

potassium nitrate were more spherical and uniformly shaped than those obtained with the 2-4-12 (2-10-15) mixed fertilizer containing potassium chloride (Figure 12). The 5-4-12 (5-10-15) mixed fertilizer also gave more cohesive, less porous, and tougher granules.

The granule product in both mixtures was relatively more homogeneous than

reported in the literature since the raw materials used in this study were of finer mesh size.

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FERTILIZER TECHNOLOGY

A One-Step Continuous Quick-Curing Triple Superphosphate Process Employing Rod Mill Grinding

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An investigation was undertaken to determine the feasibility of a one-step quick-curing continuous process for the manufacture of triple superphosphate. Bench-scale work was carried out in a 1-quart, laboratory ball mill made of stainless steel. The results from this preliminary work indicated that quick-curing triple superphosphate of high conversion could be produced. The process was investigated on pilot-plant scale with successful operation. Completely cured powdered triple superphosphate was obtained within 1 hour.

THE ADVANTAGES of a quick-curing continuous superphosphate process include the following: the product can be shipped directly, thus reducing the required storage facilities and process inventory; operating conditions in the mixing step can be chosen with more flexibility; control of the process can be essentially automatic; uncertainty as to production rates can be eliminated to some extent because a finished product can be produced in a matter of hours, instead of weeks as required by the storage curing process; and there is a possibility of lower operating labor and maintenance requirements and elimination of a final crushing and screening step since finely ground products can be obtained directly.

Previous Work

Many processes (3, 5, 9, 12) have been tried for quick-curing of triple superphosphate. None of these processes has been able to eliminate curing time entirely without loss of phosphorus availability. In some processes, both drying and storage curing are employed to shorten the period of curing. A quick-curing process is therefore desirable in which a minimum amount of phosphoric acid is needed to convert a maximum amount of rock into available form without curing. The present paper

discusses an investigation of such a process.

The development of a quick-curing, one-step process for normal superphosphate was carried out by Rounsley and Boylan (74) and Martinez (8), by grinding and drying in a single piece of equipment. This process was extended to the manufacture of triple superphosphate. Essentially the same laboratory and pilot plant equipment were used.

Process Variables

The important process variables which effect the reaction stage and curing stage of the process are acid concentration, temperature, acidulation ratio (acidulation ratio as used here is the weight ratio of acid P_2O_5 to rock P_2O_5), and time. The effects of these variables using grinding in a laboratory ball mill and a pilot plant rod mill were investigated.

The effect of acid concentration is the most important process variable. An acid concentration of about 70% H_3PO_4 has been found most suitable, considering the physical properties of the mixture during the process and the degree of completion of reaction. Higher acid concentrations result in poor conversion, probably due to excessive side reactions. Very low acid concentrations result in

slow reaction and incomplete curing with a resulting product of high moisture and free acid content.

Temperature is also an important process variable. Its effect interferes with acid concentration because the reaction is exothermic. Acid concentrations above 75% H_3PO_4 increase the rate of reaction, and an excessive amount of heat is liberated within a short time in the first stage of the reaction. Temperatures above 284° F. may decompose the monocalcium phosphate into unavailable pyrophosphate (17). Rapid rise in temperature of the freshly acidulated mass tends to drive off water, increasing the concentration of the acid. The increased concentration means further increase in reaction rate, and hence higher temperature of the mixture. Thus a balance is required between the temperature and the acid concentration such that optimum conditions are obtained in the first stage of the reaction. Various workers (2-4, 6, 15) have suggested limiting temperatures in the range of 150° to 302° F.

Acidulation ratio is less important as a process variable than as an economic factor. An acidulation ratio of 2.0 is the theoretical minimum based on stoichiometry. Generally, it is necessary to use an acidulation ratio greater than theoretical due to the loss of acid consumed by impurities and side reactions.

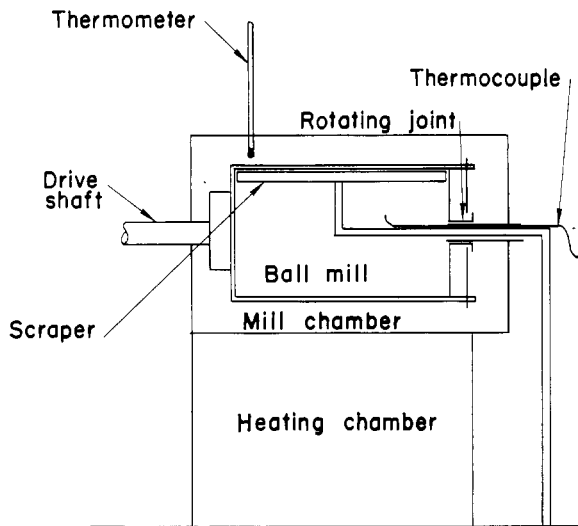


Figure 1. Cross section of ball mill and heating unit

Grinding during reaction is a new process variable introduced in this investigation. The effect of grinding the rock before acidulation has been shown to be beneficial (7, 10, 11), and rocks of porous structure can be benefited by preacidulation grinding. Rounsley (13) studied the effect of grinding during and after the acidulation of rock phosphate with sulfuric acid. The results showed considerable increase in the conversion. The process of curing is assumed to take place by the diffusion of the free acid into the pores of the unreacted rock particles. The grinding action continuously makes available new unreacted rock particle surfaces.

Time is a process variable closely associated with other variables such as acid concentration, acidulation ratio, and temperature. Higher acidulation ratios and lower concentrations introduce large amounts of excess water and require more curing time for specified final moisture and free acid contents in the product. Use of lower temperatures would mean lower drying rates, slower reaction, and longer process time. Thus selection of acid concentration, temperature, acidulation ratio, drying rate, and final product specifications, in effect, sets the time of reac-

tion. Lower drying rates are preferable to avoid side reactions and achieve complete curing.

Bench-Scale Investigation

Bench-scale experiments were carried out in a setup similar to that used by Rounsley and Boylan (14). Initial difficulties were experienced as a result of stickiness of the freshly acidulated mass. Larger steel balls, 1.5 inches in diameter, and a continuous scraper were employed to eliminate this problem.

The phosphate rock used was Florida pebble rock of the composition and size analyses given in Table I. Analytical grade phosphoric acid was used for the bench-scale work.

Phosphate rock and phosphoric acid for the desired acidulation ratio were mixed and introduced into the ball mill (Figure 1). The ball mill was heated by a gas burner below the outer shell, and the temperature of the shell was maintained constant throughout each run. A sample was taken at the end of each run for analysis.

Total water-soluble, and citrate-insoluble phosphorus were determined

Table I. Typical Analyses of Florida Phosphate Rock

		Type Sieve Size			
Screen mesh		+20	+48	+65	+100
		-20	-48	-65	-100
Weight %		0.10	3.03	9.37	3.09
Screen mesh		+150	+200	-200	
		-100	-150		
Weight %		23.79	5.95	54.67	
		Composition			
Component		Weight %			
CaO		47.20			
F		2.90			
P ₂ O ₅		34.17			
P		14.91			
SO ₃		0.30			
R ₂ O ₃		2.90			
SiO ₂		9.40			
Moisture		0.42			

by the official methods of Association of Official Agricultural Chemists (7). Moisture was determined by heating the samples at 105° C. for 5 hours in an oven. Calcium was determined using a flame photometer.

Bench-Scale Results

Experiments were carried out to study the effect of temperature, time, acid concentration, and acidulation ratio in the quick-curing process with grinding. The results are presented in Table II. Figure 2 shows that optimum acid concentration, under the process conditions employed, was about 65% H₃PO₄. The lower conversion at acid concentrations below 65% is probably due to slow reaction rate and incomplete curing. At acid concentrations above 65% the reaction rate was very fast, causing an excessive temperature rise and side reactions and thus driving off much of the water and resulting in a poor mix with high acid concentration. This condition caused a longer curing, since diffusion of highly viscous free acid is slow.

Figure 3 shows the effect of acidulation

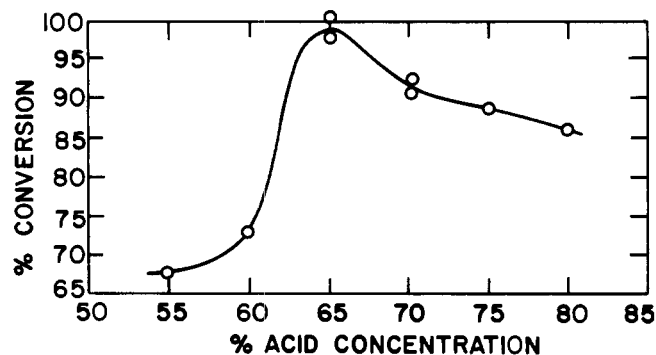


Figure 2. Effect of acid concentration on conversion

Temperature, 230° F.; time, 2 hours; acidulation ratio, 2.4

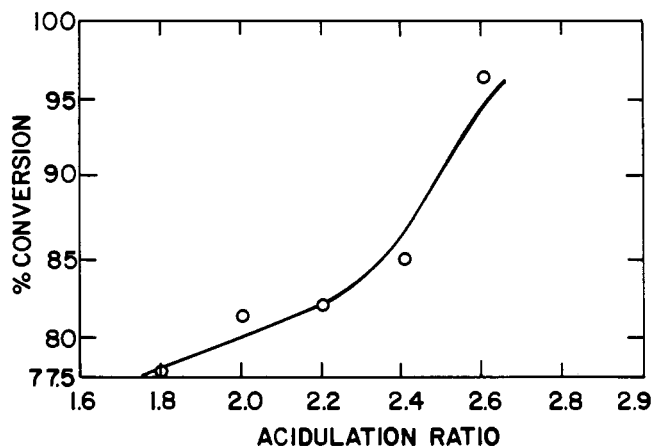


Figure 3. Effect of acidulation ratio on conversion

Acid concentration, 65%; time, 1.5 hours; temperature, 220° F.

Table II. Typical Analysis of Laboratory Ball Mill Acidulation (Dry Basis)

Run No.	Total Time (Hr.)	Temp., ° F.	Acid Conc., %	Acid Ratio	Phosphorus, %								Moist., %	Conv., %
					Total		Citrate-insoluble		Water-soluble		Available			
					P	(P ₂ O ₅)	P	(P ₂ O ₅)	P	(P ₂ O ₅)	P	(P ₂ O ₅)		
A-27	0.33	230	75	2.4	22.41	(51.30)	0.09	(0.22)	21.70	(49.70)	22.32	(51.08)	7.14	98.6
A-21	1.25	280	70	2.4	23.60	(54.00)	1.25	(2.86)	19.71	(45.10)	22.33	(51.10)	4.43	82.0
A-17	1.50	220	65	2.0	22.40	(51.27)	1.43	(3.24)	17.05	(39.06)	21.00	(48.00)	0.92	81.4
A-19	1.50	220	65	2.4	21.93	(50.20)	0.97	(2.23)	15.52	(36.58)	21.00	(48.00)	5.36	84.9
A-2	2.00	220	70	2.4	20.82	(47.70)	18.32	(41.97)	20.82	(47.70)	7.07	100.0
B-3	2.00	230	65	2.4	23.79	(54.45)	19.70	(45.05)	23.79	(54.45)	1.45	100.0
B-5	2.00	230	70	2.4	23.32	(53.40)	0.63	(1.44)	20.71	(47.44)	22.70	(51.96)	8.30	91.0
A-4	4.00	220	70	2.4	22.31	(51.10)	...	(...)	20.82	(47.70)	22.31	(51.10)	2.96	100.0

Table III. Typical Pilot-Plant Operating Conditions

Run No.	Acid Conc., %	Approx. Rock Feed Rate G./Min.	Approx. Acid Feed Rate G./Min.	Outlet Heating Gas Temp., ° F.	Drying Air Temp., ° F.			Product Temp., ° F.	Acid Temp., ° F.	Heating Chamber Gas Temp., ° F.	Drying Air Rate, Cu. Ft./Min.
					Inlet, D.B.	Outlet, D.B.	Inlet, W.B.				
3	71.6	100	161	375	225	215	65	650	0.350
4	70.6	100	161	350	200	194	68	575	0.350
5	70.6	100	161	300	135	170	68	450	0.370
6	71.0	100	161	250 ^a
7	72.4	100	174	350	150	190	...	198	66	550	0.365
8	71.6	100	148	350	156	180	85	162	68	575	0.365
9	66.0	50	87	350	177	195	100	180	71	550	0.365
10	61.0	50	94	350	160	185	...	175	72	530	0.342
11	72.8 ^b	100	174	325	73	175	48	170	66	450	0.512

^a The low heating gas temperature was insufficient for adequate curing and drying.
^b Acid concentration of 71.7% was used for the first 4 hours.

ratio on the conversion. Conversion increases with increasing acidulation ratio. The curing was incomplete as sufficient time was not allowed for the completion of reactions.

Figure 4 shows the effect of heating shell temperature. An optimum temperature of about 230° F. is indicated. Higher temperatures probably result in excessive side reactions and decomposition of monocalcium phosphate to pyrophosphate. At lower temperatures, the reaction is too slow. Processing time in these runs was insufficient for the completion of curing, and low conversions were obtained.

Figure 5 indicates the effect of time on conversion. A minimum time of about 2 hours is indicated for the completion of curing. Grinding and heating the product for a period of more than 2 hours had no detrimental effects on the

conversion under the conditions employed.

No consistent relationship between final moisture content and other process variables was indicated. Drying took place inside the ball mill, and the gases evolved escaped through the small central opening.

The results of the bench-scale work suggested that a quick-curing process based on grinding and drying was possible.

Pilot-Plant Work

Investigation of the quick curing process on a pilot-plant scale was undertaken using essentially the same equipment as used by Rounsley (13).

The pilot plant consisted of a 6-foot long, 1-foot diameter, stainless steel-lined rod mill with an external heating

jacket (Figure 6). Hot gases from the jacket were introduced into the mill to increase the drying rate. Phosphoric acid and rock were fed continuously at one end of the mill. Product was collected at the other end. The rod mill contained 10 stainless steel rods, 1 inch diameter and 6 feet long, each weighing 16 pounds. The temperature in the outside heating jacket was kept constant by a controller. The reaction gases evolved in the mill were passed through a scrubber and exhausted to the atmosphere by a blower.

The rod mill was first heated for 2 hours before each run, then rock and acid feed were started. No samples were taken during the unsteady state period. Four samples were taken every hour thereafter in the first seven runs, three per hour in run 8, and two samples per hour in the rest of the runs. The product samples were collected for 5-

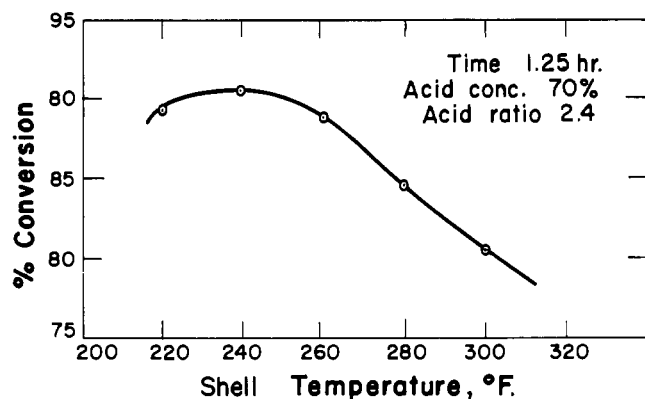


Figure 4. Effect of temperature on conversion
 Time, 1.25 hours; acid concentration, 70%; acidulation ratio, 2.4

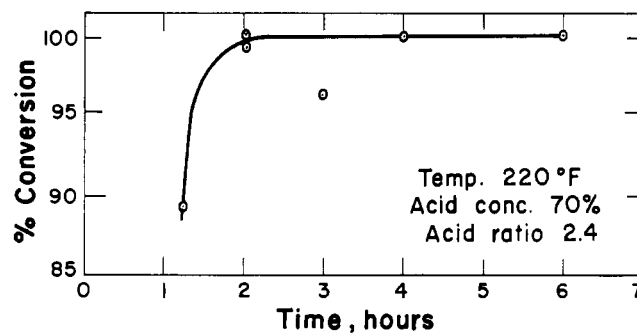


Figure 5. Effect of time on conversion
 Temperature, 220° F.; acid concentration, 70%; acidulation ratio, 2.4

Table IV. Typical Analysis of Pilot-Plant Product (Wet Basis)

Sample No.	Phosphorus, %								Moist., %	CaO, %	Calcd. Acid Ratio	Free Acid P, %	Free Acid P ₂ O ₅ , %	Conv., %
	Total		Citrate-insoluble		Water-insoluble		Available							
	P	(P ₂ O ₅)	P	(P ₂ O ₅)	P	(P ₂ O ₅)	P	(P ₂ O ₅)						
4-23	23.22	(53.17)	0.43	(0.99)	20.80	(47.63)	22.80	(52.18)	4.40	24.10	2.00	0.62	1.41	94.42
4-24	22.80	(52.17)	0.76	(1.74)	20.20	(46.26)	22.00	(50.43)	2.90	23.50	2.02	0.39	0.90	89.95
4-25	22.81	(52.20)	0.85	(1.94)	20.20	(46.26)	21.96	(50.26)	3.01	23.40	2.07	0.33	0.76	88.60
5-34	22.88	(52.37)	0.59	(1.36)	19.74	(45.19)	22.30	(51.01)	2.39	22.40	2.04	0.57	1.30	92.12
5-35	22.83	(52.26)	0.71	(1.62)	20.52	(46.98)	22.12	(50.64)	4.03	22.14	2.21	0.37	0.86	90.06
5-36	22.90	(52.41)	0.60	(1.38)	20.88	(47.75)	22.32	(51.03)	4.42	23.50	2.03	0.79	1.82	92.04
7-56	22.70	(51.98)	0.33	(0.75)	21.21	(48.55)	22.40	(51.23)	5.84	22.43	2.15	96.46
7-57	22.33	(51.55)	0.26	(0.60)	21.35	(48.85)	22.25	(50.95)	5.30	22.80	2.08	0.77	1.76	96.44
7-58	22.99	(52.63)	0.29	(0.68)	20.15	(46.12)	22.70	(51.95)	3.17	23.19	2.09	96.04
9-79	23.60	(53.97)	0.14	(0.32)	23.15	(52.97)	23.43	(53.65)	4.55	20.90	2.51	97.89
9-80	24.02	(55.00)	0.14	(0.33)	23.00	(52.66)	23.90	(54.68)	4.09	21.52	2.48	97.95
9-81	23.61	(54.05)	0.11	(0.26)	22.70	(51.97)	23.52	(53.79)	3.81	21.63	2.40	98.40
10-88	23.23	(53.20)	0.33	(0.74)	21.98	(50.26)	22.92	(52.46)	4.98	22.76	2.19	95.55
10-89	23.63	(54.15)	0.37	(0.84)	22.05	(50.50)	23.30	(53.31)	3.41	23.00	2.20	95.00
10-90	23.61	(54.05)	0.29	(0.66)	22.18	(50.71)	23.32	(53.36)	1.69	22.00	2.34	95.94
11-99	22.35	(51.13)	0.41	(0.93)	21.63	(49.53)	21.95	(50.20)	4.54	22.15	2.14	93.31
11-100	22.54	(51.58)	0.39	(0.90)	21.58	(49.41)	22.15	(50.68)	4.07	23.20	2.02	0.96	2.19	94.71
11-101	22.82	(52.24)	0.42	(0.95)	21.60	(49.49)	22.42	(51.29)	...	22.35	2.18	1.47	3.37	94.19

Table V. Pilot-Plant Size Analyses

Run No.	Tyler Sieve Size									Remarks
	+20	+28 -20	+48 -28	+65 -48	+100 -65	+115 -100	+150 -115	+200 -150	-200	
3	4.0	4.6	28.5	19.1	11.9	11.7	3.3	6.1	10.8	Screens clogged
4	4.5	4.1	33.9	33.0	8.5	4.6	4.4	4.3	2.9	Screens clogged
5	9.9	5.2	23.3	13.5	14.4	5.5	4.2	5.9	18.3	...
7	30.3	9.4	26.2	25.7	3.3	1.4	0.7	0.7	2.4	Screens clogged
9	5.0	11.0	27.0	15.9	8.0	6.0	4.1	8.6	14.4	Predried
10	7.5	13.6	27.1	10.3	10.2	4.6	2.4	6.8	17.5	Predried
11	12.1	8.4	23.6	11.7	10.9	4.2	2.6	5.7	20.8	Predried
Rock sample	0.1	0.2	2.8	9.4	3.1	23.2	0.6	6.0	54.7	As received

and 10-minute periods for rock feeding rates of 50 and 100 grams per minute, respectively.

The inside of the mill was examined under steady state conditions. A wet crust extending about 1 to 2 feet was observed at the inlet end of the mill where the first stage of reaction took place. Operating conditions of the different runs are given in Table III. Materials used were the same as those used for the laboratory studies.

Pilot-Plant Results

The results of the pilot-plant runs are given in Tables IV and V. The analyses of the samples of the first six runs were made after a few days, and analyses of the samples for the rest of the runs were made immediately to give zero day results.

The effect of acidulation ratio, acid concentration, feed rate, and temperature on the product was investigated. Other parameters for the process, such as the

source and particle size of the rock, rod mill diameter, speed, slope, and length, and the size and number of rods were kept constant, except for run 11 when the number of rods were reduced to six. This last run was carried out to examine the possible variation of operating variables.

Evaluation of Pilot-Plant Results

The results obtained in the laboratory-scale ball mill were to a large extent confirmed in the pilot-plant scale equipment (Table IV).

Analytical results of run 4 show poor consistency and reflect the poor control of the acid and rock feed rates in this run. Also, sufficient time was not allowed to reach steady state conditions. Run 5 was discontinued before steady state was reached. The acidulation ratio in the steady state period of this run was around 2.0, and conversions greater than 95% were obtained. Some analyses of samples taken during the early part of run 7 (not shown in Table IV) were as high as 99.3%.

Improper positioning of the inlet end of the acid line during run 8 resulted in poor mixing and lower conversions. In run 9 and 10, lower acid concentrations were used and the moisture content of the product increased. The effect of dilution on conversion was insignificant.

Operating conditions were changed in run 11 to test their flexibility. Only

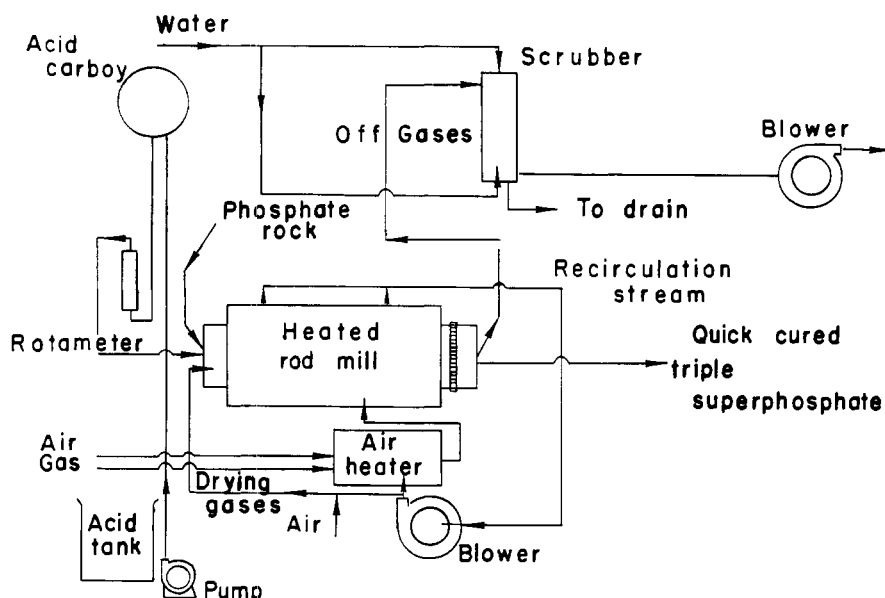


Figure 6. Flow sheet of the pilot plant for quick cured triple superphosphate

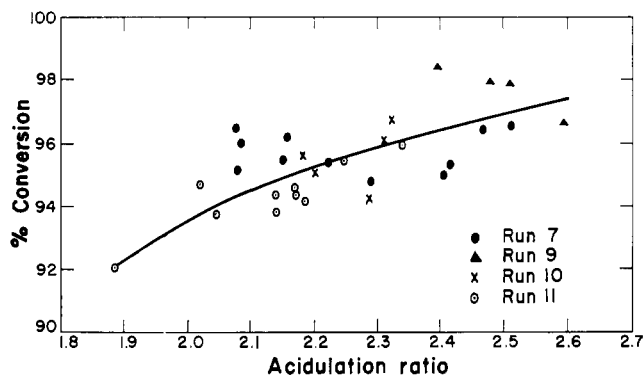


Figure 7. Effect of acidulation ratio on conversion

six rods were used instead of the 10 rods used in previous runs. A lower heating jacket temperature of 325° F. was used instead of 350° F. The drying air rate was increased from 0.365 cu. ft. per minute to 0.512 cu. ft. per minute, and the drying air temperature was decreased from about 160° to 73° F. The opposing effects of changes in these operating variables resulted in no distinguishable changes in the product, except for higher moisture and free acid content. This could be corrected either by increasing the temperature, increasing the residence time, increasing the amount of drying air or its temperature, or by decreasing the acid and rock feeding rates. Moisture content between 3 and 4% gave optimum results and satisfactory free acid contents.

Figure 7 indicates the effect of the

variation of the acidulation ratio on the conversion obtained in various runs. The particle size analysis of the rock used and the product triple superphosphate are given in Table V. Agglomeration of fine particles in the product of these runs prevented correct indication of the degree of grinding.

A residence time in the mill of about 45 minutes was indicated during run 10 by introducing ground charcoal with the rock feed and subsequent examination of the product for color.

The product was examined for storage characteristics after one month and two months. It was found free flowing and had excellent physical condition.

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GROWTH REGULATOR RESIDUES

Determination of Beta-Hydroxyethylhydrazine in Pineapples

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A microanalytical method for the isolation and determination of beta-hydroxyethylhydrazine (HEH) in pineapples is described. The method consists of blending and extracting the HEH from the fruit with water. After the interfering pigments in the extract are removed with ion exchange resins, the HEH is reacted with cinnamaldehyde to produce a yellow color. The intensity of the color is proportional to the concentration of HEH, and is measured at 420 m μ . The amount of HEH in the sample is then calculated from a standard curve.

IT is of economic importance to the pineapple growers to be able to make their plants fruit uniformly, and at a predetermined date. This can be achieved by spraying the plants with chemical agents which induce flowering and thus control the date of harvest (7). One of the very promising chemicals in this respect is beta-hydroxyethylhydrazine (Omaflora, Olin trade name) (3, 4, 6). The method presented was

developed to determine microgram quantities of Omaflora in the presence of pineapple.

Experimental

Apparatus. The apparatus included chromatographic tubes with Teflon stopcocks, Waring Blendor, International chemical centrifuge, and Beckman Model B spectrophotometer.

Reagents. DEIONIZED WATER. Dis-

tilled water was deionized using Amberlite MB-3 resin.

DILUTE HCL. Prepared by mixing 30 ml. of concentrated HCl and 70 ml. of deionized water.

ION EXCHANGE RESINS. Dowex 1-X8 and 50W-X8, 50- to 100-mesh, were used in the investigation. The Dowex 1 resin, obtained in the Cl⁻ form, was converted to the OH⁻ form according to the procedure recommended by the