspended as fine particles. This reactor design also allows water to escape at about 100°C, thereby minimizing hydrolysis of already formed estolide (Scheme 1). With combined mixing and nitrogen sparging the estolide yield was improved by 13% (Fig. 6).

The effect of stirring with a sonicator on estolide yields was: 18, 16.5; 25, 18.0; 50, 20.0, power (W) and estolide yield (%), respectively. Agitation was achieved with a high-intensity ultrasonic processor. The vibrations from the converter are intensified by the probe, creating pressure waves in the liquid. This action forms a large number of microscopic bubbles (cavities), which expand during the negative pressure excursion and implode violently during the positive excursion. These bubbles produce a powerful shearing action at the horn tip and cause the molecules in the liquid to become intensely agitated. The estolide yields in these reactions increased, as shown above, as the power of mixing increased.

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[Received April 10, 1996; accepted November 18, 1996]