SEPARATION OF LACTIC ACID

by

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INTRODUCTION

Historical

Lactic acid, α-hydroxypropionic acid is probably one of the oldest known organic acids. It is present in sour milk, in the muscles of animals, in the soil, and in sauerkraut. It is also used in beverage products. Because of its diverse distribution, its presence has been recognized for ages.

It was first isolated and identified by Swedish scientist Scheele in 1780. In 1857, Pasteur discovered that the souring of milk was due to the fermentation of milk by microorganisms.

The first commercial production of lactic acid was done by Charles E. Avery of Littleton, Massachusetts in 1881 in an attempt to replace the tartarate in baking powder with calcium lactate (1).

Properties of Lactic Acid

Lactic acid $CH_3CH(OH)COOH$, molecular weight 90.08, is usually a colorless sirupy, hygroscopic liquid or a low melting crystal in pure form. It has a slight but not unpleasant odor. The specific gravity of DL-lactic acid is $1.249^{15°/4}$. The heat of formation and free energy of formation at 25°C and 1 atm in the liquid state are -161.65 kcal/g mole and -124.40 kcal/g mole respectively (2).

Lactic acid has one assymmetric carbon atom and hence exists in three forms: L configuration L(+) lactic acid which is dextrorotary, D configuration D(-) lactic acid which is levorotary, and optically inactive DL-lactic acid, a racemic mixture of equal proportions of D-form and L-form.

Salts of L(-) isomer are levorotary and those of D(-) isomer dextrorotary. Vigorous heating of optically active forms convert them into the optically inactive racemic form. Ordinary fermentation lactic acid is in racemic form. Racemase, an enzyme produced by a number of bacteria, converts the active form originally produced by the fermentation into the racemic form.

It is completely miscible with water, and water-miscible organic solvents such as alcohol, ether and acetone. The distribution coefficients of lactic acid between water and various solvents are summarized in Table I (3). Note that the K's are always larger then one and the concentrations in the water phase are between 1.34 and 11.06 grams per 100 ml. This demonstrates that the hydrogen bonds between lactic acid and water are quite strong.

The vapor pressure data are shown in Table II. Some properties of lactic acid isomers are shown in Table III (4).

Various salts of optically active forms and racemic forms have different numbers of moles of water of crystallization, and these may be utilized for their identification. See Table IV (5).
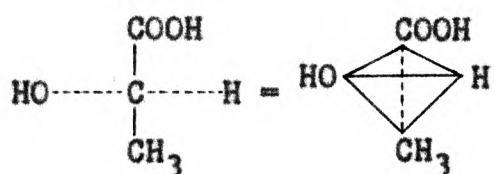
L(+) lactic acid   D(-) lactic acid
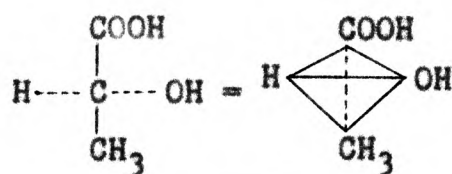
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Table I. Distribution coefficients for lactic acid
between water and various solvents(3).

Solvent	Temp.,°C	C_W	K
n-Butyl alcohol	31	1.34	1.37
n-Amyl alcohol	31	1.65	2.45
n-Hexyl alcohol	28	1.79	3.40
n-Octyl alcohol	28	1.62	5.2
Isobutyl alcohol	28	1.41	1.60
Isoamyl alcohol	31	1.59	2.22
sec-Butyl carbinol	28	1.68	2.46
Diethyl carbinol	26	3.18	2.03
	26	8.42	1.95
	90	2.00	1.77
	90	10.00	1.64
Amyl alcohols (Pentasol)	26	3.07	2.30
	26	8.79	2.01
	100	2.83	1.84
2-Ethyl butanol	28	1.81	3.64
Octanol-2	28	2.03	5.2
2-Ethyl hexanol	28	1.98	6.8
Benzyl alcohol	28	1.63	2.33
Phenyl ethyl alcohol	28	1.73	2.36
Phenyl cellosolve	28	1.68	2.41
Cyclohexanol	26	2.60	1.74
	100	2.82	1.40
Amylcyclohexanol	26	2.71	7.0
Phenol	26	2.56	1.35
Eugenol	28	1.80	14.7
Terpineol	28	1.82	3.84
Ethyl acetate	31	1.77	4.07
Butyl acetate	28	2.00	8.2
Amyl acetate (fusel oil)	28	2.15	11.0
Amyl acetate (pentacetate)	26	2.80	8.8
Cyclohexyl acetate	28	2.08	13.0
Butyl carbitol acetate	28	1.79	4.1
Butyl cellosolve acetate	28	2.78	9.3
Diethyl carbonate	28	2.12	21.0
n-Butyl lactate	28	2.56	1.88
	26	8.38	1.61
	100	3.54	1.82
Isobutyl lactate	28	1.61	1.86
n-Amyl lactate	27	1.87	2.88
Ethyl ether	28	1.88	9.8
Isopropyl ether	28	2.27	35.
n-Butyl ether	28	2.23	73.
n-Amyl ether	28	2.20	100.

Table I. Distribution coefficients for lactic acid between water and various solvents (concl.) (3).

Solvent	Temp., °C	C_W	K
Methyl isobutyl ketone	26	3.55	7.9
	26	11.06	7.5
	100	3.76	5.6
Methyl n-amyl ketone	26	3.18	9.7
	100	4.08	6.8
Diisobutyl ketone	28	2.22	36.0
Mesityl oxide	28	1.84	3.76
	100	3.56	2.74
Phorone	28	4.80	15.7
Isophorone	28	2.38	2.33
	26	8.42	2.13
	100	3.30	2.28
Acetophenone	28	2.04	8.8
Cyclohexanone	27	2.26	1.87
	100	2.92	1.75
Furfural	27	1.84	3.32
Furan	26	3.04	80.
Limonene	28	1.83	280.
Pinene	28	1.87	80.
p-Cymene	28	1.86	600.
Sulfite turpentine	28	1.87	100.
Chloroform	28	1.87	100.
Nitroethane	28	1.81	11.0

$K=C_W/C_S$
C_W=concentration of acid in aqueous phase, g. per 100 ml.
C_S=concentration of acid in solvent phase, g. per 100 ml.

Table II. Boiling point of lactic acid under different pressure.

Pressure, mm Hg.	Boiling Point, °C
760	260 (decompose)
40	158
10	125
5	112
1.0	84
0.5	72
0.1	52

Source: Correspondence, Clinton Corn Processing Company, Clinton, Iowa

Table III. Properties of lactic acid isomers (4).

	M.P., °C	$[\alpha]_{5461}^{21-22°}$	Dissociation constant at 25°C pK
L lactic acid	52.8	2.6 (c=8.0)	3.83±0.01
D lactic acid	52.8	-2.6 (c=8.0)	3.79±0.01
DL lactic acid	16.8	0.0	3.81±0.01

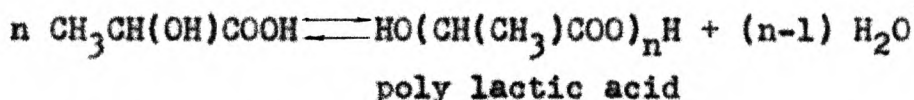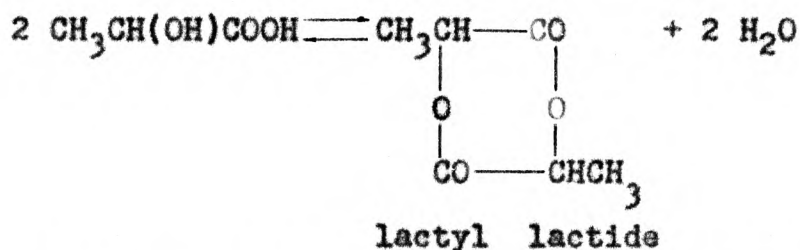*$[\alpha]=\dfrac{\text{Observed rotation in degrees}}{\text{Length of polarimeter tube in dm. x concentration in g./cc}}$

$[\alpha]_{5461}^{21-22°}=2.6$ (c=8.0) indicates the measurement of the specific rotation at 21-22°C and green light of mercury of wave length 5461Å is employed.

*$pK = -\log_{10}K$

Table IV. Water of crystallization in lactate salts (5).

	Calcium lactate	Magnesium lactate	Zinc lactate
Optically active salts	4½ molecules	3½ molecules	2 molecules
Racemic salt	5 molecules	3 molecules	3 molecules

On account of the presence of a hydroxy group and a carboxyl group in the same molecule, concentrated solutions of lactic acid undergo self-esterification to form a lactyl lactide and linear polylactic acids upon heating. Concentrated lactic acid tends to esterify with itself more readily than in dilute water solution because of the law of mass action. Figure 1 shows the equilibrium composition of lactic acid-water solutions (6).

$$2\ CH_3CH(OH)COOH \rightleftharpoons CH_3CH\!-\!\!-\!\!CO + 2\ H_2O$$

$$\begin{array}{ccc} & | & | \\ & O & O \\ & | & | \\ & CO\!-\!\!-\!\!CHCH_3 \end{array}$$

lactyl lactide

$$n\ CH_3CH(OH)COOH \rightleftharpoons HO(CH(CH_3)COO)_nH + (n-1)\ H_2O$$

poly lactic acid

Utilization of Lactic Acid

The most important uses of lactic acid are in the food industry. About half of the total acid produced is of the edible grade. It is used to adjust the pH of jelly, cheeses, egg whites etc. In the beer industry, it is used to adjust the pH of hard
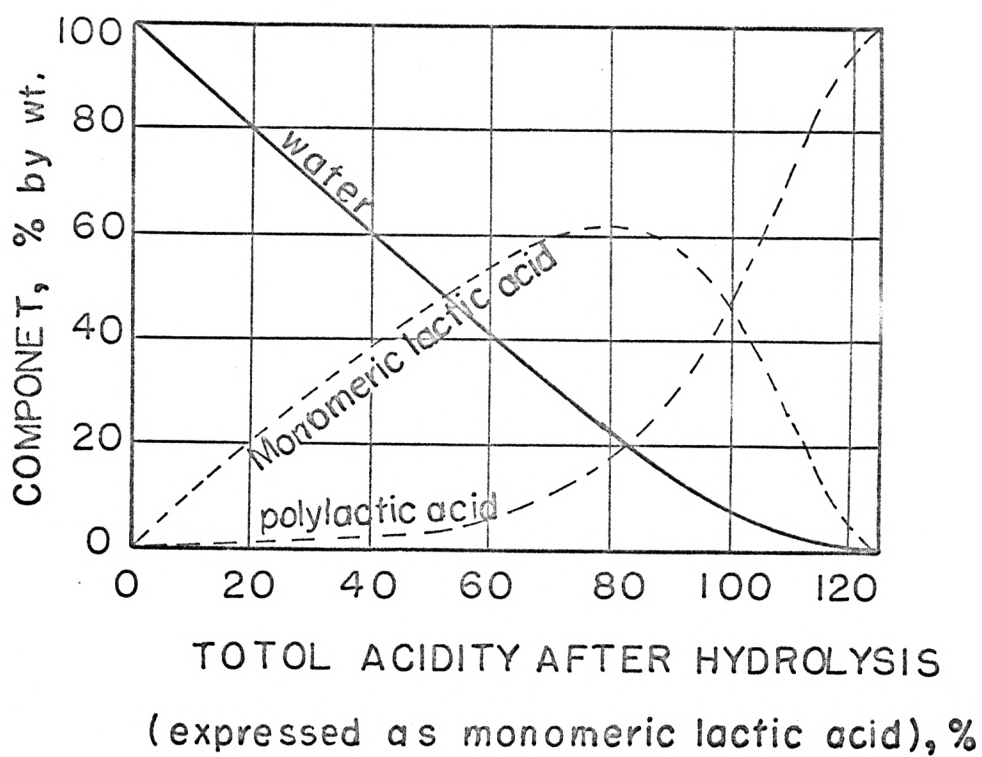
Fig. 1. Composition of lactic acid-
water systems (6).

water. It is also used as an acidifying agent in jams, olives,
sauerkraut, mincemeat, pickles, soft drinks, confectionery and
bakery products.

The largest industrial use of lactic acid is that of a
deliming agent in the tanning industry. It is also used in the
dyeing of wool with mordant and chrome colors, and in the pro-
duction of wetting agents in textile finishing.

Other applications of lactic acid are in the field of phenol-
formaldehyde resin manufacturing, lithographic developers, electro-
plating, insecticides and fungicides. It is used as a raw material
for various high boiling esters that are constituents of lacquers,
varnishes and inks. Some esters are compounded with plastic to
increase its flexibility, workability or shock resistance. They
are called plasticizers.

Preparation of Lactic Acid

There are various ways to prepare lactic acid.

(A) Carbohydrates are degraded with alkalies to produce
lactic acid. The reaction of sugar with lime or sodium hydroxide
at high temperature and pressure yields lactic acid (7, 8). It
seems probable that methyl glyoxal is first formed and then this
undergoes internal oxidation-reduction.

$$C_{12}H_{22}O_{11} \longrightarrow 4\ CH_3COCHO + 3\ H_2O$$
$$CH_3COCHO + H_2O \longrightarrow CH_3CH(OH)COOH$$
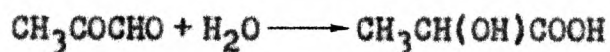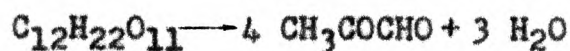
(B) Lactic acid can be synthesized by reaction of carbon monoxide and acetaldehyde in the presence of sulfuric acid at 130°C. to 200°C. under 900 atm pressure (9).
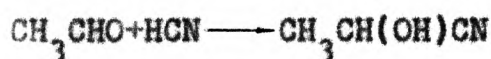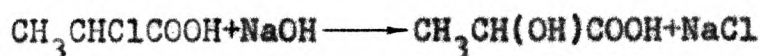
$$CO + CH_3CHO + H_2O \xrightarrow{H_2SO_4} CH_3CH(OH)COOH$$
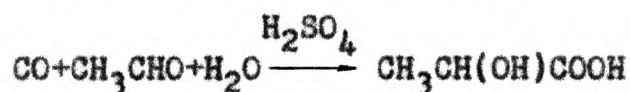
(C) Acetaldehyde reacts with hydrocyanic acid, and the product acetaldehyde cyanohydrin is hydrolyzed (8).

$$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$$

$$CH_3CH(OH)CN + 2H_2O \longrightarrow CH_3CH(OH)COOH + NH_3$$

(D) Lactic acid is formed by catalytic oxidation of 1:2-propylene glycol (8).

$$CH_3CH(OH)CH_2OH + O_2 \longrightarrow CH_3CH(OH)COOH + H_2O$$

(E) Propionic acid is chlorinated and   -chloropropionic acid formed is hydrolyzed by an alkali (8).

$$CH_3CH_2COOH + Cl_2 \longrightarrow CH_3CHClCOOH + HCl$$

$$CH_3CHClCOOH + NaOH \longrightarrow CH_3CH(OH)COOH + NaCl$$

(F) Sugars are fermented to yield lactic acid. This is the only method at present for the commercial production of lactic acid. Molasses, starch hydrolyzates and whey are considered the most potentially important raw materials. Utilization of sulfite waste liquor (3), potatoes (10), Jerusalem artichokes (11), molasses (12), whey (13), corn sugar (14), and beet juice (15) for the lactic acid fermentation have been discussed.

Whatever the raw material is used, the concentration of the sugar on starting the fermentation is kept between 10 to 15%. Suitable quantities of inorganic salts such as nitrogen compounds and calcium carbonate are added to the medium. The medium is adjusted to pH values between 5.5 and 6.0. The temperature of fermentation is generally high. For example, the optimum fermentation temperature for Lactobacillus delbrueckii is 50°C. The fermentation is usually complete in 1 to 6 days with yields of 85 to 90% based on the sugar fermented. The loss is partly due to metabolism of the carbohydrate by bacteria and partly due to the subsequent processing.

$$C_6H_{12}O_6 \longrightarrow 2\ CH_3COCHO + 2\ H_2O$$
$$\text{(Dextrose)} \quad \text{(Methyl glyoxal)}$$

$$CH_3COCHO + H_2O \longrightarrow CH_3CH(OH)COOH$$

$$\text{(Methylglyoxal)} \quad \text{(Lactic acid)}$$
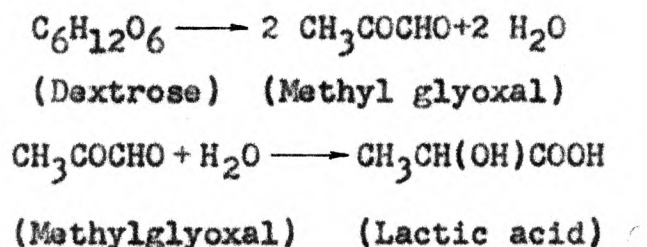
Lactic acid production from corn sugar was described by G. C. Inskeep, G. G. Taylor and W. C. Breitzke (14). The flow sheets for the production of lactic acid and calcium lactate are given in Figures 2 and 3. The details of this process as carried out by American Maize Products Co. at Hammond, Indiana are outlined below.

The inoculum, Lactobacillus delbrueckii, was cultured successively in a test tube, a 500 ml flask and a 6 liter flask containing 3 liters of media. After 24 hours of incubation, the 6 liter flasks were used to inoculate culture tanks. Each tank contained 375 gallons of media. After 24 hours at 120°F. the

culture tanks were used to inoculate fermenters. The contents of one culture tank was used for inoculating one 6,600 gallon fermenter or three culture tanks were used for one 30,000 gallon fermenter. These fermenters were filled with 4,600 gallons and 24,000 gallons of media respectively to allow for expansion and gas evolution.

The medium used in the culture tanks and fermenters consisted of an aqueous solution of 15% corn sugar; 0.375% malt sprouts and 0.25% diammonium phosphate as nutrient and 10% calcium carbonate as neutralizing buffer to maintain the pH in the optimum range of 5.8 to 6.0.

Culture tanks and fermenters were mixed vigorously to keep the neutralizing agent in suspension. The circulating water kept the temperature of the culture tank and fermenter at 120°F. This operating temperature was too high for the growth of contaminating organisms. And hence it was not necessary to pasteurize the media.

The course of the fermentation was followed daily by checking the pH and reducing sugar content of the medium. The fermentation came to an end when the reducing sugar content had decreased to 0.10%. The total time for fermentation was from 4 to 6 days. The temperature was then raised to 180°F. to kill the bacteria. During the fermentation the lactic acid produced reacted with the calcium carbonate, forming calcium lactate. Fermentation was retarded or stopped by acidity.

The liquor was then pumped to a decanter where hydrated lime was added to a pH of 10.0 and the temperature was kept at 180°F.

to coagulate the protein in the suspension. The slurry was agitated for 30 minutes and then allowed to settle for 2 to 6 hours. The clear liquor was decanted from the top and pumped to the first bleach tank. The sludge from the bottom was mixed with recycle calcium sulfate and this slurry was filtered on a continuous string vacuum filter. The filtrate went to the first bleach tank where it was mixed with decanted liquor and activated carbon. Three pounds of carbon were used to decolorize 40 gallons of 14% calcium lactate solution. The carbon-calcium lactate slurry was then filtered in a filter press. The filtrate was concentrated to 32% calcium lactate solution in a single effect evaporator. Sulfuric acid-50° Bé - was added to the concentrate in an acid conversion tank to change calcium lactate into lactic acid. Calcium sulfate thus formed was filtered off on a continuous string vacuum filter and the cake was added to the previously mentioned mud as a filter aid. The lactic acid filtrate was then bleached in the second bleach tank with re-cycle carbon filtered from the first, third, and fourth bleaching operations. The slurry went to a filter press and the filtrate was concentrated in a double effect evaporator to 52% lactic acid. In the third bleach tank, it was treated with sodium sulfide to remove heavy metals and with new carbon. This slurry was filtered in a filter press. The filtrate was checked for free acidity, heavy metals, odor and color, and the lactic acid was adjusted to 50% and some new carbon was added for the fourth or final bleaching. The filtrate from the final filter press was 50% edible lactic acid.

If 80% edible acid was desired, the 52% acid was concentrated in an vacuum evaporator to 82% lactic acid and the acid went to a third bleach. The process following this step was the same as that of producing 50% edible acid.

The 44% and 80% technical grades of lactic acid were produced in the same equipment and from the same raw materials.

Purification of Lactic Acid

Lactic acid is available in four grades: technical, edible, plastic and U. S. P. Typical analyses of these grades of acid are shown in Table V (16).

The impurities in lactic acid include heavy metals such as iron, copper; ash, especially calcium carbonate; unfermented sugar and volatile acids. These impurities come partly from the raw materials of fermentation and processing, partly from the corrosion of process equipment and some from the fermentation.

The cost of the crude technical grade of lactic acid is quite low. However, because of its corrosiveness and the difficulty of producing high purity acid, the cost of the pure acid is very high compared with competitive acids (refer to Table VI).

Several processes have been developed to produce grades of lactic acid of higher purity.

(A) Steam Distillation. This was perhaps the oldest method of purification. The lactic acid was steam distilled under high vacuum (17, 18). Macallum (18) recommended that the crude lactic acid be steam distilled preferably between 10 and 25 mm Hg

Fig.2. Flow sheet for the production of lactic acid at the Hammond, Ind. Plant of American Maize-Products Co.
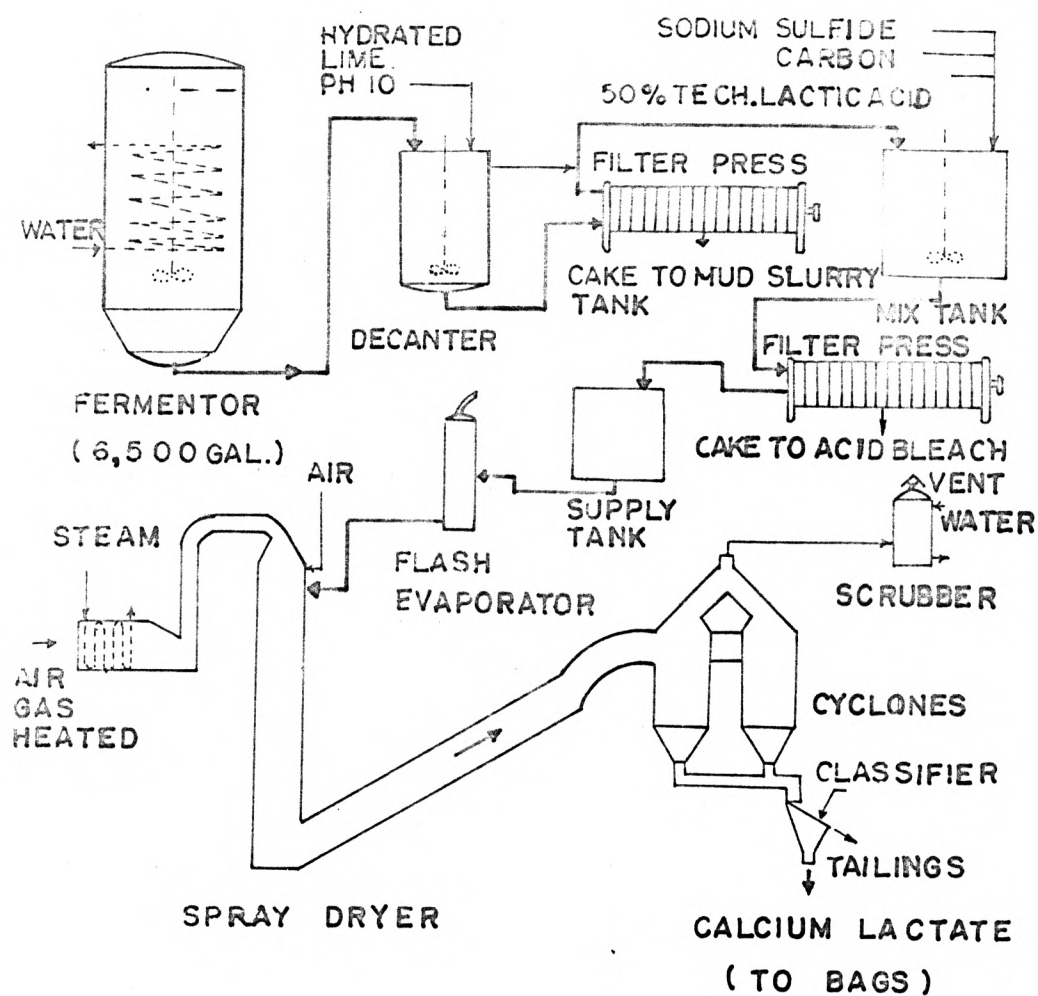
Fig.3. Flow Sheet for the Production of Calcium Lactate at the Hammond, Plant of American Maize-Products Co.

at 60 to 120°C. The vapors were passed through two condensers
in series. The temperature at the first condenser was kept
around 40 to 50°C and the second condenser around 0°C. The
product from the first condenser was 60 to 90% lactic acid
solution. The acid recovered from the second condenser was
very dilute. About 86.2% of the acid in the crude liquor could
be recovered from the first condenser.

Table V. Grades of lactic acid (16).

	Technical	Edible	Plastic	U. S. P.
Total acidity	44%	50%	50%	85%
Free acidity	40-42%	46-48%	47-49%	76-78%
Volatile acids	1-2%	1-2%	1-2%	2-3%
Ash	0.6-0.7%	0.4-0.5%	0.005-0.1%	0.05-0.1%
Carbonizable organic matters	present	present	none	none
Sulfates	present	trace	none	none
Chlorides	present	present	none	none
Color	yellow to brown	slight straw yellow	colorless	colorless
Iron	present	less than 3 p. p. m.	trace	trace
Copper	present	trace	trace	trace

Table VI. Price of lactic acid and some competing acids.

		Selling price per 100 lbs. comm. product dollars	Approx. price per 100 lbs. 100% acid dollars
Lactic acid	44%, technical	12.85	27.00
	50%, edible	20.86	41.70
	80%, edible	34.36	43.00
	50%, plastic	28.40	56.80
	80%, plastic	47.25	59.00
	85%, U. S. P.	85.00	100.00
Acetic acid	28%, commercial	4.80	17.20
	56%, commercial	8.25	14.70
	80%, commercial	10.45	13.10
	glacial, technical	10.00	10.00
	glacial, U. S. P.	13.00	13.00
Propionic acid	pure	14.75	14.75
Citric acid	U. S. P.	28.00	
Tartaric acid	N. F.	43.00	
Phosphoric acid	75%, food grade	5.60	7.50
	85%, N. F.	6.65	7.80

Source: Oil, Paint and Drug Reporter 183, No. 13 (April 1, 1963)

The sugar in the crude acid gave rise to traces of carbonizable substances in the product. The volatile acids were completely carried over to the product by this process.

(B) Recrystallization. Usually the acid had been recrystallized as the calcium salt. A small amount of water at 66°C was used to dissolve the calcium lactate crystals obtained from crude calcium lactate solution. After adding Norit activated carbon and filter aid to the solution, the slurry was filtered in a filter press. The filtrate was concentrated to 11.5° Bé and then sent to the crystallizer. The crystals were washed with several small portions of water and then sulfuric acid was added to convert them into lactic acid (13).

Another procedure made use of the zinc salt. Zinc lactate crystallizes more readily than other lactates. Calcium lactate solution reacted with zinc sulfate to form zinc lactate solution and calcium sulfate-gypsum-precipitate. Zinc lactate solution was filtered while warm giving a gypsum cake. The filtrate was concentrated by vacuum evaporation and the zinc lactate allowed to crystallize. Pure zinc lactate was obtained by repeated crystallizations.

Hydrogen sulfide was added to the zinc lactate to recover lactic acid. Alternately, lactic acid may be liberated by precipitating zinc sulfide with barium sulfide followed by the removal of barium sulfate precipitate with sulfuric acid (7).

(C) Extraction. Jenemann patented a process in which crude lactic acid, preferably a concentrated solution, was

extracted countercurrently with isopropyl ether. The isopropyl ether-lactic acid solution was then extracted countercurrently with fresh water in a second column. The aqueous solution from the second column was then concentrated by evaporation (19).

The acid thus obtained is free from ash but contains carbohydrate materials that are also extracted from the crude solution of lactic acid.

Extraction by isoamyl alcohol (3, 20, 21), amyl alcohol (3), nitroparaffins (22) and several other solvents (3, 21, 23) have been studied.

Ratchford studied the extraction of lactic acid from water solution by an amine-solvent mixture (24, 25). His study showed that tertiary amines especially triamyl and trioxyl amine were effective amines and that chloroform and various alcohols were suitable solvents for this process.

He extracted 8.7% aqueous lactic acid solution with triamyl amine-chloroform mixture. The organic layer was separated and lactic acid was recovered from it by a simple steam distillation in which the steam distilled off the chloroform and amine while the lactic acid remained in water solution.

$$CH_3CH(OH)COOH + R_3N \underset{steam}{\rightleftharpoons} CH_3CH(OH)COONHR_3$$

The amine served to improve the distribution of lactic acid favoring the chloroform layer over the aqueous layer.

Table VII. Extraction of 8.7% lactic acid at 25°C by solvent chloroform solutions of amines (24).

|	Acid in Solvent Phase %	Acid Remaining in Water Phase, % as Free Acid	C_W	K
Triamyl amine	74	22	0.27	2.7
Trioctyl amine	83.5	11	0.18	4.5

$K=C_s/C_w$; C_s, C_w are concentrations of acid in milliequivalents per ml. for solvent phase and water phase.

(D) Oxidation. The oxidizable substances in lactic acid have been removed by mildly oxidizing the crude liquor. Some reagents that have been used are: sodium or calcium hypochlorite, potassium permanganate, potassium chromate, nitric acid, hydrogen peroxide, chlorine and ozone. Hagg (26) patented a process in which he used nitric acid to purify lactic acid containing easily carbonizable matter. Lactic acid was heated with a few percent of strong nitric acid to a temperature above about 80°C. Then a few percent of activated carbon was added and the temperature maintained above 80°C to convert the remaining nitric acid to nitrogen oxides. The lactic acid was then separated from activated carbon by filtration.

(E) Precipitation of Heavy Metals and Sulfate Ion. Ordinarily iron and copper or heavy metals have been removed by adding suitable amounts of potassium ferrocyanide, hydrogen sulfide or sodium sulfide. Sulfate ion was removed by adding barium chloride.

(F) Esterification. In the presence of catalysts such as sulfuric acid, phosphoric acid, boric acid or p-toluene-sulfonic acid, lactic acid is easily esterified with methanol and ethyl alcohol.

$$CH_3CH(OH)COOH + ROH \xrightleftharpoons{\text{Catalyst}} CH_3CH(OH)COOR + H_2O$$
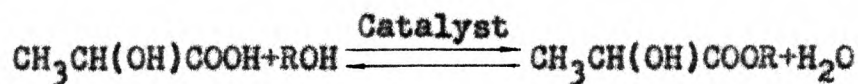
The esterification process was originally proposed by Hillringhaus (27) and was modified by Smith and Claborn (28), Weisberg and Stimpson (29), Wenker (30), Schopmeyer and Arnold (31) and Filachione and Fisher (32, 33).

According to the method of Smith and Claborn (28), 10 to 20 moles of methanol were added to 1 mole of dry calcium lactate. Undissolved precipitates were then filtered off. More than 1 mole of sulfuric acid was added. It liberated lactic acid and the excess sulfuric acid was employed as a catalyst for subsequent esterification. The mixture was refluxed for 4 to 8 hours to esterify lactic acid. After calcium sulfate was separated on a filter, methanol was stripped off under atmospheric pressure. Methyl lactate and water were distilled under vacuum. The distillate was then diluted 3 times and boiled to hydrolyze the methyl lactate. Pure water white lactic acid was obtained.

Weisberg and Stimpson patented a process for producing pure lactic acid from salts of lactic acid (29). Sulfuric acid in excess of that required for liberating lactic acid was added to a lactate. An alcohol in excess of the theoretical amount for the formation of an ester was then added and esterification

proceeded by refluxing for a suitable period. The ester was
distilled under vacuum. The ester remaining in the residue was
recovered by adding water to the residue and distilling it off
as a constant boiling mixture at 208 to 212°F, containing 30 to
35% ester. The pure lactic acid was obtained by hydrolyzing the
ester thus obtained. The yield was increased, compared to the
Smith and Claborn process, for this process recovered the ester
in the residue. About 10% of the total ester formed remained
in the residue, if not recovered. The authors claimed that the
time of hydrolysis was shortened considerably by adding about
15% by volume of lactic acid to the aqueous ester solution and
by hydrolyzing it under a pressure between about 15 to 100 psig.

Wenker's process (30) consisted of esterifying 70 to 85%
lactic acid with approximately 1½ moles methanol per mole of
lactic acid. A mineral acid was used as catalyst. A vapor
containing ester, methanol and water was delivered to the bottom
of a fractionation column. Methanol was stripped off. Ester
and water flowed to another kettle, where it underwent
hydrolysis. Methanol produced by hydrolysis passed through
the vapor line of this kettle to the bottom of the same column.
The methanol vapor was delivered from the top of the column to
a condenser. It was condensed and recycled to the esterification
reactor until almost all of the lactic acid in the crude liquor
was removed.

Schopmeyer and Arnold received a patent for continuous
esterification of lactic acid and regeneration of lactic acid by

continuous hydrolysis (31). Crude lactic acid and water were fed continuously to a kettle at such a rate as to keep a constant level and so as to keep the composition of the mixture at about 25 to 35% lactic acid, 10 to 20% alcohol, 30 to 40% methyl lactate and 10 to 20% water. Sulfuric acid was used as a catalyst. The reaction proceeded at approximately atmospheric pressure and at about the temperature of boiling water. The vapor formed by heating the mixture in the reactor contained alcohol, methyl lactate and water. Vapor was delivered to the middle portion of a fractionation column and methanol vapor was stripped and passed to a condenser on the top of the column. It was condensed and recycled to the reactor. At the same time, ester and water accumulated at the lower part of the column and the ester was hydrolyzed there by the heat supplied at the bottom of the column. Purified aqueous lactic acid was drawn off from the still continuously and concentrated to the desired concentration in a vacuum evaporator. The crude lactic acid could be of any concentration but ordinarily it was about 40 to 60% crude acid.

Filachione and Fisher patented a process (33) for recovering lactic acid by passing a stream of alcohol vapor countercurrently to an acidified fermentation liquor or a crude acid at temperatures between 50 and 135°C. Mineral acids were used as catalysts. In one of the claims made by them, the temperature was below 200°C instead of 50 to 135°C. The exit vapor contained alcohol, water and the ester. The ester was separated and hydrolyzed to lactic acid.

EXPERIMENTAL PROCEDURE

Purpose of This Research

One of the goals of this research was to find an efficient method of separating lactic acid from fermentation liquor. An efficient process should be simple and require very little equipment. The most tedious steps in the preparation of pure lactic acid, such things as filtrations, bleaches, precipitation of heavy metal ions etc. could be eliminated or reduced to a minimum by esterifying the acidified fermentation liquor without filtration of the calcium salt formed.

Chow reported in his thesis "Purification of Lactic Acid" (34) that the yield obtainable for a 7-hours run for this process was 40.75% and the maximum yield among 4-hours runs was 25.15%. The yields of this process might be improved by operating the reaction at a higher temperature and with less water present in the reactant mixture. A suitable solvent was necessary for these purposes and for the prevention of the formation of a lump of solid calcium phosphate. The coagulation of solid calcium phosphate made thorough mixing very difficult and resulted in overheating and poor temperature control. Lactic acid decomposes when it is overheated. The undesirable decomposition of lactic acid could be avoided by the introduction of a suitable solvent.

Finding a suitable solvent and some modification of the process were the goals for this research.

Materials Used

The lactic acid solution used was the 44% light technical grade (acidity 43.35%) furnished by the Clinton Corn Processing Company. The calcium hydroxide powder used was the analytical reagent grade, produced by the Mallinckrodt Chemical Company. Purity was 95.55% $Ca(OH)_2$. The orthophosphoric acid and glycerine were reagent grades, purchased from the Allied Chemical and Dye Corporation. The acidity of the orthophosphoric acid was determined to be 84.63%. Purified toluene and methanol were purchased from Fischer Scientific Company. Ethylene glycol was the regular grade, produced by Dow Chemical Company.

Equipment Used

The equipment used for the runs using ethylene glycol and glycerine solvents are shown in plate I, appendix. The first two runs with toluene were also run in the equipment shown in plate I. The flow sheet shown in plate II, appendix, was used for run numbers 4 and 5 using toluene solvent. The equipment in plate I consisted of a heated reactor flask with stirrer and a fractionating column unit. The reactor was one liter three neck Pyrex glass flask equipped with 24/40 and 34/45 standard taper ground glass joints. A stirrer passed through the center neck providing the mixing required. The stirrer was equipped with a mercury seal. The fractionating column was made of Pyrex glass, three inches outside diameter and three feet long. It was packed with ½ inch stoneware Raschig rings. The reboiler was a

one liter three necks Pyrex glass flask identical with the reactor. At the top of the column, a reflux splitter, which could be adjusted to three reflux ratios 3, 1, 1/3 was connected with 24/40 and 34/45 ground glass joints. The reflux ratio was fixed at 3 to 1 in this study. Three condensers with 24/40 ground glass joints were connected in series to condense all the vapor from the top of the column. Thermometers used to measure the temperatures at the reactor and at the top of the column were mercury in glass type with 10/30 standard taper ground glass joints. A thermocouple was used to measure the temperature of the reboiler. The connections between the reactor flask and the fractionating column were made with Teflon plastic tubing and glass tubing. Heat for the reactor and for the re- boiler was supplied by Glascol electric resistance heaters (140 watt for upper heater and 380 watt for lower heater at 115 volts). Variable transformers were used to adjust the heat inputs.
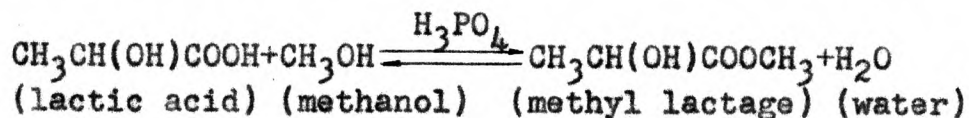
The equipment shown in plate II consisted of a reactor and three fractionating column units. The reactor and the first fractionating unit were the same as that described above except that the reboiler had an outlet to let the upper part of the contents overflow to the middle section of column 7. Columns 7 and 11 were made of Pyrex glass, 3 inches outside diameter, 2 feet high and were packed with ½ inch stoneware Berl saddles. They were connected with reboilers and a cross. The connections were made with 24/40 ground glass joints. The decanter under

the cross was 3 inches outside diameter, 5 inches high, and made
also of Pyrex glass. A cross which had 4-24/40 ground glass
joints connected the condenser 10, decantor 9 and the tops of
the columns 7 and 11. The decanter had two 3/8" O. D. glass
outlets which were joined to columns 7 and 11 by Teflon and glass
tubings. The reboilers 8 and 12 were also Pyrex glass three
necks one liter flasks. They had 24/40 and 34/45 ground glass
joints. A 3/8" O. D. glass tubing outlet at reboiler 12
permitted the toluene accumulating to be pumped back to the
reactor. The heat required for the reactor and three fraction-
ating columns was supplied by Glascol electric resistance
heaters. Variable transformers were used to adjust the heat
input required.

Description of the Process

To simulate the crude liquor obtained from lactic acid
fermentation, 400 grams of distilled water and 38.8 grams of
calcium hydroxide were added to 208 grams of light technical
grade 44% lactic acid. The calcium lactate solution thus
obtained was of concentration 16.85%. Some 85% orthophosphoric
acid was then added to the solution. Part of the orthophosphoric
acid was employed as an acidifying agent to liberate lactic
acid from the calcium lactate. The excess of orthophosphoric
acid was utilized as the catalyst for the subsequent esteri-
fication. Solvents, toluene, ethylene glycol and glycerine
were used to get a suspension of calcium phosphate. The solvent

both dissolved the lactic acid liberated and avoided the formation of a lump of solid calcium phosphate. Methanol was used to esterify lactic acid. The esterification reaction follows:

$$CH_3CH(OH)COOH + CH_3OH \xrightleftharpoons{H_3PO_4} CH_3CH(OH)COOCH_3 + H_2O$$
(lactic acid) (methanol) (methyl lactage) (water)

Methyl lactate forms a minimum boiling azeotrope with water. The vapor mixture of methyl lactate, methanol and water was formed in the reactor and led to a fractionation column. The removal of methyl lactate formed by esterification shifted the equilibrium toward the formation of methyl lactate. Since methanol is the low boiler, it was distilled overhead and methyl lactate and water collected in the reboiler of the column. The methyl lactate hydrolyzed to lactic acid in the reboiler and the methanol formed distilled to the top of the column. The product was a purified aqueous solution of lactic acid.

Procedure (A). Most of the experiments (runs 6 through 20) were carried out as described below.

Four hundred grams of distilled water, 38.8 grams of calcium hydroxide and 208 grams of 44% lactic acid were mixed to obtain a solution similar to the product of lactic acid fermentation. The reaction can be represented by the following equation:

$$2\ CH_3CH(OH)COOH + Ca(OH)_2 \longrightarrow Ca(CH_3CH(OH)COO)_2 + 2\ H_2O$$

Orthophosphoric acid, 85%, was added in excess to liberate lactic acid.

$$3\ Ca(CH_3CH(OH)COO)_2 + 2\ H_3PO_4 \longrightarrow Ca_3(PO_4)_2 \downarrow + 6\ CH_3CH(OH)COOH$$

Then, a suitable solvent (ethylene glycol or glycerine) was added. This mixture was heated in the reactor to evaporate the water. This was called the concentration period. The lower Glascol heater was kept at 110 volts throughout the concentration and reaction periods, while the upper heater was turned on at 70 volts during the first part of the concentration period and then turned off. The temperature of the reactor was recorded from time to time. When the temperature of the reactor reached a temperature about 10°C. higher than the temperature chosen for the esterification, methanol was introduced slowly into the reactor. The recycle methanol stopcock was opened to allow it to return to the reactor. The flow rate was so controlled that the temperature in the reactor was kept at the preselected temperature. The esterification was catalyzed by the excess orthophosphoric acid. When about 50 cc of methanol was left at the feeder, the heater of the reboiler was turned on. The vapor from the reactor consisted of methanol, methyl lactate and water. This vapor was introduced as feed to the middle section of the fractionating column. There the methanol distilled up the column. Part of the methanol was refluxed to the column, the other part was recycled to the reactor. The reflux ratio of the column was kept at 3 to 1 all the time during this study. After all the methanol was fed to the reactor, the temperature of the reactor was controlled by changing the rate of methanol recycled to the reactor. The amount of methanol recycled was, in turn, controlled by the heat input to the reboiler. During

the concentration and reaction steps the stirrer kept the reactor contents well mixed. Methyl lactate and water accumulated at the lower part of the column and in the reboiler. Methyl lactate was hydrolyzed there by the heat supplied from the reboiler. The reaction occurring at the reactor was:

$$CH_3CH(OH)COOH + CH_3OH \xrightleftharpoons{H_3PO_4} CH_3CH(OH)COOCH_3 + H_2O$$
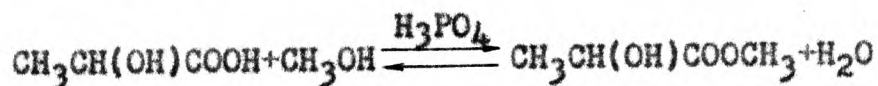
The reaction occurring at the lower part of the column and the reboiler was:

$$CH_3CH(OH)COOCH_3 + H_2O \rightleftharpoons CH_3CH(OH)COOH + CH_3OH$$

Procedure (B). The process was modified for runs 1 and 2 on account of the formation of a minimum boiling azeotrope between toluene and water. Simulated fermentation liquor was formed as before. It was acidified with 85% orthophosphoric acid. Then it was concentrated in the reactor by evaporation. After the temperature of the reactor reached 103°C., toluene was introduced to the reactor to help further concentration. Toluene and water formed an azeotrope and this was fractionated in the column. Part of the azeotrope went overhead and was recycled to the reactor. When the temperature of the reactor reached 105°C. methanol was fed to the reactor. The flow rate of the methanol was so controlled that the temperature of the reactor was maintained within the range of the preselected esterification temperature. After the total amount of methanol was fed to the system, the temperature of the reactor was controlled by adjusting the voltage input for the Glascol heater

which supplied heat to the reboiler. The rest of the operation was essentially the same as procedure (A). The product obtained in the still separated into two layers. The upper layer was the toluene layer; the lower layer was the water layer. Lactic acid in the water layer was titrated and reported as recovered lactic acid.

Procedure (C). The equipment shown on plate II was used for this procedure. Most of the procedure was the same as (B), but toluene was recycled through line 13 instead of through cock 4. In this process, toluene and part of the water overflowed from reboiler 6 to the middle section of packed column 7. Water accumulated at reboiler 8. While toluene and a small part of the water were vaporized and condensed by condenser 10. The condensate accumulated and separated into two layers in the decantor 9. The water layer refluxed to column 7, while the toluene layer overflowed to column 11. Dry toluene accumulated in reboiler 12 and was pumped back to reactor 1. The flow rate was so controlled that the level in the reactor was kept constant during the esterification.

Analytical Methods

To compute the percent recovery of lactic acid, determinations of free acidities and total acidities were made according to the titrimetric method proposed by Fetzer and Jones (35). These determinations were made on crude lactic acid and recovered pure lactic acid solutions.

According to their method, a suitable quantity of lactic acid was weighed in a weighing bottle. The acid was transferred to a 500 ml. Erlenmeyer flask using 75 to 100 ml. of distilled water. An additional 100 ml. of distilled water and 9 drops of phenolphthalein indicater were added. A buret was filled with 0.5 N NaOH solution to the zero mark. The sample was titrated with 0.5N NaOH solution to a pale pink color. The NaOH solution was added slowly and the sample solution was shaken vigorously to avoid over neutralization. A reading was taken for the calculation of free acidity. Then an excess of 0.5N NaOH solution was added until a total of 50 ml. had been used. The flask was shaken vigorously and allowed to stand for 20 to 30 minutes. This sample was then back titrated with 0.5N H_2SO_4 solution to a faint pink color. The reading was recorded for the total acidity calculation. In this experiment the actual normality of standard NaOH and H_2SO_4 solutions were 0.5042N and 0.5041N respectively. The calculation for the free acidity and total acidity were as follows:

Free Lactic Acid =

$$\frac{(\text{ml. of 0.5042N alkali solution}) \times 0.04542}{\text{sample weight}} \times 100\%$$

Total Lactic Acid =

$$\frac{(50.01 - \text{ml. of 0.5041N acid solution}) \times 0.04541}{\text{sample weight}} \times 100\%$$

The ash content of the recovered acid solutions was also determined as an indication of their purities. A crucible of 50 ml. capacity was heated to redness and weighted after

cooling. Approximately 35 grams of the sample was weighed in the crucible to the nearest 0.0001 grams. The crucible was heated gently at first in a muffle furnace (below a temperature of 400°F) and then the temperature was raised to 1600°F and maintained at this temperature until the carbonaceous substance formed disappeared. The crucible was weighed after cooling briefly. The heating was repeated until a constant weight was obtained. The calculation of ash content was as follows:

Ash Content =

$$\frac{(\text{weight of crucible} + \text{ash}) - (\text{weight of crucible})}{\text{weight of sample}} \times 100\%$$

DISCUSSION OF RESULTS

Solvents

In runs 1, 2, 4 and 5, toluene was used as a solvent. Procedure (B) was followed in runs 1 and 2. For runs 4 and 5, procedure (C) was adopted. The total times (time of concentration plus time of esterification) required were run 1-2 hours 25 minutes, run 2-3 hours 19 minutes, run 4-2 hours 41 minutes and run 5-4 hours 34 minutes. The maximum yield obtained among these four runs was that of run 2-19.26%. The reaction temperature was 76 $\pm$ 6°C. To speed up the reaction rate, the temperature of the reaction should be raised.

Ethylene glycol was then chosen as a solvent, because it had a higher boiling point. Runs 6 through 9 were made by procedure (A). Run 8 gave the best result among the four runs. The yield was 38.6%. The concentration time was 1 hour 14 minutes and the time of esterification was 2 hours 19 minutes. Reaction temperature was 118 $\pm$ 10°C. Some ethylene glycol was distilled over and mixed with pure lactic acid, because its vapor pressure was fairly high.

Glycerine, which has a lower vapor pressure was then tried for runs 10 through 20. These runs were also made by procedure (A). The maximum yield obtained was 84.5% in run 18. This required 1 hour and 29 minutes for concentration and 2 hours 30 minutes for esterification. The reaction temperature was the

Table VIII. Experimental results.

Run No.	Feed 44% lactic acid, gms	Ca(OH)$_2$ gms	H$_2$O gms	85% H$_3$PO$_4$ gms	CH$_3$OH gms	Solvent gms	Total gms	Pure lactic acid, gms	Excess 85% H$_3$PO$_4$, gms	Product Product gms	Residue gms	Total gms	Loss gms	Pure lactic acid, gms	Ash %	Operating Variables Loss %	Lactic acid recovered, %	Concentration time	Temp. at end of concn., °C	Esterification time	Esterification temp., °C
1	208.0	38.8	400.0	40.0	100.0	Toluene 300.0	1086.8	90.1	1.4	u.l 284.3 l.l 556.1	191.8	1032.2	54.6	12.8	0.0383	5.03	14.20	1 hr. 7 min. + 48 min.	106	30 min.	105±3
2	208.0	38.8	400.0	40.0	100.0	Toluene 200.0	986.8	90.1	1.4	u.l 131.2 l.l 586.6	226.1	943.9	42.9	17.4	0.0304	4.35	19.26	1 hr. 31 min. + 18 min.	105	1 hr. 30 min.	76±6
4	208.0	38.8	400.0	40.0	100.0	Toluene 2800.0	3586.8	90.1	1.4	u.l 797.8 r. 416.8 l.l. 613.8 s. 1651.1		3479.5	107.3	9.16	0.0241	2.99	10.17	1 hr. 14 min. + 20 min.	102.5	1 hr. 7 min.	97±7
5	208.0	38.8	400.0	40.0	100.0	Toluene 3032.9	3819.7	90.1	1.4	u.l 1240.5 r. 270.8 l.l. 642.4 s. 1606.7		3760.5	59.3	16.1	0.0260	1.55	17.80	1 hr. 48 min. + 16 min.	96.5	2 hr. 30 min.	95±11
6	208.0	38.8	400.0	40.0	100.0	Glycol 300.0	1086.8	90.1	1.4	654.7	410.3	1065.0	21.8	16.9	0.0418	2.01	18.80	1 hr. 24 min.	111	1 hr. 30 min.	120±12
7	208.0	38.8	400.0	40.0	100.0	Glycol 100.0	886.8	90.1	1.4	601.4	265.9	867.3	19.5	16.0	0.0328	2.20	17.72	1 hr. 21 min.	131	1 hr. 1 min.	126±10
8	208.0	38.8	400.0	40.0	200.0	Glycol 100.0	986.8	90.1	1.4	812.6	159.7	972.3	14.5	34.8	0.0300	1.47	38.6	1 hr. 14 min.	106.5	2 hr. 19 min.	118±10
9	208.0	38.8	400.0	40.0	200.0	Glycol 100.0	986.8	90.1	1.4	751.2	191.4	942.6	44.2	34.8	0.00924	4.48	38.6	1 hr. 16 min.	110	3 hr. 23 min.	120±10
10	208.0	38.8	400.0	40.0	200.0	Glycerine 100.0	986.8	90.1	1.4	691.6	276.6	968.2	18.6	25.4	0.01162	1.88	28.2	1 hr. 16 min.	103.5	2 hr. 30 min.	125±10
11	208.0	38.8	400.0	40.0	200.0	Glycerine 100.0	986.8	90.1	1.4	748.1	193.7	941.8	45.0	35.1	0.00928	4.56	39.0	1 hr. 16 min.	102	4 hr. 30 min.	125±10
12	208.0	38.8	400.0	40.0	200.0	Glycerine 100.0	986.8	90.1	1.4	689.5	263.4	952.9	33.9	33.6	0.00807	3.44	37.3	1 hr. 13 min.	107.5	2 hr. 30 min.	125±13
13	208.0	38.8	400.0	40.0	200.0	Glycerine 100.0	986.8	90.1	1.4	680.2	266.4	946.6	40.2	31.1	0.0150	4.08	34.5	1 hr. 22 min.	125	2 hr. 30 min.	125±6
14	208.0	38.8	400.0	40.0	200.0	Glycerine 100.0	986.8	90.1	1.4	695.3	238.0	933.3	53.5	31.9	0.0104	5.41	35.4	1 hr. 33 min.	165	58 min.	150±10
15	208.0	38.8	400.0	40.0	200.0	Glycerine 100.0	986.8	90.1	1.4	766.6	186.8	953.4	33.4	42.1	0.0294	3.38	46.8	1 hr. 20 min.	130	4 hr. 30 min.	135±8
16	208.0	38.8	400.0	50.0	200.0	Glycerine 100.0	996.8	90.1	11.4	727.3	201.0	928.3	68.5	36.9	0.0155	6.87	40.9	1 hr. 24 min.	145	2 hr. 30 min.	140±8
17	208.0	38.8	400.0	50.0	200.0	Glycerine 200.0	1096.8	90.1	11.4	810.6	230.7	1041.3	55.5	65.6	0.0157	5.07	72.9	1 hr. 29 min.	147	2 hr. 30 min.	142±8
18	208.0	38.8	400.0	50.0	200.0	Glycerine 300.0	1196.8	90.1	11.4	824.5	297.6	1122.1	74.7	76.2	0.0138	6.82	84.5	1 hr. 29 min.	146	2 hr. 30 min.	157±7
19	208.0	38.8	400.0	50.0	200.0	Glycerine 200.0	1096.8	90.1	11.4	726.0	350.8	1076.8	20.0	27.4	0.0291	1.83	30.4	1 hr. 18 min.	131	2 hr. 33 min.	122±7
20	208.0	38.8	400.0	50.0	200.0	Glycerine 300.0	1196.8	90.1	11.4	759.3	424.3	1183.6	13.2	20.9	0.0191	1.21	23.2	1 hr. 21 min.	131	2 hr. 30 min.	122±7

Notes: u.l. = upper layer of the product; l.l. = lower layer of the product; r. = residue in the reactor; s. = solvent in the system except that in upper layer of the product; 1 hr. 7 min. + 48 min. = concentration time without adding toluene, 1 hr. 7 min.; another 48 minutes concentration time with toluene as entrainment agent.

highest of all runs--157 $\pm$ 7°C. Less carbon was formed when glycerine was used as a solvent than when ethylene glycol was used. No carbon was formed when 200 or 300 grams of glycerine were used.

Losses of Materials

The maximum loss of material occurred in run 4, where 107.3 grams of materials, or 2.99%, disappeared. The maximum percentage loss occurred in run 16, 6.87%. Next was a 6.82% loss for run 18. The temperature of the reaction for runs 16 and 18 was 140 $\pm$ 8°C. and 157 $\pm$ 7°C. respectively. The material lost was mainly methanol, which has a very high vapor pressure at these temperatures. The methanol may have escaped through the overhead condenser. It was also observed in several runs, such as runs 14, 16 and 18, that vapors escaped through the mercury seal for the stirrer due to pressure surges. This was probably due to friction in the small vapor line from the re-actor to the fractionating column.

Yields

Yields of purified lactic acid ranged from 10.2% to 84.5%. For runs 10 through 20, where glycerine was used as a solvent, the yields ranged from 23.2% to 84.5%. The contributions of the different factors to the variation of yields will be discussed later.

The Effect of Temperature

The temperature of the reaction had a most pronounced effect upon the yields obtained. Run 11 and run 15 had the same raw materials, and the same time of esterification, 4 hours 30 minutes, though they had 4 minutes difference in the concentration step, 1 hour 16 minutes and 1 hour 20 minutes respectively. The main difference was in the temperatures of esterification. Run 11 was made at a temperature of $125 \pm 10°C$. and run 15 at $135 \pm 8°C$. This changed the yield from 39.0% to 46.8%. Runs 17 and 19 also had the same conditions, the same raw materials and the same time of esterification, although the time of concentration was 11 minutes different, 1 hour 29 minutes and 1 hour 18 minutes respectively. The difference in yields, 72.9% in run 17 and 30.4% in run 19, was due to the different temperatures of esterification, $142 \pm 8°C$. for run 17 and $122 \pm 7°C$. for run 19. Another example was found between runs 18 and 20. Run 20 had a temperature of reaction of $122 \pm 7°C$. and the yield obtained was 23.2%. Run 18 had a temperature of reaction of $157 \pm 7°C$. and the yield was 84.5%. This is a tremendous increase in yield caused by an increase of 35°C.

Effect of Time of Run

Runs 10 and 11 showed that an increase in the time of esterification resulted in an increase in the yield. These had the same raw materials, the same time of concentration, 1 hour

16 minutes, and the same reaction temperature 125 ± 10°C. The times of esterification were 2 hours 30 minutes for run 10, and 4 hours 30 minutes for run 11. The yield for run 10 was 28.2%, while that for run 11 was 39.0%.

The Effect of Quantity of Solvent Used

The quantity of solvent used gave conflicting results. Different quantities of solvent were used in runs 19 and 20. They had similar conditions, but 200 grams of glycerine were used for run 19 and 300 grams of glycerine in run 20. The yields were 30.4% for run 19 and 23.2% for run 20. On the other hand, run 16 used 100 grams of glycerine and run 17, 200 grams of glycerine, the yield of the second run was higher than that of the first-40.9% for run 16 and 72.9% for run 17.

It might be supposed that the increase in contact time between methanol and lactic acid due to the deeper liquid head would increase the amount of esterification. On the other hand, the lower concentration of the reactants in the larger quantity of solvent might reduce the rate of esterification. Perhaps there is an optimum quantity of solvent to use for this size flask.

Purity of the Product

The ash content of the products were determined. They were used as an index of purity. Ash content ranged from

0.00807% to 0.0418%. Products were straw yellow and needed decolorization by carbon bleaches if a colorless product was desired.

Summary of Results

Glycerine was found to be the most efficient solvent in our process. Its high boiling point gave us convenience in operation. The simplest procedure (A) could be used. The higher reaction temperatures desired were obtained without the formation of char, the result of overheating the reactants.

Using less solvent would give us higher concentrations of reactants and higher yield would be expected, an extremely small amount of solvent gave a smaller yield than a moderate amount of solvent. This resulted from the small contact time between methanol and lactic acid in the solvent due to a smaller liquid depth.

The process gave a favorable yield if it took place at a temperature over 140°C. But the extremely high vapor pressure of methanol at these temperatures induced leakage of vapor through the mercury seal due to pressure surges. Another loss occurred at the condenser because of incomplete condensation of methanol vapor. The high vapor pressure of methanol was reflected in a fairly large temperature fluctuation for the reaction. To avoid unnecessary loss of materials through the mercury seal and the condenser, the methanol recycle rate should not be too large and should not be changed suddenly. The time

lag following a change of recycle rate made temperature control very difficult.

Although the purities obtained were good, concentration of the product would boost the ash content. If very low ash content in the final product was desired, lower ash contents than attained here would be necessary.

RECOMMENDATIONS

The experience obtained in this research suggests that it may be desirable to perform the concentration and esterification in different sized flasks. If a total of about 1,000 grams of raw material are to be processed, a flask of about 1.5 to 2 l. capacity should be used in the concentration step. The product of the concentration, now about 300 grams, should be transferred to a 0.5 l. flask for esterification. To simplify the step involved, a reactor shaped like that shown in Figure 4 is recommended. This reactor gives a fairly high liquid depth after the concentration and hence, a higher yield is expected.

The control of the recycle methanol rate is very critical. Any variation affects the temperature in the reactor. It is not satisfactory to attempt to control this by means of the reboiler heat control, because there is too much time lag in the operation of the fractionating column. To reduce this lag, accumulator tank shown in Figure 5 is recommended. In operation, valve W should be fully open. Methanol flows through valve W to the reactor. If a decrease of temperature is desired, the voltage of the transformer for the heater of the reboiler is stepped up. Valve V is opened slightly to give an immediate reduction of temperature. When the response of the heat input is felt from the rotameter, valve V should be throttled. The voltage should be so changed that the valve V can be closed in usual operation. If an increase of temperature is desired, the voltage at the heater of the reboiler should be stepped

down. Valve W can be throttled slightly to give an immediate
increase in temperature. When conditions return to normal, valve
W should be fully open. The overflow line O. L. is required for
smooth operation; it vents the tubing to the reactor.

To increase the purity, a cyclone should be added between
the reactor and the fractionating column. The liquid accumulat-
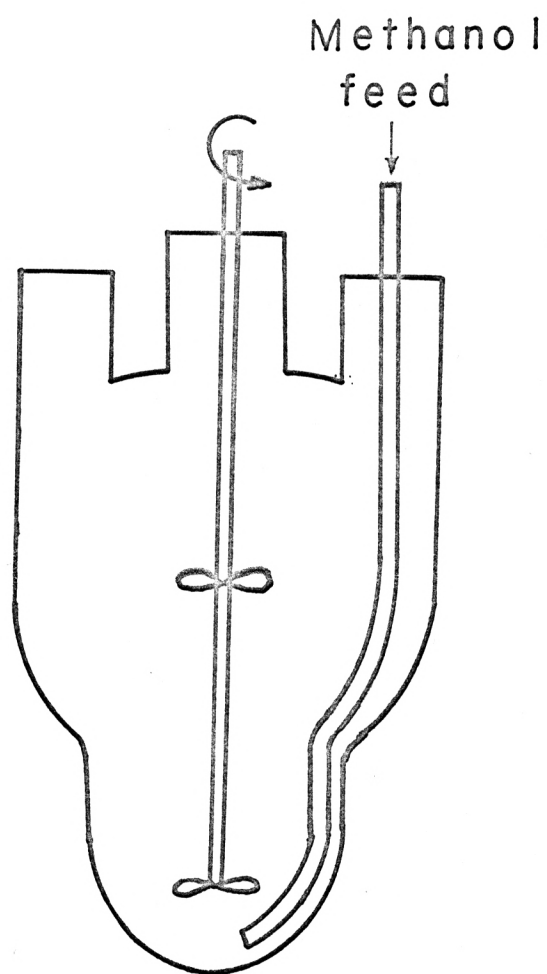ing in the cyclone would be recycled to the reactor.

Methanol
feed

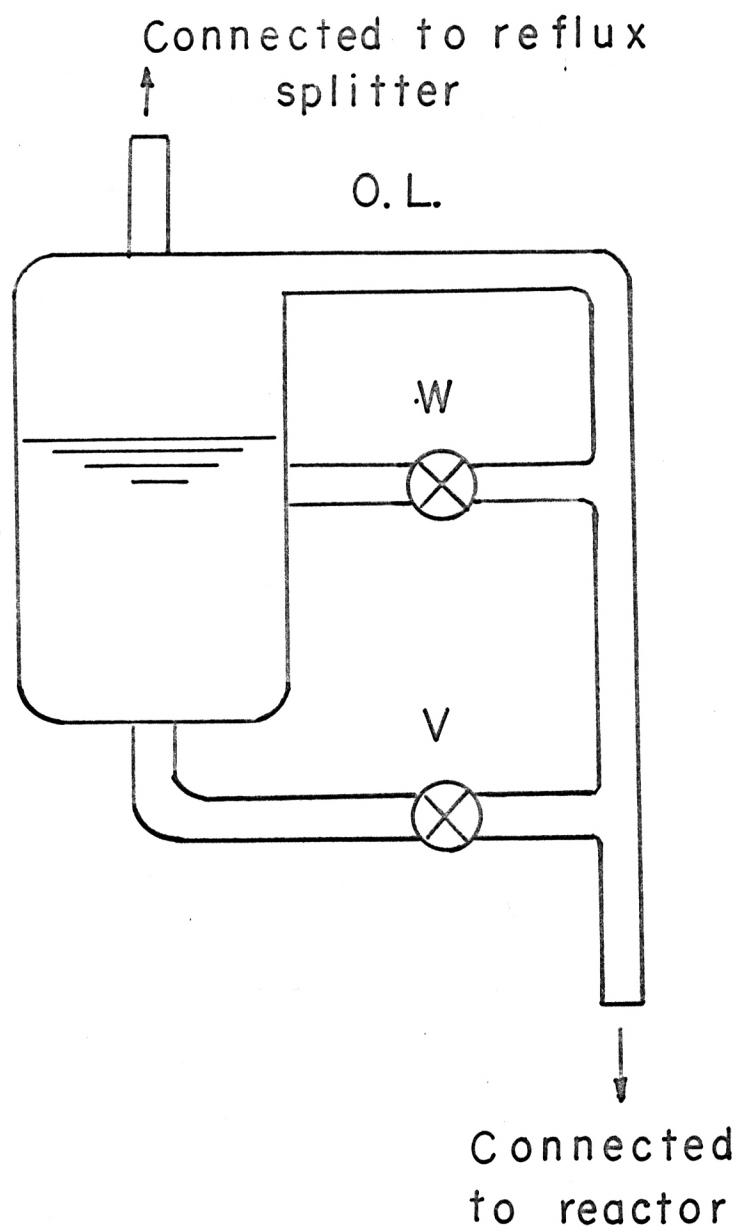Fig.4. Improved reactor

Connected to reflux
splitter

O. L.

W

V

Fig. 5. Accumulator tank

Connected
to reactor

ACKNOWLEDGEMENTS

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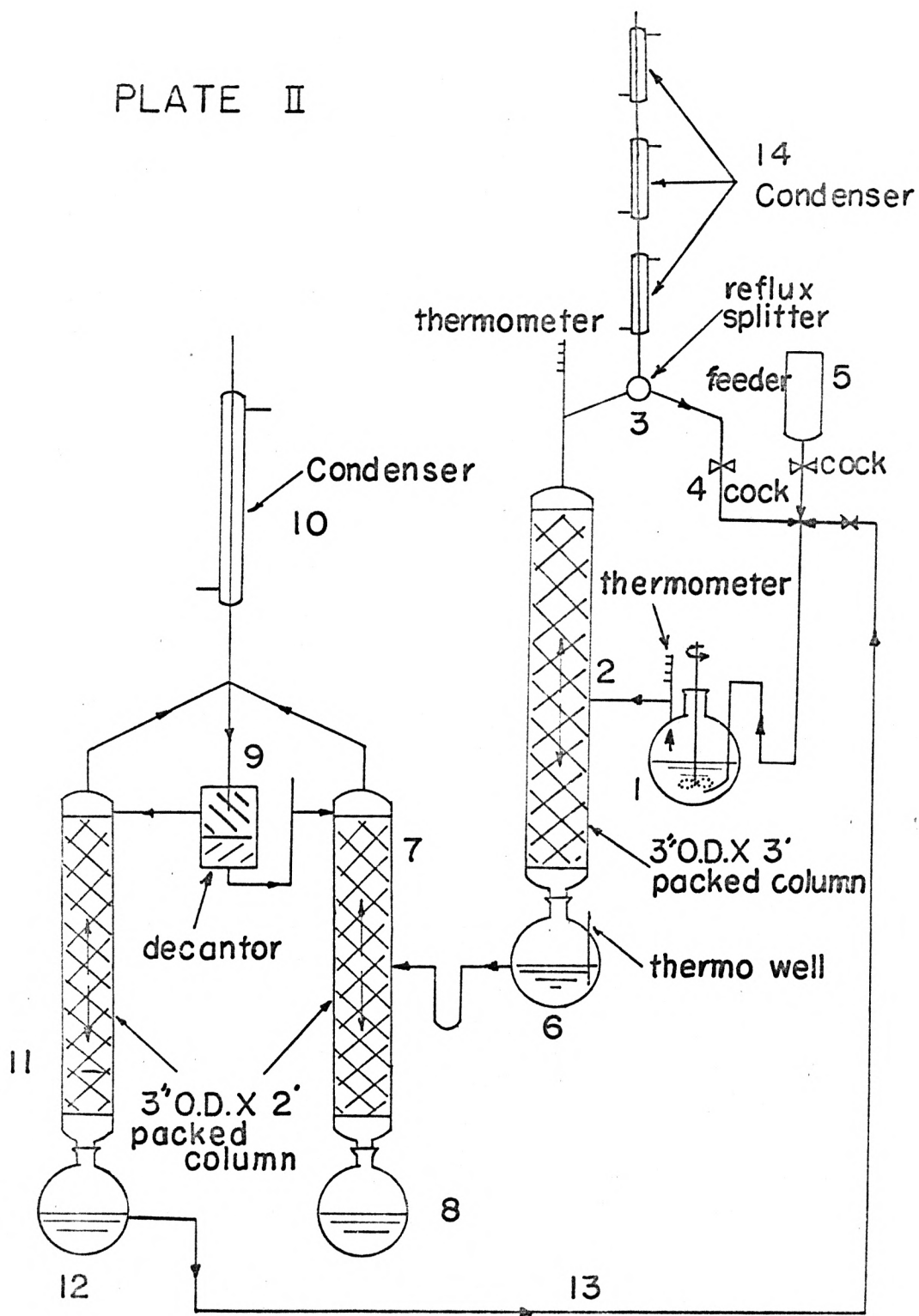   Lactic Acid, Analytical Chemistry, 24, 835 (1952).

APPENDIX

EXPLANATION OF PLATE I

Photograph of the Equipment

for Procedures (A) and (B)

PLATE I

EXPLANATION OF PLATE II

Flowsheet

for Procedure (C)

PLATE II

SEPARATION OF LACTIC ACID

by

CHAO-HSIUNG TSAI

B. S., National Taiwan University, 1958

AN ABSTRACT OF

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

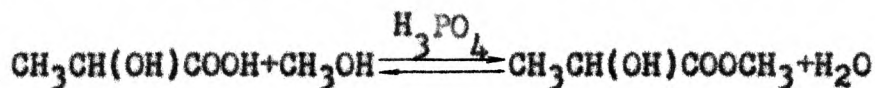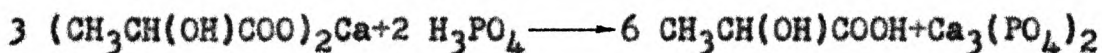KANSAS STATE UNIVERSITY

Manhattan, Kansas

1963

ABSTRACT

The cost of 44% crude technical lactic acid is about 27¢ per pound of 100% acid while the purified 85% U. S. P. grade costs about $1.00 per pound of 100% acid. This big difference in prices comes from the difficulty of purification. It is clear that by simplifying the process of purification, the cost of the high purity acid will be reduced, thus stimulating its industrial usage and production. The present investigation is aimed at removing the steps of filtration, crystallization of calcium lactate, precipitation of heavy metals, and oxidation of carbonizable substances.

Orthophosphoric acid was added to fermentation liquor in excess of the amount required to liberate lactic acid. A suitable solvent was used to obtain a suspension of calcium phosphate and to dissolve the liberated acid in the solution. This suspension was concentrated by evaporation until most of the water was removed. Then methanol was introduced to the reactor where the esterification of lactic acid proceeded employing excess orthophosphoric acid as catalyst. Vapor, consisting of methanol, methyl lactate and water was evaporated and introduced into the middle section of a fractionating column. This was fractionated in the column. The methanol was withdrawn from the top, condensed and recycled to the reactor for further esterification. Methyl lactate and water accumulated in the reboiler, where hydrolysis occurred

liberating the methanol and leaving a solution of lactic acid and water. The reactions involved in this process were:

In the reactor:

$$3 \ (CH_3CH(OH)COO)_2Ca + 2 \ H_3PO_4 \longrightarrow 6 \ CH_3CH(OH)COOH + Ca_3(PO_4)_2$$

$$CH_3CH(OH)COOH + CH_3OH \underset{}{\overset{H_3PO_4}{\rightleftarrows}} CH_3CH(OH)COOCH_3 + H_2O$$

In the lower part of the column and in the reboiler:

$$CH_3CH(OH)COOCH_3 + H_2O \rightleftarrows CH_3CH(OH)COOH + CH_3OH$$

Toluene, ethylene glycol and glycerine were used as solvents in this study. Some modifications in the process were made to utilize toluene as solvent. Without these solvents, it was impossible to increase the temperature sufficiently for a satisfactory reaction rate and it was difficult to remove water without the coagulation of calcium phosphate. The coagulation made mixing difficult and there was some decomposition due to overheating.

The result of the investigation showed that much improvement was made by using glycerine as solvent and by concentration of the suspension before esterification. The maximum yield was 84.5% and the total time required was 3 hours 59 minutes. The best that could be done without extra solvents and without preconcentration was 25.2% in a total time of 4 hours and 40.8% in 7 hours (34).