

# Potassium Acid Saccharate by Nitric Acid Oxidation of Dextrose

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**P**ATENT literature contains descriptions of many processes for the nitric acid oxidation of carbohydrates to organic acids, principally tartaric and oxalic (1, 12, 15, 16). Previous investigators (2-9, 14) prepared saccharic acid from various carbohydrate materials as early as 1833, using relatively weak nitric acid for the oxidation. Work conducted in the Starch and Dextrose Division of the Northern Regional Research Laboratory resulted in an improved patented process (10), in which dextrose was oxidized with concentrated nitric acid to produce saccharic acid. Conditions of oxidation were carefully controlled so that excessive decomposition of the carbohydrate was avoided, and a comparatively high yield of saccharic acid was obtained. The product was recovered as the potassium acid salt.

This paper describes experiments in which potassium acid saccharate was produced by the improved process on a pilot plant scale. The work was undertaken to develop operating conditions suitable for commercial scale operations. A proposed plant process and cost estimates are based on engineering data obtained in the pilot plant.

## Safety Features of Process and Adequate Cooling Maintain Reaction Control

**Equipment.** Figure 1 shows the layout of the pilot plant, and Figures 2 and 3 are photographs of it. Pieces of equipment which came into contact with the acidic liquors were constructed of Type 316 stainless steel. All piping, with the exception of service lines, was constructed of stainless steel, Type 304. The reactor used for the oxidation was a 50-gallon jacketed kettle equipped with a motor driven agitator,  $\frac{3}{8}$ -inch cooling coils with a surface area of approximately 15 square feet, pressure filled expansion type thermometer, and several flanged top openings. The thermometer bulb extended 26 inches into the reactor, but only the 2-inch tip was sensitive. The shell-and-tube-type condenser had a surface area of approximately 25 square feet.

Absorption of the nitrogen oxides was conducted in a column consisting of a jacketed stainless steel pipe, 6 inches in diameter. The column was packed with  $\frac{3}{4}$ -inch Karbate Raschig rings and included a cast-iron spray nozzle for introducing the caustic solution.

In addition to the 50-gallon reactor, two 30-gallon jacketed kettles (one with agitator) and one 50-gallon jacketed kettle with an anchor-type agitator were used for precipitation and crystallization.

Three pumps were available for transferring nitric acid, caustic, and sugar solutions, respectively. The casing and impeller of the centrifugal pump used for handling acid were constructed of a high-nickel, high-chrome stainless steel and employed a blue-African-asbestos type packing. A duplex reciprocating pump

was used for the caustic solutions, and a conventional centrifugal pump was used for sugar solutions.

Crystalline products were filtered on a stationary vacuum filter made of chemical stoneware and employing a fibrous-glass filter cloth. Vacuum was applied to the chamber below the cloth.

A horizontal screw feeder, shown in Figure 3, was used for introducing the solid dextrose into the reactor. The rate of dextrose addition was controlled by a variable-speed drive mechanism. A small quantity of air was introduced at the discharge end of the feeder to maintain the dextrose in a dry state so that it would flow freely.

Instruments for the pilot plant were centrally located on a panelboard and consisted of dial thermometers, solenoid switches, and motor controls.

Nitric acid was pumped from carboys to an overhead tank, measured, and then pumped to the reactor. Acid used later in the process was fed by gravity to the precipitating kettle.

**Safety Features.** The reaction between dextrose and nitric acid is strongly exothermic, and at high temperatures it proceeds very rapidly, with vigorous evolution of gases. Hence, special attention was given to safety in the design and operation of the equipment.

Under normal operating conditions the temperature of the reaction was controlled adequately by passing tap water through the cooling coils in the reactor. However, for sudden increases in the reaction temperature it was sometimes necessary also to pass cooling water through the jacket of the kettle. The jacket was piped so that it could be used for either steam heating or water cooling. Solenoid valves in the lines could be controlled instantaneously from a single switch mounted on the panelboard so that red or green pilot lights indicated the cycle in which the jacket was operating.

As a further precaution, another line containing a solenoid valve was installed so that, in an emergency, cold water could be admitted quickly to the reactor, thereby flooding and diluting the reaction mixture.

Finally, a 3-inch pop safety valve was installed in the vapor line leading from the reactor to the condenser. The valve was set for a relief pressure of 5 pounds per square inch gage but it also could be opened manually.

**Raw Materials.** The acid used for all the experiments was 40° Bé., technical grade, containing 61.4% nitric acid by weight. Sugar used in the oxidations was granular dextrose hydrate, commercial grade, containing approximately one molecule of water of crystallization. Hydrol, the concentrated mother liquor obtained in the crystallization of dextrose, was employed in experiment 23. This sirup had a dextrose equivalent of 51.2% by weight and a density of 45° Bé. Potassium hydroxide, as 45% by weight liquid, technical grade, was used for precipitation of the potassium acid saccharate. For the absorption of

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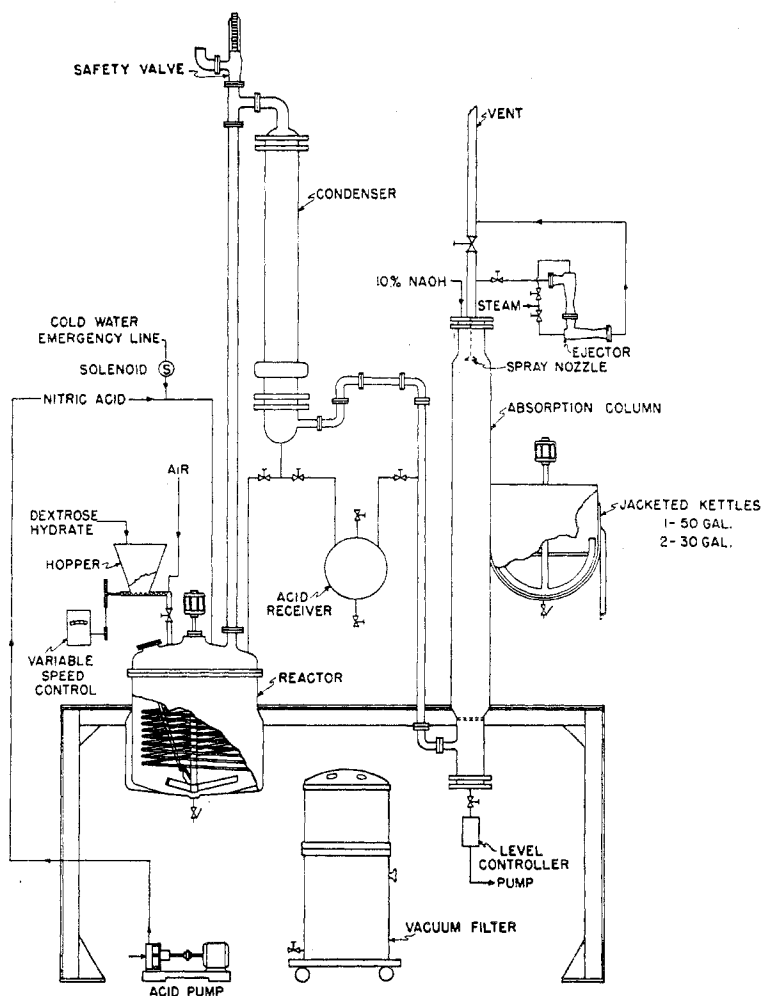


Figure 1. Layout of Pilot Plant Equipment

nitrogen oxides in the gas scrubber, 10% by weight sodium hydroxide solution was fed countercurrently to the gases.

**General Procedure.** The procedure generally followed in the pilot plant consisted of three phases of operation—namely, the dextrose oxidation, the recovery of potassium acid saccharate, and the recovery of potassium nitrate.

In starting the oxidation, the required amount of acid was pumped to the reactor where it was heated to 130° F. Granular dextrose was then introduced by the screw feeder. The dextrose was added slowly at the beginning (approximately 40 pounds per hour), but the rate was gradually increased to 100 pounds per hour. The time required for the addition of 0.5 pound-mole (approximately 100 pounds of commercial dextrose) was 2 hours. During this period, the temperature was held at 130° F. by regulating the flow of cooling water through the coils. The oxides of nitrogen being evolved continuously were passed to the absorption column. After all the dextrose had been added, the temperature of the mixture was raised to 158° F. and maintained at that value for an additional 2 hours to complete the reaction.

The liquor was cooled and transferred to a 50-gallon jacketed kettle used for crystallization. Potassium hydroxide solution was slowly stirred into the acid liquor. During this period, the temperature increased to approximately 158° F., and the pH of the liquor was finally adjusted to 9.0. The temperature and pH were held constant for a period of 20 minutes. The solution was then cooled to room temperature, and its pH was adjusted

to 3.4 with 40° Bé. nitric acid. At this pH, potassium acid saccharate precipitated as needle-shaped crystals. After the reaction mixture had stood overnight, the crystals were removed by vacuum filtration, and the cake was washed with water. The wet cake contained approximately 50% moisture, and it was dried in a forced circulation air dryer at 105° F.

Potassium nitrate was recovered from the mother liquor and washings by adjusting the pH of the combined liquors to 2.0 with 40° Bé. nitric acid. This step was necessary to convert organic potassium salts to potassium nitrate. The liquor was then concentrated to two thirds of its original volume and was cooled to room temperature over a period of 2 hours, with slow stirring. Potassium nitrate crystallized from solution and was filtered or centrifuged, washed, and dried in a manner similar to that used for saccharate crystals. This procedure was repeated to obtain a second crop and, in some cases, a third crop of potassium nitrate.

**Control of Reaction Temperature.** The oxidation reaction became violent if not carefully controlled. The reaction was most sensitive during the first half of the dextrose addition at 130° F. and again during the first hour of oxidation after the temperature was raised to 158° F. If the temperature was allowed to rise above 185° F., the reaction became exceedingly difficult to control.

Adequate control of the reaction was maintained by fulfilling the following requirements:

Sufficient time was allowed for oxidation of the dextrose.

Adequate cooling capacity was available.

A sensitive-type thermometer with quick response was used.

For the protection of operating personnel and equipment, in case the reaction should become too violent, adequate safety values were provided, as described.

#### 4-Hour Oxidation at Acid to Dextrose Ratio of 3 to 4 Gives 43% Yield of 98 to 99% Pure Saccharate

The following factors involved in the production of potassium acid saccharate were studied on a pilot plant scale. Weight yields reported throughout this paper are actual weights of the materials obtained, corrected to a purity of 100%. Yields of potassium acid saccharate referred to as per cent of theoretical are based on the weights of dextrose used in the oxidations.

**Sugar Concentration.** The effect of sugar concentration on yield is shown in Table I. The yield of saccharate obtained when solid dextrose was used in the oxidation was considerably higher than that obtained with 75% dextrose sirup. Consequently, solid dextrose was used in subsequent experiments. Dilution of the acid resulting from the use of dextrose sirup decreases the oxidizing power of the nitric acid.

**Rate of Dextrose Addition and Time Required for Oxidation.** The rate at which dextrose may be added to an excess of acid is limited by the reaction rate which, in turn, depends on the cooling capacity available for removing the heat of reaction. In the pilot plant equipment, a period of 1½ to 2 hours was required for the addition of 0.5 pound-mole of dextrose.

Oxidation periods, including dextrose acid addition, varied from 4 to 7 hours. Yields equal to those obtained in laboratory investigations were obtained in a period of 4 hours.

**Excess Nitric Acid Used for Oxidation.** A series of six experiments was conducted in order to correlate saccharate yield with the mole ratio of acid to dextrose. The results of the experiments are given in Table II and shown graphically in Figure 4. The yield of saccharate increased with an increase in the mole ratio of acid to dextrose. Satisfactory yields were obtained when the mole ratio was in the range of 3.0 to 4.0.

**Intermediate Distillation Step for Recovery of Nitric Acid.** The liquor remaining after 4 hours of oxidation contains residual nitric acid amounting to between 10 and 20% of that added originally, and most of this can be recovered by distillation. In experiment 3 the liquor was concentrated to a thick sirup by vacuum distillation over a 2<sup>3</sup>/<sub>4</sub>-hour period. Sparging steam was introduced, and the mixture was steam stripped for 4<sup>1</sup>/<sub>2</sub> hours at 130° F. By this procedure, 95% of the nitric acid remaining after oxidation was removed. Recovery of potassium acid saccharate from the stripped liquor amounted to 39.9% of the theoretical yield.

**Precipitation of Potassium Acid Saccharate in Two Steps.** The conventional laboratory procedure (10) employing a single precipitation, was replaced by a two-step precipitation developed during the pilot plant work. When the pH of the oxidized liquor was being adjusted to 9.0, it was observed that potassium acid saccharate crystals precipitated at a pH of 3.8. As a result of this observation a new procedure was developed. The pH of the oxidized liquor was adjusted to 3.8 with potassium hydroxide solution, while the temperature was maintained at 85° F. A crop of potassium acid saccharate was precipitated, allowed to stand overnight, filtered, washed, and dried. The mother liquor was concentrated to one-half volume, and its pH adjusted to 9.0 with more alkali solution. The temperature rose to 158° F. and was maintained at this value for 20 minutes. The liquor was then cooled to 85° F. and its pH was reduced to 3.4 by the addition of 40° Bé. nitric acid. Potassium acid saccharate crystals separated and were recovered the following morning by filtering, washing, and drying. The mother liquor was processed, as described previously, for the recovery of potassium nitrate. A quantitative flow sheet of this process, based on data from experiment 25, is shown in Figure 5.

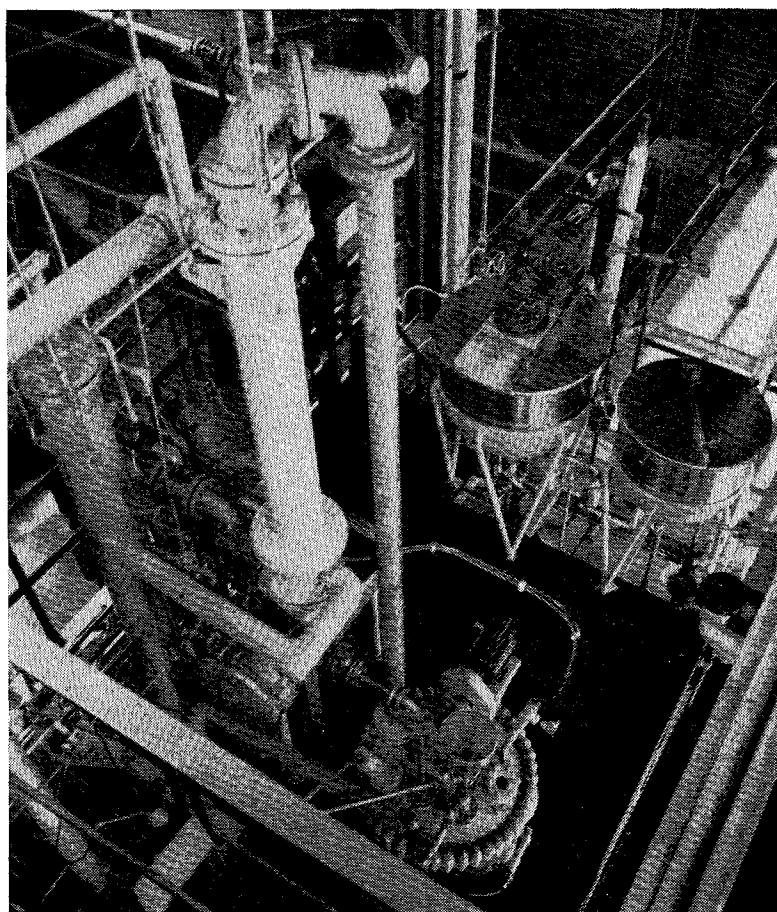


Figure 2. View of Pilot Plant

An important advantage was gained by the two-step procedure in that smaller quantities of alkali and acid were required for processing. Table III shows the alkali and acid requirements for the one- and two-step procedures.

**Re-use of Residual Mother Liquors.** Mother liquors remaining at the end of the process were recycled into subsequent oxidations in an effort to increase the yield of saccharate. In a typical series, an oxidation was conducted and the saccharate and nitrate products recovered. The residual mother liquor from the potassium nitrate crystallization was then concentrated to a sirup and introduced along with the dextrose charge into a second oxidation. The residual liquor from this cycle was then concentrated and introduced into a third oxidation.

Data for a typical series are given in Table IV. Yields by this procedure were considerably lower than those employing the standard procedure.

Table I. Effect of Sugar Concentration on Yield of Potassium Acid Saccharate

Expt. No.	Dextrose Hydrate	Dextrose Hydrate (100%), Lb.	Nitric Acid (100%), Lb.	Yield of Potassium Acid Saccharate (100%)	
				Pounds	Per cent of theoretical <sup>a</sup>
1	75% Sirup	99 <sup>b</sup>	126 <sup>c</sup>	45.3	36.5
3	75% Sirup	99	126	49.4	39.9
4	Solid	99	126	53.4	43.0

<sup>a</sup> Theoretical yield is 1 pound mole of potassium acid saccharate, 248.2 pounds per pound-mole of dextrose.

<sup>b</sup> Equivalent to 0.5 pound-mole.

<sup>c</sup> Equivalent to 2 pound-moles.

Approximately 60% of the total yield of potassium acid saccharate was obtained in the first crop, which consisted of large crystals with purity in the range of 99 to 100%. The second crop consisted of smaller crystals with purity in the range of 98 to 99%.

Table II. Effect of Mole Ratio of Acid to Dextrose on Yield of Potassium Acid Saccharate

Expt. No.	Dextrose Hydrate		Nitric Acid <sup>a</sup> (100%)		Acid Dextrose, Mole Ratio	Yield of Potassium Acid Saccharate	
	Pounds	Pound-mole	Pounds	Pound-moles		Pounds	Per cent of theoretical
4	99	0.5	126	2.00	4.00	53.4	43.0
5	99	0.5	111	1.75	3.50	51.7	41.7
6	99	0.5	94.5	1.50	3.00	50.7	40.8
9	99	0.5	86.6	1.375	2.75	43.2	34.8
7	99	0.5	79	1.25	2.50	40.5	32.7
8	99	0.5	79	1.25	2.50	39.5	31.9

<sup>a</sup> Concentration was 40° Bé.



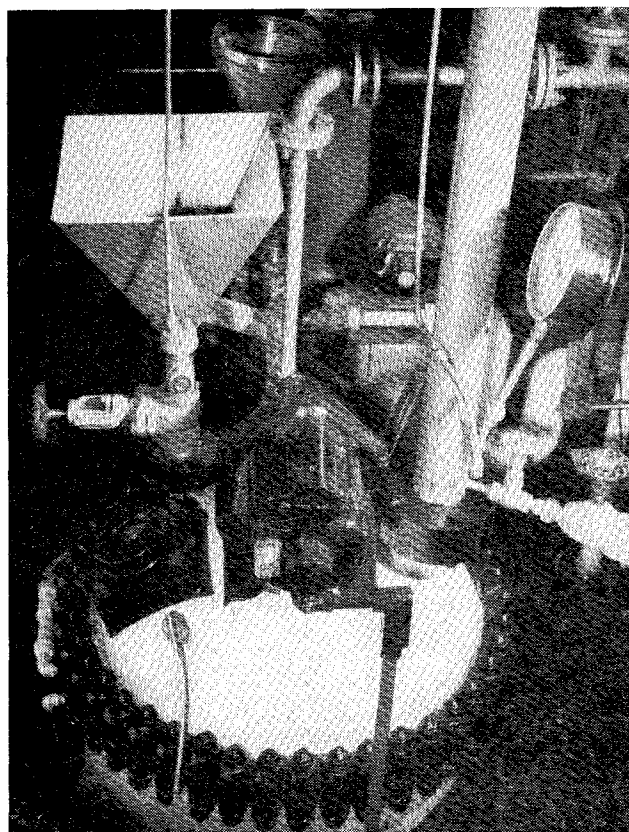


Figure 3. Reactor and Dextrose Screw Feeder

**Absorption of Nitrogen Oxides.** In order to dispose of the nitrogen oxides produced in the pilot plant operations, they were passed through a packed column countercurrent to the flow of 10% sodium hydroxide solution. Little work was conducted on this phase of the process, since absorption methods for nitrogen oxides are well known. In a commercial plant they would undoubtedly be recovered as nitric acid.

**Oxalic Acid from Residual Mother Liquors.** Laboratory studies (11) have shown that the residual mother liquors from the process may be further oxidized to give good yields of oxalic acid.

The process was investigated on a pilot plant scale, using the mother liquor from experiment 3. The oxidation products of dextrose (other than saccharic acid) equivalent to 0.3 pound-mole of dextrose were available for conversion to oxalic acid. A charge of 40° Bé. nitric acid weighing 157 pounds was pumped to the reactor where it was heated to 85° F., and  $\frac{1}{3}$  ounce of

Table III. Comparison of Chemical Requirements for One-Step and Two-Step Precipitation Procedures

Expt. No.	Acid Dextrose, Mole Ratio	Precipitation Steps	Yield of Potassium Acid Saccharate, Lb.	Total Chemicals Required	
				Nitric acid (100%), lb.	KOH (100%), lb.
5	3.5	1	51.7	156.4	66.0
6	3.0	1	50.7	143.5	64.6
13	3.0	2	50.7	115.0	43.2
25	3.0	2	49.0	120.7	41.0

Table IV. Re-use of Residual Mother Liquors by Recycling (Experiment No. 16)

Cycle No.	Acid/Dextrose, Mole Ratio	Potassium Acid Saccharate Yield, % of Theoretical
1	3.0	40.6
2	3.0	34.7
3	3.0	25.3
Average		33.5

sodium vanadate was added. The mother liquor, concentrated previously to a sirup, was fed slowly to the reactor over a  $\frac{1}{2}$ -hour period. Oxidation was continued for 22 hours at 85° F. The temperature was then raised to 130° F. and held at that value for 4 hours. Oxalic acid crystals were formed when the mixture was cooled to 70° F. over a 2-hour period. The crystals were filtered on the vacuum filter. The yield was 22.5% of theoretical, and the dried crystals analyzed 99.5% oxalic acid dihydrate. This value was lower than that obtained in the laboratory.

**Recovery of Potassium Nitrate.** Potassium nitrate was recovered in many of the experiments by concentrating the saccharate mother liquors and crystallizing. Two crops were usually recovered by successive procedures. The purity of the first crop of crystals averaged 94.1%, the second crop averaged 90.9%. In commercial production only one crop of nitrate would be removed from the process; the second crop would be redissolved and recycled to the evaporator. Table V lists the recovered yields of potassium nitrate for a series of experiments.

**Substitution of Hydrol for Dextrose.** The use of commercial Hydrol as a raw material for the oxidation was investigated. Hydrol sirup was used in place of solid dextrose for the oxidation. The quantity of Hydrol used was equivalent to 0.5 pound-mole of dextrose. Sufficient 40° Bé. nitric acid was used to provide a mole ratio of acid to dextrose of 4.0. The process was conducted in a manner similar to that employed in the experiments using dextrose sirup as a raw material. The yield of potassium acid saccharate obtained was 16.6% of theoretical. With such a low yield, Hydrol would not be suitable as a raw material for the process.

Table V. Recovery of Potassium Nitrate

Expt. No.	Nitric Acid Used in Oxidation (100%), Lb.	Precipitation Steps	Total KOH, Lb.	Potassium Acid Saccharate Yield (100%), Lb.	Yield, lb.	Potassium Nitrate (100%) Purity, %		Recovery, % of theoretical <sup>a</sup>
						1st crop	2nd crop	
4	126	1	63	53.4	63.4	94.0	90.0	69.0
5	111	1	66	51.7	68.8	96.5	90.0	70.0
6	94.5	1	64.6	50.7	42.3	96.8	...	44.2
9	86.6	1	51.7	43.2	43.9	89.0	90.0	58.0
7	79	1	47.8	40.5	39.0	97.4	98.3	55.8
8	79	1	48.2	39.5	39.3	90.9	86.0	55.4
13	94.5	2	43.2	50.7	15.6	100.0	98.5	27.1
25	94.5	2	41.0	49.0	32.0	100.0	71.7	59.0

$$^a \text{ \% of theoretical} = \frac{\text{KNO}_3 \text{ yield} \times 100}{\text{total KOH used} \times \frac{101}{56} - \left( \text{potassium acid saccharate yield} \times \frac{101}{248} \right)}$$

Table VI. Chemical Requirements and Yields in Production of Potassium Acid Saccharate

Expt. No.	Mole Ratio of Acid to Dextrose	Precipitation Steps	Dextrose Hydrate (100%), Lb.	Nitric Acid (100%), Lb.				Potassium Hydroxide (100%), Lb.			Potassium Nitrate Yield, Lb.	Potassium Acid Saccharate Yield, Lb.
				Oxidation	To pH 3.4	To pH 2.0	Total	To pH 3.8	To pH 9.0	Total		
7	2.50	1	99	79.0	22.0	10.4	111.4	...	47.8	47.8	39.0	40.5
8	2.50	1	99	79.0	23.4	16.5	118.9	...	48.2	48.2	39.3	39.5
9	2.75	1	99	86.6	29.7	16.5	132.8	...	51.7	51.7	43.9	43.2
6	3.00	1	99	94.5	40.2	8.9	143.6	...	64.6	64.6	42.3	50.7
5	3.50	1	99	111.0	35.7	9.5	156.2	...	66.0	66.0	68.8	51.7
4	4.00	1	99	126.0	27.1	11.8	164.9	...	63.0	63.0	63.4	53.4
13	3.00	2	99	94.5	14.6	6.0	115.1	32.3	10.9	43.2	15.6	50.7
25	3.00	2	99	94.5	16.8	9.4	120.7	35.5	5.5	41.0	32.0	49.0

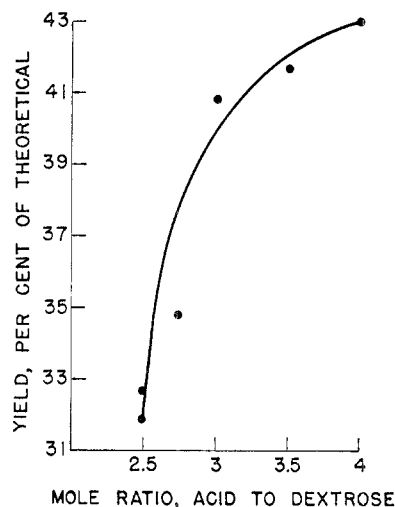


Figure 4. Effect of Mole Ratio of Acid to Dextrose on Yield of Potassium Acid Saccharate

**Color Formation in Process Liquors.** It was found that the addition of alkali to the process liquors in the precipitation steps produced considerable darkening. The process liquors varied in color from deep red to dark brown. Crystals from the dark process liquors were more difficult to filter and were lower in purity. The literature contains some references to this problem (13, 17). Laboratory investigations revealed that color formation was minimized by the use of lower temperatures and shorter processing times in the precipitation steps. These measures were incorporated into the pilot plant procedures.

**Effect of Procedure on Yield and Purity of Recovered Potassium Acid Saccharate.** In comparative experiments, slightly higher yields were obtained in the pilot plant than in the laboratory when the mole ratio of nitric acid to dextrose was less than 4. The purity of the first crop of potassium acid saccharate crystals produced by the two-step precipitation procedure was in the range of 99 to 100%. Precipitates obtained by the one-step procedure varied in purity from 97 to 99%. With suitable operating conditions, potassium acid saccharate yields obtained using either precipitation process were consistently in the range of 40 to 43% of theoretical when the mole ratio of nitric acid to dextrose was 3 to 4.

A typical analysis of the pilot plant product is as follows:

Purity (by neutral equivalence), %	98.5
Moisture, %	0.10
Nitrogen, %	0.023
Oxalate, %	0.10
Ash ( $K_2SO_4$ ), %	34.8
Bulk density, grams per ml.	0.45
pH of saturated solution (20° C.)	3.9
Solubility in water (20° C.), grams per 100 ml.	2.0

The product is obtained in the form of white, nonhygroscopic, needlelike crystals, insoluble in alcohol. The solubility of the crystals in water increases with temperature and alkalinity.

#### With Nitric Acid Recovery, Estimate of Commercial Production Cost Is 35 Cents per Pound

**Mole Ratio of Nitric Acid to Dextrose and Precipitation Procedure.** The mole ratio of acid to dextrose used for the oxidation had some effect on the yield and the chemical requirements of the process. Table VI gives the chemical requirements and the yields of products obtained in a series of experiments, and Table VII shows the net cost of chemicals per pound of potassium acid saccharate. Recovery of any nitric acid has been neglected in these calculations. Using the one-step precipitation process, the lowest net chemical cost of 42.0 cents per pound of saccharate was obtained at a mole ratio of acid to dextrose of 3.5. With the two-step procedure, a net chemical cost of 40.3 cents per pound of saccharate was obtained at a mole ratio of acid to dextrose of 3.0.

**Nitric Acid Recovery.** Recovery of nitric acid in this process is important because of the requirement of a large excess over that theoretically needed. If a conventional nitric acid recovery plant can be provided, costs can be reduced considerably.

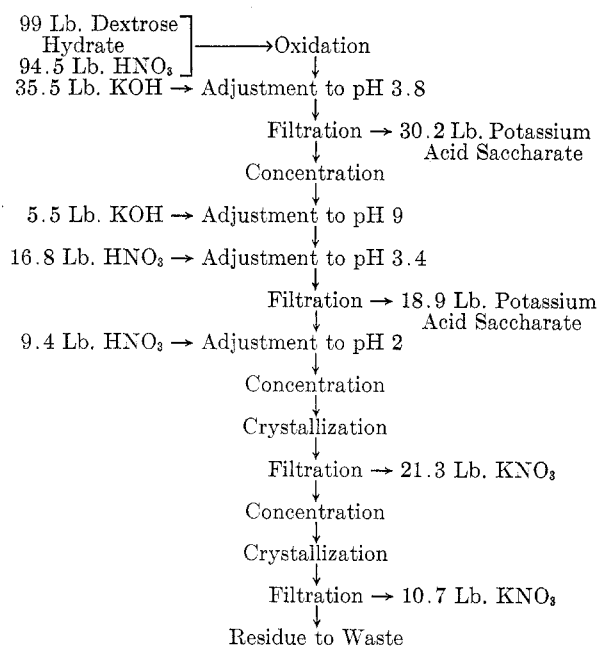


Figure 5. Quantitative Flow Sheet for Two-Step Precipitation Process

Weights are for pure substances

Table VII. Net Cost of Chemicals for Producing Potassium Acid Saccharate

Expt. No.	Mole Ratio of Acid to Dextrose	Precipi- tation Steps	Total Nitric Acid (40% Bé.)		Total KOH (45% Soln.)		Commercial Dextrose Hydrate Cost at 7.5 Cents/Lb.	Total Chemical Cost	Potassium Nitrate Value at 10 Cents/Lb.	Net Chemical Cost	Net Chemical Cost <sup>a</sup> /Lb. Potassium Acid Sac- charate
			Pounds	Cost at 6 cents/lb.	Pounds	Cost at 4 cents/lb.					
7	2.50	1	181	\$10.88	106	\$4.24	\$7.50	\$22.80	\$3.90	\$18.70	\$0.461
8	2.50	1	194	11.64	107	4.28	7.50	23.42	3.93	19.49	0.494
9	2.75	1	216	12.96	115	4.60	7.50	25.06	4.39	20.67	0.478
6	3.00	1	234	14.04	144	5.76	7.50	27.30	4.23	23.07	0.455
5	3.50	1	254	15.24	147	5.88	7.50	28.62	6.88	21.74	0.420
4	4.00	1	269	16.14	140	5.60	7.50	29.24	6.34	22.90	0.429
13	3.00	2	187	11.22	96	3.84	7.50	22.56	1.56	21.00	0.414
25	3.00	2	197	11.82	91	3.64	7.50	22.96	3.20	19.76	0.403

<sup>a</sup> No credit has been allowed for nitric acid recovery.

Table VIII. Estimated Investment Cost of Potassium Acid Saccharate Plant

(Daily capacity 9600 lb. from 19,200 lb. dextrose hydrate)

Equipment	Item	Estimated Delivered Cost	Land: Property, improvements, railroad siding Building: Factory, office, and laboratory, 3 stories (40 × 70 ft., 30 × 40 ft., 30 × 40 ft.) at \$10/sq. ft.	\$ 25,000    62,400
1	Absorption column: 3 × 40 ft., with bubble caps, cooling coils in each plate, stainless steel, No. 316	\$ 25,000		
1	Compressor: NO <sub>2</sub> , 100 cu. ft./min., 20 hp., stainless steel No. 302, single stage, reciprocating	4,200		
1	Compressor: air, 200 cu. ft./min., 40 hp., single stage, motor driven	4,500		
1	Compressor: air, 10 hp., turbo driven (stainless steel No. 302, turbine side)	2,500		
1	Pump: (absorber) steel, reciprocating, 60 gal./hr. at 100 lb./sq. inch gage, 1/2 hp.	300		
1	Storage tank: HNO <sub>3</sub> , 10,000 gal., stainless steel, No. 347	11,500		
1	Storage tank: KOH, 10,000 gal., steel	3,200		
1	Pump: HNO <sub>3</sub> , centrifugal, duriron, 3/4 hp., 10 gal./min. at 35-ft. head	600		
1	Pump: KOH, centrifugal, cast iron, 10 gal./min. at 35-ft. head, 3/4 hp.	400		
1	Pump: reactor, centrifugal, stainless steel No. 302, 1 hp., 30 gal./min. at 15-ft. head	600		
1	Pump: holding tank, 3/4 hp., 10 gal./min. at 35-ft. head, stainless steel No. 302	500		
2	Pumps: filter, 1/2 hp., 5 gal./min. at 22-ft. head, stainless steel No. 302	1,000		
3	Tanks: precipitation, open, jacketed, agitators, 1/2 hp., stainless steel No. 302 (pH 3.8 step = 300 gal.; pH 9-3.4 step = 300 gal.; pH 2 step = 250 gal.)	4,700		
7	Reactor vessels: 150 gal., stainless steel No. 316, complete with jackets, cooling coils, agitators, and controls, 1 hp.	17,500		
1	Holding tank: steel, open, rubber lined, 200 gal.	650		
2	Holding tanks: steel, open, rubber lined, with agitator, 1/2 hp., 250 gal.	1,500		
7	Hoppers and screw feeders: 3/4 hp. variable speed drives	4,200		
1	Holding tank: steel, open rubber lined, 500 gal. with agitator, 1/2 hp.	1,200		
1	Filter: rotary vacuum, 1 1/2 hp., 3-ft. diameter × 3-ft. face, stainless steel No. 302	6,500		
1	Filter: rotary vacuum, 1 1/2 hp., 3-ft. diameter × 2-ft. face, stainless steel No. 302	5,000		
2	Holding tanks: open, steel, rubber lined, (one 250 gal. and one 350 gal.)	1,500		
1	Rotary dryer: saccharate, 6-ft. diameter × 20-ft. length, 7 hp., steam heated with inside lining of stainless steel No. 302	12,000		
1	Rotary dryer: nitrate, 4-ft. diameter × 15-ft. length, 4 hp., steam heated, with inside lining, stainless steel No. 302	8,000		
1	Holding tank: open, steel, 250 gal., rubber lined	700		
1	Evaporator feed tank: open, steel, 250 gal., rubber lined	700		
1	Evaporator: single effect, vertical tube, stainless steel No. 302, 53 sq. ft., vacuum	10,000		
2	Evaporators: single effect, vertical tube, stainless steel No. 302, 24 sq. ft., vacuum	14,000		
2	Centrifugals: basket, suspended, vertical shaft, with 26-inch basket, stainless steel No. 302, 3 hp.	11,400		
1	Pump: rotary, evaporator, 1/2 hp., stainless steel No. 302, 3 gal./min. at 15-ft. head	400		
1	Pump: rotary, evaporator, 1/4 hp., stainless steel No. 302, 2 gal./min. at 15-ft. head	350		
1	Crystallizer: Swenson Walker, 1/2 hp., stainless steel No. 302, 24 inches wide × 26 inches deep × 20 ft. long	9,300		
1	Crystallizer: Swenson Walker, 1/2 hp., stainless steel No. 302, 24 inches wide × 26 inches deep × 10 ft. long	6,300		
1	Tank: open, mixing, conical bottom, 1/2 hp., stainless steel No. 302, 200 gal., with agitator	750		
Equipment	Item			Estimated Delivered Cost
1	Tank: open, mixing, conical bottom, 1/2 hp., stainless steel No. 302, 100 gal., with agitator			500
1	Tank: slurry, steel, 60 gal., with agitator, 1/2 hp.			250
1	Pump: centrifugal (slurry tank), 1/4 hp., 1 gal./min. at 25-ft. head			125
1	Screen: vibrating, 20 × 48 inch, 1/2 hp., totally enclosed			750
1	Screen: vibrating, 3 × 2 ft., 1/2 hp., totally enclosed			650
2	Hammer mills: capacity 1000 lb. saccharate/hr.			8,000
2	Screw conveyor elevator lifts: steel, 1/2 hp., 10 ft., with 4-inch screw, with reduction drives to 20 r.p.m.			1,400
1	Storage bin: conical bottom, steel, 40 cu. ft. capacity			300
1	Storage bin: conical bottom, steel, 10 cu. ft. capacity			100
2	Bagging machines: automatic, 1/2 hp.			1,000
	Equipment delivered			\$184,025
	Allowance for installation, 30 % of delivered cost			55,298
	Equipment installed			\$239,233
	Piping, electrical wiring, and instrumentation, 30 % of cost of equipment installed			71,770
	Equipment, piping, etc., installed			\$311,003
	Contingencies, engineering and contracting fees, 25 % of cost of equipment, piping, wiring installed			77,751
	Total cost of equipment			\$388,754
	Total capital investment			\$476,154

Nitrogen oxides released in the process can be oxidized and absorbed in water in a pressure tower operating at 100 pounds per square inch gage to yield 40° Bé. nitric acid. The nitric acid from the intermediate distillation step from the oxidized liquors can also be passed to the acid absorption tower for recovery.

**Cost Estimates.** The proposed process is based on the two step precipitation procedure. Nitric acid is recovered by oxidation and absorption of nitrogen oxide gases in a conventional nitric acid tower. It is estimated that the recovery will amount to 80% of the acid used in the oxidation step, with no acid recovered from the oxidized liquors by intermediate distillation. Residual mother liquors are considered a waste material and are given no value. A diagrammatic flow sheet for the proposed process is shown in Figure 6. Daily production is 9600 pounds of potassium acid saccharate and 4800 pounds of potassium nitrate. Rubber lining or stainless steel is required in most pieces of equipment.

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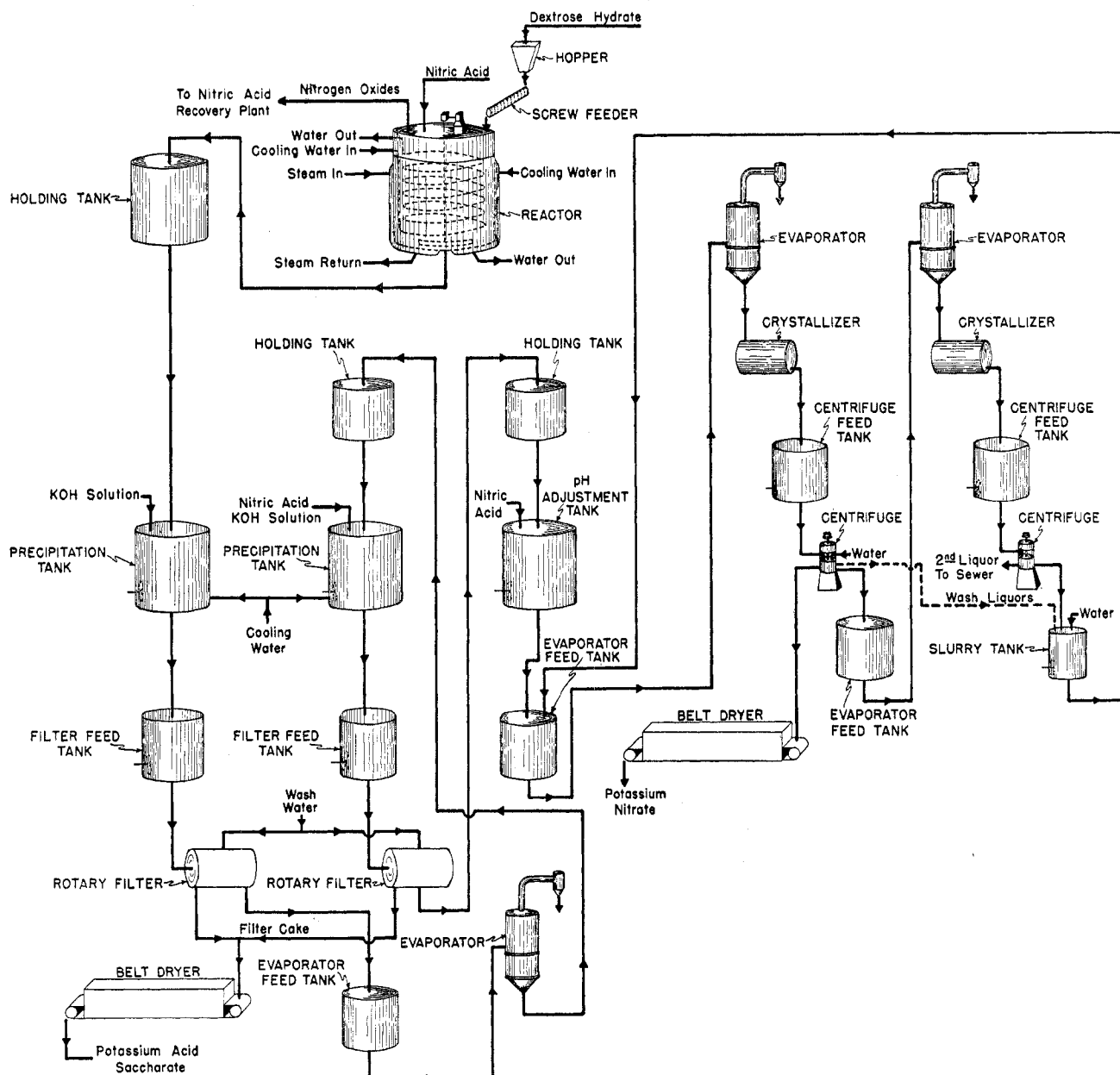


Figure 6. Flow Sheet for Production of Potassium Acid Saccharate

while the seventh is being emptied and recharged. The operating cycle for each reactor is 3 hours, which permits two reactors to be discharged per hour. A charge of 400 pounds of dextrose and 620 pounds of 40° Bé. nitric acid is made to each reactor.

Table VIII lists the land, building, and equipment necessary for a plant producing 9600 pounds of potassium acid saccharate and 4800 pounds of potassium nitrate per day. The total investment cost is estimated at \$476,154. Production costs are given in Table IX. The production cost for manufacturing potassium acid saccharate is estimated at 35.2 cents per pound, with corn sugar at 7.5 cents per pound. These are plant production costs only and do not include administrative or selling expenses.

#### Summary and Conclusions

Results from the pilot plant experiments indicate that potassium acid saccharate may be prepared successfully on a com-

mercial scale by the oxidation of dextrose with 40° Bé. nitric acid.

The oxidation is conducted as a batch process, preferably in small batches of 500 gallons maximum, to obtain better temperature control and to provide a steady supply of nitrogen oxides for conversion to nitric acid. Commercial grades of granular dextrose hydrate and 40° Bé. nitric acid are used. The mole ratio of nitric acid to dextrose should be 3.0 for suitable yield, moderate requirements for precipitating chemicals, and a small amount of potassium nitrate by-product.

Nitric acid is heated to 130° F., and dextrose is added over a period of 1½ hours. The temperature is raised to 158° F., and the oxidation is continued for an additional 1½ hours. The oxidized liquor may be vacuum distilled to recover the residual nitric acid.

Recovery of potassium acid saccharate is accomplished in two precipitation steps. Potassium hydroxide solution is added to

Table IX. Estimated Daily Production Costs for Manufacturing Potassium Acid Saccharate

(Daily capacity 9600 lb. from 19,200 lb. dextrose hydrate; operating 24 hr./day, 300 days/year)

	Daily Costs	Cost/Lb. Saccharate
Raw materials:		
Nitric acid, 40° Bé. (make-up), 12,432 lb. at \$0.065/lb.	\$ 808.00	
Potassium hydroxide, 45% liquid, 18,400 lb. at \$0.045/lb.	828.00	
Dextrose hydrate, 19,200 lb. at \$0.075/lb.	1,440.00	
Total cost of raw materials	\$3,076.00	
By-product credit, potassium nitrate, 4800 lb. at \$0.09/lb.	432.00	
Total net cost of raw material	\$2,644.00	\$0.275
Utilities:		
Steam, 78,300 lb. at \$0.75/1000 lb.	\$ 58.50	
Water, 361,000 gal. at \$0.075/1000 gal.	27.10	
Electricity, 2640 kw. at \$0.0125/kw.-hr.	33.00	
Total cost of utilities	\$ 118.60	\$0.012
Labor and supervision:		
Reactor operators, 3 per shift at \$1.75/hr.	\$ 126.00	
Neutralizer operators, 1 per shift at \$1.75/hr.	42.00	
Centrifuge and filter operator, 1 per shift at \$1.75/hr.	42.00	
Evaporator and crystallizer operator, 1 per shift at \$1.75/hr.	42.00	
Drier, bagging and dumping operator, 1 per shift at \$1.50/hr.	36.00	
Helpers, 1 per shift at \$1.25/hr.	30.00	
Oilier and repairman, 1 per day at \$1.50/hr.	12.00	
Foreman, 1 at \$16.00/day	16.00	
Superintendent, 1 at \$25.00/day	25.00	
Chemist, 1 at \$16.00/day	16.00	
Clerk, 1 at \$12.00/day	12.00	
Total labor and supervision	\$ 399.00	\$0.042
Maintenance:		
Building and land at 2% of \$87,400	\$ 5.80	
Equipment at 5% of \$311,003	51.80	
Total maintenance	\$ 57.60	\$0.006
Fixed charges:		
Taxes and insurance, 3%/year on total capital investment of \$476,154	\$ 47.60	
Depreciation		
Building, 5%/year on \$62,400	\$ 10.40	
Equipment, 10%/year on \$311,003	108.60	
Total fixed charges	\$ 161.60	\$0.017
Total	\$3,380.80	\$0.352

the oxidation liquor while the temperature is maintained at 85° F. by cooling. The first crop is precipitated at pH 3.8, filtered, washed, and dried. Combined mother liquor and washings are concentrated to one-half volume and then adjusted to pH 9.0 with potassium hydroxide. The temperature is allowed to rise to 158° F. and is held at this value for 20 minutes, after which it is cooled and adjusted to pH 3.4 with 40° Bé. nitric acid. The

resulting crystals are filtered, washed, and dried. The purity of the first crop of crystals is in the range 99 to 100%, while that of the second crop is approximately 98%.

Potassium nitrate recovery is accomplished by acidifying the mother liquor to pH 2.0 with nitric acid and removing two successive crops of crystals by concentration, crystallization, and centrifugation. The second crystals are recycled with the first mother liquor to be concentrated.

Reuse of mother liquors in subsequent oxidations for the production of saccharate was unsuccessful, but they may be oxidized with 40° Bé. nitric acid and vanadium catalyst to convert the residual carbohydrates to oxalic acid. When Hydrol was used in place of dextrose in the oxidation, low yields of potassium acid saccharate were obtained.

Cost estimates indicate that potassium acid saccharate may be produced for 35.2 cents per pound in a plant having a daily capacity of 9600 pounds of potassium acid saccharate with a nitric acid recovery unit. The total investment cost for the plant is estimated at \$476,154.

#### Acknowledgment

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