Continuous Esterification of Citric and Aconitic Acids

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Tributyl citrate, trihexyl citrate, and tributyl aconitate have been produced in the continuous esterification equipment described herein. It is evident from this work that a continuous process for the esterification of citric acid and aconitic acids is available, but additional work will have to be done before a commercial unit can be designed.

CONTINUOUS methods have been developed for both unit operations and unit processes in the field of chemical engineering. Esterification as a unit process, however, has lagged far behind in conversion to continuous methods. The object of this investigation, therefore, was to esterify citric and aconitic acids continuously.

Equipment

A great many factors had to be considered in the design of equipment to carry out this reaction. The main object was attainment of high rates of conversion of acid to ester. As a corollary to that, side reactions were to be held to a minimum so that no undesirable decomposition products could be formed.

The reaction chamber, as finally assembled (Figure 1), consisted of 180 feet of Monel metal tubing, inside diameter 0.05 inch. This tubing was coiled into two concentric circles, the outside 9 inches and the inside 8 inches in diameter. These coils were supported in oil in a 5-gallon circular metal container. The system was insulated and two 1000-watt immersion heaters provided the necessary heat.

FOR CONTINUOUS *vs.* BATCH ESTERIFICATION

here's the box score on small scale tests:

. . . conversions better than 99% in contact times of from 2 to 3 minutes compared with usual 24-hour batch runs

. . . no measurable decomposition of citric acid at 200° C.

. . . up to 7.5% sulfuric acid catalyst can be used without product decomposition

. . . quality and color of citrates are equal or superior to those of the commercial product

The feed unit consisted of two 3-gallon capacity stainless steel tanks. Pressure on the system was provided by a cylinder of nitrogen.

The flash chamber followed a control valve. The flash chamber and length of tubing outside the oil bath were wound with Nichrome resistance wire to provide heat necessary to compensate for radiation losses.

To reduce the danger of plugging the small diameter tubing, a wire mesh strainer was inserted into the feed line before the reactor.

The reaction mixture, as it entered the flash chamber, consisted of both liquid and vapor. This mixture was separated therein; the vapor made up of alcohol and water went overhead; the liquid (ester, excess alcohol, unreacted acid, catalyst, and some water) was drawn off. The flash chamber also proved to be an efficient entrainment separator since no free acidity was found in the overhead.

When the equipment was designed, the needle valve was to have been used to throttle the reaction mixture at the exit. It was found, however, that no throttling was needed. In fact, the pressure on the system had to be increased to provide the desired flow rate. This feature proved to be an advantage. The tubing was of such length and diameter that the drop through the reactor resulted in atmospheric pressure at the outlet at the desired flow rates.

The high pressure drop through the unit was caused by progressive vaporization of a portion of the reaction mixture as it flowed through the tubing. The temperature of the bath was above the boiling point of the water and alcohol at atmospheric pressure. Therefore, as the pressure decreased over the length of the coil, increasing amounts of alcohol and water were flashed off. The equilibrium was shifted in favor of the ester due to the removal of water from the reaction mixture.

A large increase in linear velocity resulted from the vaporization taking place; hence, the high pressure drop through the unit.

At the operating conditions, better than 99% of the citric

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and aconitic acids have been reacted in 2 to 3 minutes. In addition, at these short reaction times there was no measurable decomposition of the citric acid. This had heretofore been a problem when reaction temperatures above 150° C. were employed in industry.

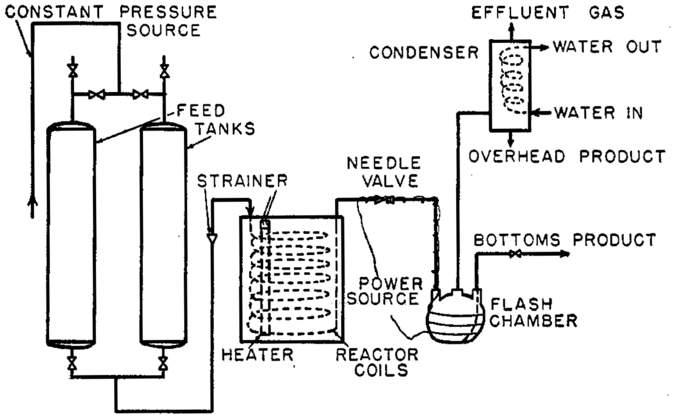

Figure 1. Continuous esterification equipment

Another novel feature of this process was that relatively large quantities of sulfuric acid could be used as a catalyst with no apparent product decomposition. In batch commercial production of citric acid esters, it has been customary to use 1% of sulfuric acid as a catalyst, based on the weight of citric acid. (The percentage concentration of all catalysts hereafter is based on the weight of the polycarboxylic acid used in the experiment.)

In these studies it was found that as much as 7.5% of sulfuric acid could be used as a catalyst without adversely affecting the product color or promoting any decomposition.

Both these features—namely, the high temperature (up to 200° C.) and high catalyst concentrations (7.5% sulfuric acid) were permissible because of the short contact time. This reaction time of 2 to 3 minutes compared most favorably with a contact time of 24 hours for a batch run on an industrial scale. In addition, higher purity and improved color were obtained than were achieved in similar commercial production.

Experimental Procedure

The feed used during these runs was prepared outside of the equipment. Citric acid was added to the alcohol and the sulfuric acid catalyst was added immediately thereafter. This was done to obtain as much conversion to the ester as possible before the reactor. The reaction mixture was heated to 50° C. for 30 minutes to dissolve the citric acid, the esterification was 33% complete at this point.

The feed was then added to one of the 3-gallon tanks, and the pressure on the system was raised to 250 pounds per square inch. The reactor had been preheated previously to the desired operating temperature.

The needle valve at the coil outlet was opened and the time noted. The reactor temperature was maintained throughout the run by controlling the heat input to the oil bath. The desired temperature was also maintained on the tubing leading from the oil bath to the flash chamber and on the chamber itself.

The overhead and bottoms from the flash chamber were measured. The water content of the overhead was determined. The bottoms were analyzed for free acidity and saponification value. In such a way the compositions of both streams could be fixed.

After each pass, fresh alcohol was added to the bottoms to reestablish the initial ratio of 12 moles of alcohol per mole of polycarboxylic acid. The product of the first pass was then reintroduced into the reactor. The feed mixture thus made from three to six passes through the equipment in this manner, fresh alcohol being added after each pass.

On an industrial scale, of course, a series of reactors or a recycle operation could be employed. Provision would be made for recovery of the alcohol-water mixture obtained as overhead

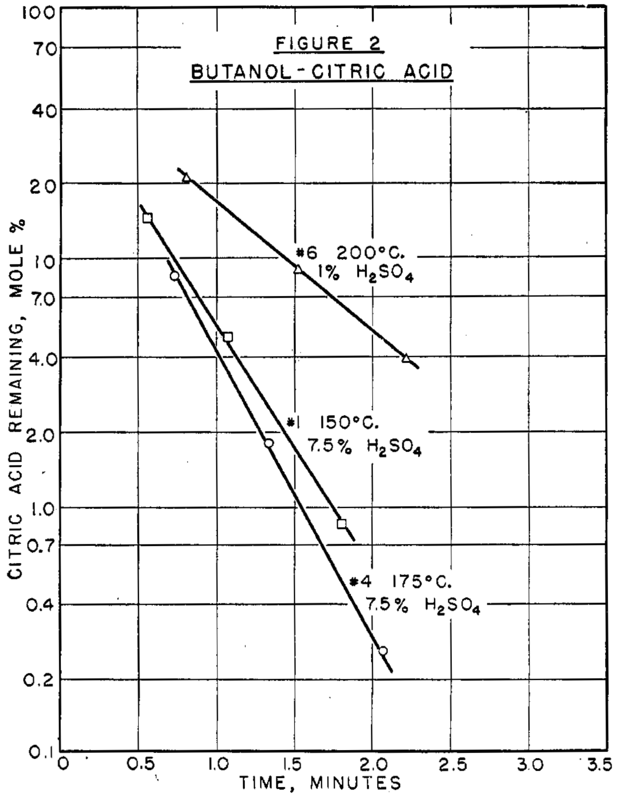
FIGURE 2

BUTANOL-CITRIC ACID

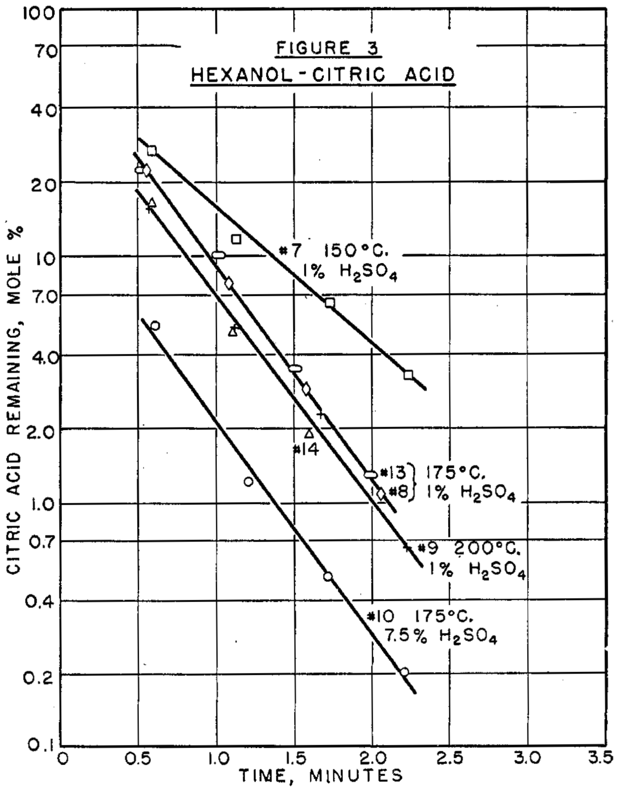
FIGURE 3

HEXANOL-CITRIC ACID

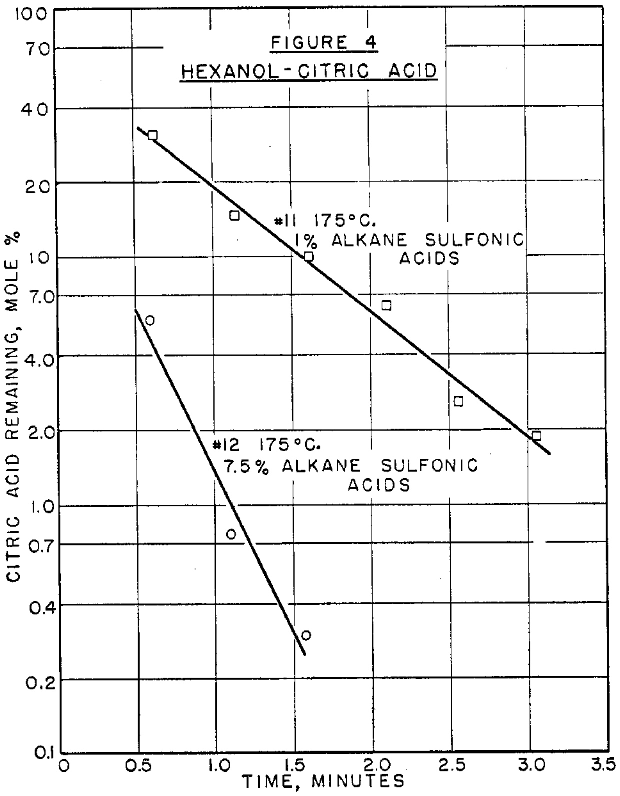

FIGURE 4
HEXANOL-CITRIC ACID

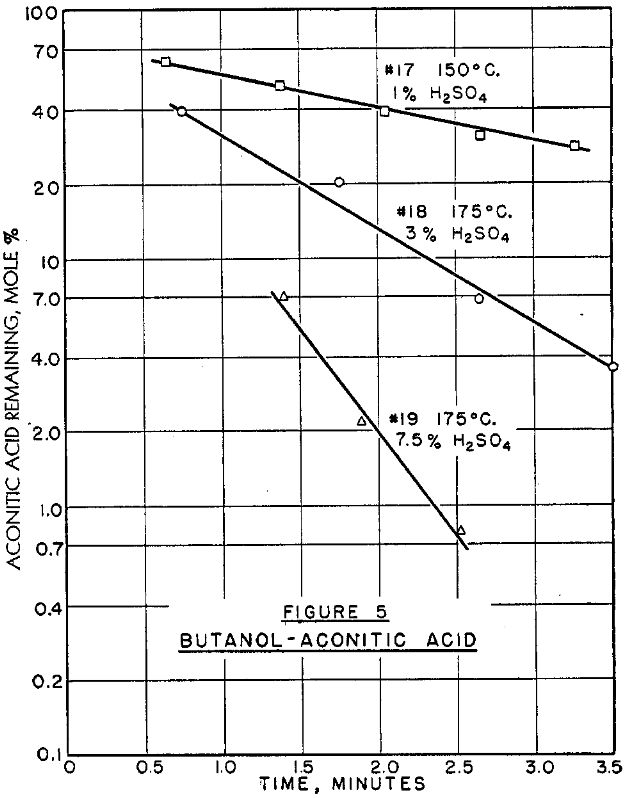

FIGURE 5
BUTANOL-ACONITIC ACID

from the individual passes. The alcohol could then be purified and re-used.

At the start of the experimental work it was decided to fix the alcohol to acid ratio at 12:1, for two reasons:

1. At a ratio smaller than 12:1—that is, less alcohol per given quantity of citric acid—difficulty was experienced in obtaining complete solution of the acid.
2. On an industrial basis a large quantity of alcohol requires a large recovery system. Therefore, on the basis of economy, the amount of excess alcohol should be kept to a minimum.

The temperature range to be investigated was set at 150° to 200° C. This was fixed when initial runs gave good conversions in short contact times. Little or no decomposition was expected as a result of the short contact times.

A catalyst concentration of 1% sulfuric acid was recommended as industrial practice. Because of the short contact times involved, however, the catalyst concentration was increased to 7.5% in some runs.

Runs were made not only with butanol and citric acid, but also with hexanol and citric and with butanol and aconitic acid.

Material Balances

An over-all material balance was made for each run. The feed and product for each pass were tabulated. From the internal volume of the reactor and the average volume of feed and product, the residence time in the reactor was calculated.

For each pass in the run the over-all values of feed and product were broken down to give the weight per cent of the various constituents. From the detailed data on each stream the rate of flow was expressed in grams per minute and moles per minute.

The weight per cent of carboxylic acid was obtained from the free acidity titration. The amounts of diester and triester present were calculated from the combination of free acidity titration and saponification value. It was assumed that all the carboxylic acid was converted to diester before any triester was formed.

The amount of water in the overhead was determined from the refractive index of the butanol-water mixture. Since hexanol is substantially insoluble in water, the water in this mixture was determined by direct measurement.

The quantity of sulfuric acid was measured by a gravimetric sulfate determination.

More than 80% of the material balances around each pass closed within 2%.

A material balance for a typical run is:

Run 9

Temperature: 200° C.
Mole ratio: Hexanol/citric acid, 12:1
Catalyst: 1% H_2SO_4

Pass No.	Feed, G.	Product, G.	Loss, G.	Residence Time, Min.
1	4244	4066	178	0.56
2	3957	3929	28	0.57
3	3890	3873	17	0.54
4	3850	3848	2	0.55

Discussion of Results

Runs 1 and 4 were made to show the effect of temperature on residence time. As shown in Figure 2, after 1.8 minutes the amount of citric acid remaining in run 4 made at 175° C. was 40% less than that remaining in run 1 made at 150° C. The catalyst concentration in both runs 1 and 4 was 7.5% sulfuric acid.

An increase in temperature, however, may more than be offset by a decrease in catalyst concentration. In run 6, after the same time had elapsed, the amount of citric acid remaining was eight times greater than the amount left in run 1 at 150° C.

Tributyl citrate, therefore, has been produced in less than 2 minutes at 150° C. and catalyst concentration of 7.5% sulfuric acid. Within the limits of the determination (<0.5%) no tributyl aconitate, a measure of citric acid decomposition, was present in the product.

Tributyl citrate esters produced were of high purity and were better in color than the normal commercial product.

It was then decided to investigate the system hexanol and citric acid. Run 7 was made at 150° C. and catalyst concentration of 1% sulfuric acid. In 2 minutes, 95.5% of the citric acid had been esterified, as shown in Figure 3. From this relatively low conversion, it was evident that a higher temperature or larger catalyst concentration would have to be used. Run 8, therefore, was made at 175° C. and catalyst concentration of 1% sulfuric acid. At 2 minutes, 98.8% of the citric acid had been reacted—a decrease of 70% in the citric acid remaining under run 7.

Run 9 was then made at 200° C. and a catalyst concentration of 1% sulfuric acid. In a residence time of 2 minutes in the reactor, 99% of the citric acid had been converted to trihexyl citrate. To make a comparison between hexanol-citric acid and butanol-citric acid systems at the higher catalyst concentration, run 10 was made at 7.5% sulfuric acid and 175° C. At the end of 2 minutes more than 99.7% of the citric acid had been converted to trihexyl citrate.

An increase in catalyst concentration at 175° C., therefore, reduced the citric acid left unconverted by more than 75%. In run 4 of the butanol-citric acid series, at the same temperature and catalyst concentration, a conversion identical to that of run 10 was reached at the end of 2 minutes.

Runs 13 and 14 were made to duplicate runs 8 and 9. As may be seen, there is very good agreement between runs 8 and 13 and also runs 9 and 14.

A different and reportedly milder catalyst was now tried. A mixed alkanesulfonic acid catalyst obtained from the Indoil Corp. of Chicago was employed in runs 11 and 12.

At 175° C. and catalyst concentration of 1% mixed alkanesulfonic acids (run 11), 98% conversion of citric acid to trihexyl citrate was obtained in 3 minutes (Figure 4). In run 12, at the same temperature and 7.5% mixed alkanesulfonic acids, 99.7% of the citric acid disappeared in only 1.5 minutes. At the same time, in run 11 only 90% conversion had been reached. Thus, by increasing the catalyst concentration from 1 to 7.5%, the amount of citric acid left was decreased by 97%.

The final system run in the experimental work consisted of butanol and aconitic acid. At the start, relatively mild conditions were employed because of the ever-present hazard of polymerizing the aconitic acid.

Catalyst concentration of 1% sulfuric acid and temperature of 150° C. were used in run 17, Figure 5. At 2.5 minutes only 65% of the aconitic acid had been reacted. This conversion was much lower than that obtained under similar conditions in the system hexanol-citric acid. To increase the rate of conversion the temperature was raised to 175° C. and the catalyst concentration was increased to 3% sulfuric acid. In run 18, after 2.5 minutes, 91.5% of the aconitic acid had been esterified.

Run 19 was made at 175° C. and 7.5% sulfuric acid concentration. After a residence time of 2.5 minutes, 99.25% of the aconitic acid was converted to tributyl aconitate. Thus, by increasing the temperature 25° and raising the catalyst concentration from 1 to 7.5% sulfuric acid at the same time, the conversion was raised from 65% to over 99%.

Conclusions

Tributyl citrate, trihexyl citrate, and tributyl aconitate have been produced in the continuous esterification equipment described herein. Contact times of 2 to 3 minutes resulted in conversions of better than 99%. These times may be compared with a usual run length of 24 hours in a commercial unit. At temperatures greatly above those employed in industry (200° C.), there was no measurable decomposition of citric acid. In addition, the tributyl citrate produced was of high quality, superior to the commercial product. The trihexyl citrate produced was also of high quality and had a much better color than the commercial product.

It is evident from this work that a continuous process for the esterification of polycarboxylic acids is feasible. In order to design a commercial unit, however, additional work on a larger size unit would have to be done.

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Pyridine-*N*-Oxide

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Pyridine-N-oxide, first made by Meisenheimer in 1926, is now available in commercial quantities. Although it is too early to predict its impact on methods of producing pyridine compounds, many of the possibilities are known: The nitration of pyridine-N-oxide proceeds under normal conditions and 4-nitropyridine-N-oxide is obtained in 90% yield. An almost quantitative yield of 2-pyridone is obtained by heating pyridine-N-oxide with acetic anhydride. Halogenation of pyridine-N-oxide offers a good route to 2- and 4-chloropyridines. 2-Picoline-N-oxide reacts with *p*-toluenesulfonyl chloride to give a good yield of 2-(chloromethyl)pyridine. An analogous reaction is the formation of 4-pyridylmethanol from 4-picoline-N-oxide and acetic acid.

AN IMPORTANT element in the continued rapid growth of the chemical industry is the attitude of the industry toward its processes. The procedure for manufacturing a chemical is not considered sacred and unalterable. On the contrary, chemical processes are constantly modified to utilize technological advances.

Most changes in chemical processes are a result of either the development of a new technique or the availability of a new raw material. Pyridine-*N*-oxide is a new raw material that may alter existing processes for the manufacture of pyridine compounds.

Pyridine-*N*-oxide became commercially available in June 1954. Although it is too early to predict the impact pyridine-*N*-oxide will have on methods of making pyridine derivatives, it may be of interest to mention some of the changes that are in the offing.

Substitution reactions in the pyridine ring are much more