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UNIVERSITY OF LOUISVILLE

A RESINOUS MOLDING COMPOUND FROM CITRUS WASTE
" PREPARATION OF CITRUS WASTE FOR PRESSING
DISPOSAL OF DISTILLERY SLOP
and
DEHYDRATION OF BEEF BY INFRA-RED RADIATION

A thesis
submitted to the faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of
MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

by
Wilbur P. ^{Little} Adams
1943

A RESINOUS MOLDING COMPOUND FROM CITRUS WASTE
PREPARATION OF CITRUS WASTE FOR PRESSING
DISPOSAL OF DISTILLERY SLOP
and
DEHYDRATION OF BEEF BY INFRA-RED RADIATION

by

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14 Feb 67

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ABSTRACT

^{work}
This thesis is a report on three investigations; Citrus Waste Disposal, Distillery Slop Disposal, and Dehydration of Beef by Infra-red Radiation.

The work on citrus waste consisted of the production of a resin from citrus waste and phthallic anhydride. The optimum molding conditions for this cellulosic resin were established, and the effect of variation in the percentage of citrus waste to phthallic anhydride was determined.

In the second part of the work, on the Disposal of Citrus Waste, the possibility was investigated of using soluble salts in the treatment of citrus waste prior to pressing. A series of experiments were run to determine the optimum amounts of the salts to use.

A process for the complete disposal of distillery wastes was investigated. The waste was concentrated to the maximum viscosity that would permit spraying and burned with stack gases in a combustion chamber.

Efforts to coagulate the suspended solids in distillery slop with chlorine produced in situ were not completely satisfactory from an economic viewpoint. The chlorine was produced by electrolyzing the slop after the addition of sodium chloride or calcium chloride.

Removal of the suspended solids in distillery slop by filtration was unsuccessful. Addition of various chemical reagents did not improve to any great extent the filtration rate or the quality of the filtrate.

In the third investigation, a process for the rapid dehydration of beef with infra-red radiation was developed.

THE PREPARATION OF A RESINOUS
MOLDING COMPOUND
from
CITRUS WASTE

INTRODUCTION

This investigation consisted of two distinct parts. In the first, the manufacture of resin from citrus waste and phthallic anhydride was studied. In the second, the use of soluble salts in the preparation of citrus waste for pressing was investigated.

Previous experiments by Ernst and Hunter (1) showed resin to be a practical product for the utilization of citrus waste. This work is an extension of these experiments and was designed to obtain more accurate operating conditions for the preparation of these materials and to establish the best ratio between citrus waste and phthallic anhydride. In determining this ratio, all factors were taken into consideration including the economic as well as the effect of the composition upon the physical properties of the plastic.

The second part of this investigation was an extension of the work of Ernst and Bumstead (2). In 1940 they reported the successful use of soluble salts in producing pressability of citrus waste. It was the purpose of this work to determine the best procedure and conditions of treatment.

HISTORICAL

Established practice in the field of plastics has followed the principle of preparation of a compound, followed by molding. Often the molding materials are mixed with wood flour or other fillers before molding in order to improve their strength. It would be much cheaper if, during the molding operation, the reaction could be brought about in situ between the materials from which the plastics are made, and the filler.

It is desired to produce a plastic-like resin using citrus waste, a cellulosic material, and phthallic anhydride, an esterifying agent. Several investigators (3) have studied the reaction of phthallic anhydride and cellulose, but their interest has been mainly a study of the compound, its preparation, and properties.

None of these investigators have suggested their product as a plastic material. They have been interested in the ester from its theoretical aspect as a new cellulose compound. They prepared it in most cases by heating the pure cellulose with phthallic anhydride in the presence of a carrier and a catalyst.

THEORETICAL

The chief chemical characteristic of cellulose is the hydroxy groups that it contains. The cellulose molecule is made up of building units of this structure formula, according to Degering (4).

Figure I

The average molecular weight of the cellulose molecule as determined by the ultra-centrifuge method was found to be approximately 40,000. Each unit of this chain, or cellobiose, contains two secondary alcohol groups and one primary alcohol group. The similarity of the cellobiose to the glycerol molecule is quite obvious in that each cellobiose contains three hydroxy groups as does the glycerol molecule. Glycerol reacts with phthallic anhydride or other dibasic acid to form the important alkyd group of resins.

Figure II

From Fig. II, it is apparent that a chain results from the tying together of two or more glycerol molecules. It is also possible that the phthallic anhydride molecule may act as a bridge to produce three dimensional polymers of great complexity. This grouping into larger molecules is characteristic of resins.

The similarity of cellulose and glycerol has been pointed out. Cellulose can undergo a similar reaction with dibasic acids. The logical result, as in the case of alkyds, would be a resinous compound. Since cellulose is already a large chain molecule, the derivative might be expected to have some even more desirable characteristics than the familiar alkyds. The cross linkages produced by the phthallic anhydride would give three dimensional polymers of great complexity. Experience with other polymerization reactions would cause one to expect a very low solubility in all types of solvents from such a polymer, and the findings of Levey (5) confirm this.

The esterification reaction of the cellulose units is characteristic, because of the hydroxy groups present. It is difficult, however, to esterify cellulose completely. From Fig. I, it can be seen that one of the hydroxy groups is enclosed and protected by the cellulose ring. This difficulty, of bringing the protected hydroxy group into a reaction, was experienced in the development of cellulose acetate (3) but was overcome by the use of catalysts. Without

complete esterification the product will tend to form a chain type molecule as is formed in the esterification of glycol. This type of resin is soluble and thermoplastic. The type that was desired in this work was the insoluble, thermosetting type that is characteristic of the three dimensional, or net-work molecule. This result can be obtained only if esterification is complete.

If the above esterification reaction can be carried to completion and can be made to take place directly, the result should be a cheap, durable plastic.

EXPERIMENTAL

Equipment:

The apparatus used in these experiments consisted of an Adolph Beuhler Metallographic Mounting Press equipped with an electrically heated mold, Tyler Screens, laboratory size ball mill, and a hydraulic press for testing the compression strength of the plastic.

Procedure:

Thoroughly dried citrus waste was ground in the ball mill until it would pass a 40 mesh screen. It was then mixed with phthallic anhydride and the batch ground in the ball mill until an intimate mixture was obtained. This operation was found to require about 4 hours at approximately 40 r.p.m.

A series of tests were run in which time, temperature, and pressure were varied to determine the optimum molding conditions.

The composition of the mixture used in these tests was 60% phthallic anhydride and 40% citrus waste. This ratio is a stoichimetric proportion if the citrus waste is assumed to be 100% cellulose and all three of the hydroxy groups in the cellulose molecule are assumed to react.

The selection of the optimum operating conditions was made on the basis of a microscopic examination of the samples in the series. Homogeneity was assumed as a criterion of quality. The results of these tests with the best value for each variable underlined, are given in Table I.

The composition of the plastic was then varied to determine the effect of phthallic anhydride content on the compression strength of the plastic. The samples were molded under the optimum conditions as shown in Table I, and the compression tests were made on samples of .25 sq.in. area and 0.5 in. high. The pressure was applied transversely to the molding pressure.

Three of the accelerating agents used by Hunter (4), sodium benzene sulfonate, zinc chloride, and aluminum chloride, were tested and were found to have little effect when present in amounts up to 2%, which was the maximum amount used in the tests.

Aluminum stearate, a water-proofing material used in protective films, was added to the plastic to improve its resistance to water, but the effect did not justify its continued use.

D A T A

TABLE I

EFFECT OF TEMPERATURE, PRESSURE, AND TIME ON MOLD-
ING OF CITRUS WASTE-PHTHALLIC ANHYDRIDE RESIN.

<u>Time</u>	<u>Temperature</u>	<u>Pressure</u>
20 min.	115°C	2250 #/sq.in.
20 min.	115°C	<u>3000 #/sq.in.</u>
20 min.	115°C	3750 #/sq.in.
20 min.	<u>100°C</u>	3000 #/sq.in.
20 min.	115°C	3000 #/sq.in.
20 min.	130°C	3000 #/sq.in.
15 min.	115°C	3000 #/sq.in.
<u>20 min.</u>	115°C	3000 #/sq.in.
30 min.	115°C	3000 #/sq.in.

TABLE II

EFFECT OF COMPOSITION ON COMPRESSION STRENGTH OF
CITRUS WASTE-PHTHALLIC ANHYDRIDE RESIN.

<u>% phthallic anhydride</u>	<u>% citrus waste</u>	<u>Pounds per sq.in. at failure</u>
60	40	15,000
50	50	14,500
40	60	14,000
25	75	6,000
15	85	1,200

RESULTS AND CONCLUSIONS

The data show that the best molding conditions for this citrus waste-phthallic anhydride plastic are 3000 lbs./sq.in. pressure, 20 min. time, and a temperature of 100°C.

The compression strength, as can be seen in Table II, increases with an increase in the per cent phthallic anhydride. This increase is very rapid up to a composition of 40% phthallic anhydride, but very slow afterward. This would indicate that the reaction is complete when this amount of phthallic anhydride has been used in the esterifying of the cellulose molecule. If this is true, then it is logical to assume that the equivalent of only two, of the three hydroxy groups in the cellulose unit, has been affected, since 60% of phthallic anhydride by weight would be required to esterify all three hydroxy groups.

With only two of the hydroxy groups esterified, the chain type of molecule results, and this type of resin is soluble. This structure would account for the low resistance of the plastic to the action of solvents.

Although the cost of such a plastic would seem prohibitive when the amount of phthallic anhydride is considered, there are factors which tend to make such a plastic economically feasible. The simplicity of the preparation of the molded compound, considering that the compound can be made in one operation, is so outstanding that it more than compensates for the slightly higher raw material costs.

Future work on this problem should include a study of accelerating agents, which could be used to catalyze the reaction. The success of the acetylation of cellulose resulted from the discovery of the catalyzing effects of zinc chloride on the reaction. A similar accelerating agent may be found to produce the same effect in this case.

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PREPARATION OF CITRUS WASTE
FOR PRESSING

HISTORICAL

Citrus waste is a product of the cannery industry. The waste consists of the rag and peel resulting from the juicing of the fruit prior to the canning. This waste can be disposed of as garbage where facilities for such disposal are available, but the established practice is to dry the waste and sell it as cattle feed.

The waste prior to drying is partially dehydrated by pressing. Patents (1) on the treatment of this waste in preparation for the pressing operation have been the subject of considerable discussion. The procedure accepted today is the treatment of the waste with lime followed by a short aging period. The material is then pressed and dried.

It is necessary to have an aging period in the lime treatment because of the time required for the reaction. If the lime were a soluble salt instead of an insoluble one, this aging period would be reduced or completely eliminated. With an insoluble salt time is required for dispersion of the material throughout the mass. As a result the reaction is delayed.

In a previous investigation, Ernst and Bumstead (4) reported that soluble salts could be used as well as the insoluble salts of the alkaline earth group in the preparation of citrus waste for pressing. Their work, however, was not extended at that time to cover all optimum operating conditions. They reported that it was necessary to bring the waste into the alkaline range before any satisfactory results could be obtained.

THEORETICAL

Although the exact nature of the reaction between citrus waste and lime, or the soluble salts, is not known with certainty, it is believed that a reaction involving pectin is the one producing the pressability.

Pectin is a high molecular weight, organic compound of great complexity. The methoxy groups in the molecule is one of the chemical characteristics of this compound. It is these methoxy groups that differentiates between pectin and pectic acid. One of the pectin molecules is shown in Fig. III.

Figure III

When citrus waste is brought into the alkaline range, it is believed that the methoxy groups on the pectin molecule are removed, thus forming the soluble pectic acid. If the waste is now brought back into the acid range by the addition of calcium chloride and hydrochloric acid, an insoluble calcium pectate is formed. It is this calcium pectate that gives the tissues the firmness necessary for pressing.

When the standard lime treatment is used, the mechanism of the reaction is slightly different. When the lime is added, the waste is brought into the alkaline range. During this period of alkalinity the hydrolysis of pectin to pectic acid takes place. The waste, however, approaches the acid range rapidly because of the reaction of the lime with the excess citric acid. It is this reaction rate which determines the length of the mixing time.

The cycle which the citrus waste passes during the lime treatment is duplicated in the process using the soluble salts.

EXPERIMENTAL

Equipment:

The apparatus used in these experiments consisted of a Beckman pH Meter, a small mill for the grinding of the rag and peel of the citrus fruit, and burettes for adding the solutions of sodium carbonate and calcium chloride to the waste.

Procedure:

The citrus waste was ground until it would pass approximately an eight mesh screen.

A series of experiments were run using this waste to determine the proper amounts of soda ash and calcium chloride to use, if best results were to be obtained. The soda ash was varied from 0.15% to 0.55% and the calcium chloride from 0.02% to 0.08%. Both the soda ash and calcium chloride were technical grades and were added to the waste in the form of 10% solutions.

The soda ash was added to the waste and the mass mixed vigorously for approximately one minute. The pH of the sample was taken with a Beckman pH meter. Calcium chloride was then added to the waste and the batch mixed for three minutes. The pH of the waste was again taken and the mass tested for pressability. The total time required for the process was less than five minutes, which is considerably less than the two hours required by the process using the lime treatment. The results of these experiments using sodium carbonate and calcium chloride are given in Table III.

A study was also made of the pH change in citrus waste immediately following the standard lime treatment in an attempt to discover the sequence of the reactions which cause the citrus waste to become pressable. Three hundredths of a per cent lime was added to the waste and the samples were mixed vigorously for lengths of time varying from 20 to 120 seconds. The results of these experiments are given in Table IV and Fig. IV.

D A T A

TABLE III

ESTABLISHMENT OF BEST CONDITIONS FOR PRESSABILITY

<u>Sample No.</u>	<u>Per cent Soda ash added</u>	<u>Per cent Calcium Chloride added</u>	<u>pH after addition of Soda ash</u>	<u>pH after addition of Calcium Chloride</u>	<u>Results</u>
1	.15	.020	4.7	4.3	Non-pressable
2	.15	.035	4.7	4.0	Non-pressable
3	.15	.050	4.7	3.1	Non-pressable
4	.15	.065	4.7	2.9	Non-pressable
5	.15	.080	4.7	2.8	Non-pressable
6	.25	.020	5.8	4.9	Non-pressable
7	.25	.035	5.8	4.8	Non-pressable
8	.25	.050	5.8	4.6	Non-pressable
9	.25	.065	5.8	4.0	Non-pressable
10	.25	.080	5.8	3.8	Non-pressable
11	.35	.020	6.2	6.1	Pressable
12	.35	.035	6.2	5.6	Pressable (excellent)
13	.35	.050	6.2	5.5	Pressable
14	.35	.065	6.2	5.4	Non-pressable

TABLE III - (Continued)

ESTABLISHMENT OF BEST CONDITIONS FOR PRESSABILITY

<u>Sample No.</u>	<u>Per cent Soda ash added</u>	<u>Per cent Calcium Chloride added</u>	<u>pH after addition of Soda ash</u>	<u>pH after addition of Calcium Chloride</u>	<u>Results</u>
15	.35	.080	6.2	5.3	Non-pressable
16	.45	.020	7.4	6.4	Pressable (good)
17	.45	.035	7.4	6.3	Pressable (excellent)
18	.45	.050	7.4	5.2	Non-pressable
19	.45	.065	7.4	4.6	Non-pressable
20	.45	.080	7.4	4.5	Non-pressable
21	.55	.020	7.9	6.6	Pressable (good)
22	.55	.035	7.9	6.6	Pressable (excellent)
23	.55	.050	7.9	5.9	Non-pressable
24	.55	.065	7.9	5.1	Non-pressable
25	.55	.080	7.9	4.8	Non-pressable

TABLE IV

VARATION OF PH OF CITRUS WASTE WITH TIME AFTER
TREATMENT WITH LIME

<u>Time of mixing in seconds</u>	<u>pH at end of mixing</u>	<u>pH at end of 2 min.</u>	<u>pH at end of 4 min.</u>	<u>pH at end of 6 min.</u>	<u>pH at end of 8 min.</u>	<u>pH at end of 10 min.</u>
20	9.20	8.90	8.50	8.10	7.90	7.70
30	8.95	8.50	8.00	7.50	7.20	7.10
60	8.80	8.40	7.90	7.40	7.00	6.90
90	8.30	7.65	7.30	7.00	6.80	6.70
120	7.70	7.10	6.70	6.50	6.40	6.30

FIG. IV. VARIATION OF pH OF CITRUS WASTE WITH TIME AFTER TREATMENT WITH LIME

RESULTS AND CONCLUSIONS

The data indicate that good pressability can be obtained with a maximum of thirty-five thousandths of a per cent calcium chloride and a minimum of thirty-five hundredths of a per cent sodium carbonate.

The amount of calcium chloride should be controlled very carefully since a slight deviation on either side of the above value will produce inferior pressing.

This process using soluble salts instead of lime eliminates the aging period, and reduces the mixing time to 20% of that with the standard lime treatment. Altogether this new process requires approximately 5% of the time required by the other process.

An explanation of the pH change in citrus waste following the commercial lime treatment can possibly be made on the following basis.

From an examination of the curves in Fig. IV, it can be seen that the acidity of the waste is immediately neutralized on the addition of the lime. This indicates an immediate reaction of the acid with the lime, causing the low pH of the waste. If this reaction included all of the acids in the citrus waste, the pH would rise to some value in the alkaline range, depending upon the amount of lime added, and remain constant. This is not true, however, for once the pH has reached its maximum, it begins to decrease and continues to do so for a considerable period of time. This leads one to believe that an acid which reacts much more slowly than the acid causing the acidity of the original

waste is reacting with the excess lime. If too much lime has not been added i.e., not enough to neutralize all acids present, the pH value of the waste will decrease until the mass is again in the acid range. This would happen if the slower reacting acid could replace the acid which reacted with the lime initially. Since the two principal acids in citrus waste are citric and pectic acids, this cycle as explained above could be followed. Citric acid is a relatively strong organic acid which reacts much more rapidly than the very weak pectic acid. Also the original low pH value of the citrus waste could be produced only by the citric acid. Thus it must be the reaction between the lime and the citric acid which produces the rapid change in the pH after the lime is added. Since calcium pectate is less soluble than calcium citrate, the citric acid would be slowly displaced from the product of the lime reaction, and the calcium pectate would take its place. The citric acid freed in this manner would increase the acidity of the citrus waste as it was displaced with the pectic acid in calcium citrate.

In the case of the process using soluble salts, these same pH changes occur, but they are not automatic as in the process using the lime. In the process using the soluble salts, the waste is neutralized completely with a base such as sodium carbonate which would react more rapidly than the lime. The calcium salt is then added in the form of an acidified solution which brings the pH of the waste

down into the acid range where the insoluble calcium pectate is formed.

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DISPOSAL OF DISTILLERY SLOP

I N T R O D U C T I O N

The purpose of this investigation was the development of a process for the disposal of distillery slop that may be used by the small distiller during this emergency. This process could not involve the use of critical or strategic materials and must of necessity have low operating costs.

This work did not have as its objective a permanent solution of the slop disposal problem for the industry, but rather temporary relief during the emergency. For large distilleries, the multi-effect evaporator is still the best solution of the slop disposal problem.

HISTORICAL

Disposal of Distillery Slop has been a problem for many years. The larger distilleries have installed evaporators to handle their wastes. The small distilleries, however, can hardly afford the cost of such an installation and have continued to dispose of their slop by running it into nearby streams. Most states now have statutes which forbid the pollution of their streams. Thus, it has become necessary to find a cheap method of disposal.

Much research has been done to find a simple solution, but without success. It would seem that most of these attempts to find a simple solution have involved some type of filtering operation. The Louisville Drying Machine Co. (1) has obtained a patent on a filtration process in the name of A. W. Lissauer. It also has had the Mellon Institute investigate the possibility of using chlorine as a means of coagulating the suspended solids in the slop and reducing the B.O.D. of the liquid until it can be emptied into streams without polluting them. This latter method was partially successful in the coagulating of the solid, and did destroy the B.O.D. sufficiently to permit the decanted liquid to be run into the streams of most states. This process can not be used now, during the war, because of the shortage of chlorine.

Urbain and Stemen (2) have developed a method for the coagulation and precipitation of suspended solids by the use of magnetic materials. Magnetite, nickel, cobalt, or an alloy of these will produce a magnetic field of sufficient strength to bring about the precipitation.

THEORETICAL

The solids contained in distillery slop after the starch has been fermented and removed consist of cellulose, proteins and albumins. The solids are divided into two classes, soluble and insoluble. In the insoluble category are included the cellulose which composes the larger part of the suspended solids and the proteins and albumins which have been converted into the insoluble state by heat. These latter solids form a colloidal solution and present the chief difficulty in any method for the removal of suspended solids. The soluble materials include those proteins and albumins that still remain soluble after the cooking and distilling operations, and are the source of the high B.O.D. of liquid in the distillery slop. Any satisfactory method for disposal of distillery slop must be able to offer a solution of both these problems.

The removal of the larger suspended solids does not present a difficult problem, since they can be removed almost completely by screens and can be removed completely by a filtering operation. The smaller of these suspended solids, those of colloidal size, do present a problem that has more or less defied solution. It has been possible to precipitate them by the proper adjustment of the pH with acids, bases, or salts of the electrolyte group, but after their precipitation, their removal or separation from the liquid is a very difficult problem. Because of their gelatinous nature, filtration is a costly and time consuming process which has not found any commercial applications.

Centrifuging also presents difficulties, The nature of the makes a continuous operation almost impossible.

To remove the colloidal particles completely by a centrifuging operation, before they have been discharged and precipitated, is impossible. The following equation gives the concentration of the suspended solids at any point in the sample:

$$\log_e \frac{N}{N_0} = - \frac{A}{RT} \frac{4}{3} \pi r^3 (P - P_0) gh$$

where N_0 is the number of particles per cm^3 at the bottom of the sample,

N is the number of particles per cm^3 at a distance h above the bottom,

A is Avogadro's number,

r the radius of an average size particle,

P the density of the solids,

P_0 the density of the medium, and

g the gravitational force or force being exerted by the centrifuge upon the sample.

It can be seen from the equation that regardless of the force on the system, a complete removal of the solids could never be accomplished. An increase in the force on the system causes a new distribution of the particles toward the bottom to take place, but regardless of the force, all of the particles cannot be removed by this method.

The settling of the suspended solids does make it possible to reduce the duty of the evaporators in a plant that has means of reducing the B.O.D. of the decanted liquid to a very low number, e.g., 400. With this procedure, however, the soluble materials are lost, and it is these that command the highest price as cattle feed.

Coagulating the dissolved proteins and albumins may be partially done by the addition of mineral acids, ammonium alum, potassium aluminum sulfate, or ferric chloride, but not all of the dissolved proteins or albumins can be coagulated by these methods. After the coagulation of the dissolved solids there is a tendency for them still to remain in suspension and it is sometimes difficult to centrifuge them out.

The oxidation of the whole slop by the use of chlorine causes a precipitation of the suspended solids, and reduction of the B.O.D. of the liquid from a prohibitive value of 28,000 to the considerably lower value of 4,000. This method cannot be used at this time because of the shortage of chlorine.

If chlorine could be produced in situ in the slop, by an electrolysis after the addition of a chloride salt, this process would work in three ways. The chloride salt, being an electrolyte, would cause a precipitation of the suspended solids. The chlorine generated would also have a similar effect, and at the same time oxidize the soluble solids until they would no longer have such a high B.O.D. value.

EXPERIMENTAL

Equipment:

The experimental work was carried out on both laboratory and pilot plant scale. The apparatus used consisted of a De Laval Centrifuge, Sparkler Filter, screens both 100 mesh and 200 mesh, and electrolytic cell, ammeter, variable resistance, combustion chamber, gear pump, gas burner with a forced feed, and laboratory glass ware consisting of graduated cylinders and beakers.

The electrolytic cell was composed of a glass container, two carbon electrodes, and a diaphragm. The diaphragm was an unglazed porcelain jar and prevented excessive amounts of sodium hydroxide or calcium hydroxide formed at the cathode on electrolysis of the treated slop from mixing with the rest of the bath.

The combustion chamber was a cylinder 3 feet in diameter and four feet long with a conical bottom. There was a circular opening approximately eight inches in diameter in the center of the top, and an opening of about the same area in the conical end. A baffle was welded in the chamber directly in front of the opening and approximately 1 foot from the end.

Procedure:

Four methods for the removal of suspended solids in distillery slop were tested experimentally.

Preliminary to the application of any of these methods, the slop was screened thru 100 mesh and 200 mesh screens.

The screens were supported at approximately a 30° angle with the horizontal, and a fine spray of water was directed against the top side of the screen to prevent the closing of the openings by particles of the slop. This stream of water caused all of the solids retained on the screen to move slowly toward the lower end where they were removed.

The first method consisted of the addition of various chemicals to the slop, followed by a filtration to remove the solids that had been precipitated. These chemicals were all electrolytes, since only this class has any precipitating effect on the colloids in the slop. They included potassium aluminum sulfate, calcium chloride, sodium hydroxide, and ammonium sulfate. Two of these, potassium aluminum sulfate and ammonium sulfate, were chosen because they are used in the precipitation of the solids in sewage and in the purification of water, in numerous waste disposal and water purification plants throughout the country. The others were chosen at random from the vast number of electrolytes it would have been possible to use.

Filter aids such as sil-o-cel and celite were added to the slop to increase the filtration rate.

The second method involved an electrolysis and a settling operation. The slop was treated with sodium chloride and electrolyzed. The time of electrolysis was varied from five minutes to thirty minutes, the amount of sodium chloride from 0.5% to 5%, and the current density was held constant at 0.15 amperes per square centimeter. Two experiments were

run using 0.5% and 1% calcium chloride, with a current density of 0.15 amperes per square centimeter and a time of 15 and 10 minutes respectively. In some of the experiments coagulating agents such as ammonium sulfate, lime, sulphuric acid, and ferric chloride were added to the slop after the electrolysis to aid in the coagulation.

The third method was a mechanical separation. However, a small amount of a coagulating agent was used to improve the results.

The slop, after being screened, was fed into the De Laval Centrifuge. The speed of the centrifuge was 10,000 r.p.m. and the inside bowl diameter was approximately 4 inches. The rate of feed was approximately 100 ml. per minute. In order to get good separation, the slop was recycled thru the centrifuge again. The effluent from the centrifuge was treated with a small amount of potassium aluminum sulfate, and passed thru the centrifuge again.

The fourth method consisted of concentrating the slop to the maximum viscosity that would permit spraying, and burning it in a combustion chamber with gas. The slop was concentrated until it contained approximately 15% solids and was sprayed into the top of the combustion chamber, described under equipment. A gas flame was entering the combustion chamber at the same opening as the slop and impinging against the baffle in the chamber. The spray of slop was directed against the hot baffle. On striking it, the water in the slop was evaporated and the solids burned.

The steam and carbon dioxide left the chamber thru the opening in the conical end.

The slop was concentrated in open kettles and a relation between viscosity and per cent solids determined. The following conditions and standards were used. The viscosity was taken as the time in seconds for a 25 ml. pipette to empty itself under the pressure produced by the head of slop in the pipette. The temperature of the slop when these viscosities were taken was maintained at 190°F.

Figures V and VI show the relation between the viscosity and per cent solids for corn and wheat slop.

The data from the above viscosity-per cent solids determination were used in determining the optimum solid content of the slop to be sprayed into the combustion chamber.

DATA AND RESULTS

TABLE V

PRECIPITATION AND REMOVAL OF SOLIDS IN DISTILLERY SLOP

<u>Sample No.</u>	<u>Treatment</u>	<u>Results and Comments</u>
1	.5% $\text{KAl}(\text{SO}_4)_2$, .1% NaOH	No Good
2	.5% $\text{KAl}(\text{SO}_4)_2$, 2.5% lime, .06% NaOH	No Good
3	1% lime	Filter rate good, filtrate turbid
4	2% lime	No Good
5	3% lime	Suspended solids removed, poor filter rate
6	4% lime	Filtered easily with 2% celite, filtrate clear
7	5% lime	Inferior to 6
8	1% lime, .5% $\text{KAl}(\text{SO}_4)_2$	Average rate, clear filtrate
9	2% lime, .5% $\text{KAl}(\text{SO}_4)_2$	No Good
10	3% lime, .5% $\text{KAl}(\text{SO}_4)_2$	Average rate, colored filtrate
11	4% lime, .5% $\text{KAl}(\text{SO}_4)_2$	Good rate, free of suspended solids
12	5% lime, .5% $\text{KAl}(\text{SO}_4)_2$	Average rate
13	.45% NaOH	No Good
14	.9% NaOH	No Good

TABLE V - (Continued)

PRECIPITATION AND REMOVAL OF SOLIDS IN DISTILLERY SLOP

<u>Sample No.</u>	<u>Treatment</u>	<u>Results and Comments</u>
15	1% $KAl(SO_4)_2$, .45% NaOH	Rate good with celite, filtrate clear
16	1% $KAl(SO_4)_2$, .9% NaOH	No Good
17	1% $KAl(SO_4)_2$, 1.85% NaOH	No Good
18	Filtrate from No. 6 treated with $KAl(SO_4)_2$	Caused precipitation, reduced dissolved solids from 1.5% to 1.1%
19	1% $KAl(SO_4)_2$, 4% lime, stand 18 hrs.	Rate average, filtrate turbid
20	34 lb. slop treated with 34 gms. NaOH allowed to stand several hrs.	Sparkler filter, results no good
21	Centrifuged as received for 10 min. at 1700 r.p.m.	No Good
22	1% NaOH, centrifuged, 25% by volume of saturated Alum solution, centrifuged 5 min.	Best of all centrifuged samples
23	.04% NaOH, centrifuged 5 min. 25% by volume Alum solution	No Good
24	1% NaOH, 25% Alum solution	No Good
25	.2% NaOH, 25% Alum solution	No Good
26	.3% NaOH, 25% Alum solution	Good coagulation
27	.4% NaOH, 25% Alum solution	No Good

TABLE V - (Continued)

PRECIPITATION AND REMOVAL OF SOLIDS IN DISTILLERY SLOP

<u>Sample No.</u>	<u>Treatment</u>	<u>Results and Comments</u>
28	.5% NaOH, 25% Alum solution	No Good
29	.09% NaOH, boiled .5 hour stand 12 hrs.	80 mesh screen removed most of suspended solids
30	.18% NaOH, boiled .5 hour stand 12 hrs.	Inferior to No. 29
31	.45% NaOH, boiled .5 hour stand 12 hrs.	Inferior to No. 29
32	Slop brought to pH of 4.3 with NaOH, boiled .5 hour stand 12 hrs.	80% of suspended solids were removed by screening with 60 mesh screen

TABLE VI

COAGULATION AND PRECIPITATION OF THE SOLIDS IN DISTILLERY SLOP

<u>Sample No.</u>	<u>Treatment</u>	<u>Results and Comments</u>
1	5% NaCl and lime, electrolyzed 10 min.	Fair
2	2% NaCl and lime, electrolyzed 10 min.	Fair
3	1% NaCl and lime, electrolyzed 10 min.	Good, rapid settling rate
4	2% NaCl and lime, electrolyzed 30 min.	Poor
5	1% NaCl, electrolyzed 5 min.	Poor
6	Electrolyzed 10 min.	Poor
7	2% CaCl_2 and lime, electrolyzed 10 min.	Poor
8	5% NaCl, electrolyzed 10 min.	Poor
9	Chlorination	Fair
10	2% NaCl and lime, electrolyzed 20 min.	Fair
11	1% NaCl and lime, electrolyzed 20 min.	Fair
12	.5% ammonium Alum (stand 24 hrs.)	Poor
13	100 p.p.m. FeCl_3 (stand 24 hrs.)	Fair
14	1% NaCl electrolyzed	Good, 80% of volume decanted, free of suspended solids

TABLE VI - (Continued)

COAGULATION AND PRECIPITATION OF THE SOLIDS IN DISTILLERY SLOP

<u>Sample No.</u>	<u>Treatment</u>	<u>Results and Comments</u>
15	33% volume evaporated lime added	Poor
16	33% volume evaporated	Poor
17	1% NaCl (stand 18 hrs.)	60% volume decanted, best removal of suspended solids
18	5% by volume formaldehyde (stand 18 hrs.)	Poor
19	.5% CaCl ₂ , electrolyzed 15 min.	Fair
20	1% CaCl ₂ , electrolyzed 10 min.	Fair
21	5% by volume concentrated H ₂ SO ₄ (Stand 18 hrs.)	Poor

.5% of lime was added to the samples above that specified lime treatment

FIG. V. VARIATION OF VISCOSITY WITH SOLID CONTENT
FOR WHEAT SLOP

FIG. VI. VARIATION OF VISCOSITY WITH SOLID CONTENT
FOR CORN SLOP

Fig V Corn slop

The results from the first method for the disposal of distillery slop by chemical precipitation and filtration, did not indicate that this method, as applied in these tests, could be used profitably on a commercial scale. The filtration rate is in general very poor. Even the best filter rates obtained with the use of sil-o-cel and celite diminished rapidly as the thickness of the cake became appreciable.

The second method for the disposal of distillery slop by electrolytic coagulating and settling, could be used commercially to reduce the duty of the evaporators. The cost of the sodium chloride and the current used in the electrolysis would be considerably less than the cost of evaporating the liquid that can be decanted in this method. The method, of course, was devised to be used during the emergency and would be replaced with evaporators, once they are obtainable. The recovery of the soluble solids is very important when apparatus that is capable of doing it can be obtained. The price that these solids command as cattle feed can not be ignored by the distiller.

The third method of disposal by mechanical separation of the solids from the liquid, did not show promise as a commercial process from the results obtained with the De Laval type of centrifuge. It was very difficult to obtain a clear effluent with this method, and to do so at all required an extremely low rate of feed. If the suspended solids could be removed completely, the disposal problem

would not be complete. The effluent has not had its B.O.D. partially destroyed, as happens in the second method, but has a value as high as the initial. The disposal of the effluent could be solved in the case of some distilleries by pouring it on the ground and allowing it to be absorbed and evaporated. With others, located close to centers of population, it would require an additional process.

The fourth method, of burning the slop with flue gases in a combustion chamber, is cheap and effective. It offers a method of complete disposal at a very low initial cost. If stack gases could be used instead of a gas burner, as was used in these tests, the operating cost would be negligible. There is one disadvantage which would limit its use to the emergency period. None of the solids, either soluble or insoluble, are recovered. During normal times, this would constitute a considerable loss for any distiller.

CONCLUSIONS

The results show that removal of the solids in distillery slop by filtration is not feasible in a press type of filter. The rate of filtration diminished too rapidly with an increase in cake thickness. It is possible, however, that an Oliver type filter could be used successfully. With this type of filter the cake would not be allowed to accumulate and reduce the filtration rate.

The second method of electrolytic coagulation and settling of the solids in distillery slop was intended as an emergency method. It will enable some distilleries to handle their increased waste output with their present evaporator capacity, at a time when it is impossible to obtain evaporators to increase the capacity of their waste disposal facilities.

The third method, of mechanically separating the insoluble solids in the distillery slop from the liquid, did not give satisfactory results with a De Laval centrifuge. It is possible that centrifuges of other types would give better results. This method was tested in the full realization that it was impossible to separate the solids completely from the slop, but it was hoped that enough of them could be removed to allow the liquid to be poured on the ground and absorbed.

The fourth method, that of burning the slop, can be used effectively and cheaply. This method will probably not be used by the large distilleries when the emergency is over, but it may be used permanently by the small distiller

who cannot afford the cost of an evaporator installation.

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DEHYDRATION OF BEEF BY
INFRA-RED RADIATION

INTRODUCTION

The objective of this investigation was the development of a process for the dehydration of beef that would not cause the usual crusting and darkening that are experienced with the present commercial processes. The use of radiant heat in these experiments was the first known attempt to utilize this method, infra-red radiation, of energy transmission for the dehydration of foods. These tests were, consequently, of a preliminary nature but should show if dehydration of food by this method is a solution to the problem.

HISTORICAL

Dehydration of foods has been of major importance only since the outbreak of war. The critical shipping shortage has made it imperative that the burden on our transportation facilities be reduced as much as possible. By removing all bone and moisture from the meat, the weight can easily be reduced to one-fourth of the original value.

As yet no method has been perfected that will give a product that compares favorably with fresh meat in flavor and tenderness, but these disadvantages may be overcome with additional research. It must be remembered that this problem is relatively new, having been of importance only recently, and may recede in importance with the end of the war.

Swift and Company (1) have probably conducted more research on the dehydration of meats than all other firms combined. Their work resulted in the design of a special steam tube dryer that successfully dehydrates the meat without the usual crusting. However, to do this, the meat is first cooked to make the release of the water more spontaneous.

So far as could be determined, no attempt had been made to dehydrate meat with radiant energy in the form of infra-red radiation.

THEORETICAL

The paint industry in recent years has been using infra-red radiation as a means of drying films in a very short time.

The problems in the drying of beef can hardly be compared to the problems in the drying of a protective film. However, they have some points in common. Heat to both must be transmitted by either convection or by radiant energy. Conduction as a means of heat transfer to beef causes crusting and hardening that lowers the value of the product.

Convection can be used as a means of transferring heat to either, but relatively small quantities of heat can be transferred in this manner and then only with great losses.

Radiant energy can be transferred with a very small loss, and a high concentration of energy can be obtained in a definite area in a very short time. This makes it desirable as a means of drying beef.

Infra-red rays can be used for drying because the rays are converted into heat when they strike an object. Some materials transmit most of them while others reflect or absorb them. Air will transmit infra-red radiation with a very small conversion, polished silver will reflect them, while a very thin layer of water will absorb them almost quantitatively.

Beef will absorb these rays and convert them into heat. It is this heat that will produce the dehydration.

EXPERIMENTAL

Equipment:

The apparatus used in this experiment consisted of a Leeds and Northrop potentiometer, two copper-constantan thermocouples, an infra-red radiation unit, a vacuum oven, and a balance.

Procedure:

A cube of beef of one inch dimension, had a thermocouple placed in its center and another one placed about three sixteenths of an inch from the upper surface. The temperatures of these thermocouples were read simultaneously every five minutes, for thirty-five minutes.

After noting the rate of heat transfer in the beef, it was decided to cut the beef into one-half inch cubes.

The sample of beef to be dried was composed of several one-half inch cubes of beef. It was weighed before placing under the infra-red lamp and was removed from the light every five minutes and weighed during the drying period so that a relation between drying time and loss in weight could be obtained.

The total moisture content of a beef sample similar to the one used in the experiment was determined in the vacuum oven, and was found to be 74.4%. The conditions used in the vacuum oven were 29" of vacuum, and a temperature of 60°C. The sample was kept in the oven until it reached constant weight.

D A T A

TABLE VII

TIME-TEMPERATURE RELATION OF BEEF
BEING HEATED BY INFRA-RED RADIATION

<u>Time in minutes</u> <u>sample exposed to rays</u>	<u>Temperature</u> <u>No. 1 Thermocouple</u>	<u>Temperature</u> <u>No. 2 Thermocouple</u>
5	20°C	20°C
10	47.5°C	28°C
15	55°C	35°C
20	66°C	43°C
25	72°C	49°C
30	76°C	54°C
35	78°C	56.5°C

No. 1 Thermocouple is placed 3/16" under surface of beef

No. 2 Thermocouple is placed 1/2" under surface of beef

TABLE VIIILOSS IN WEIGHT OF BEEF DURING
HEATING WITH INFRA-RED RADIATION

<u>Time of heating</u> <u>in minutes</u>	<u>Per cent of weight</u> <u>lost by sample</u>
5	4.8
15	21.8
20	27.8
25	36.5
30	42.8
35	48.5
40	54.0
45	57.2

FIG. VII. LOSS IN WEIGHT OF BEEF DURING HEATING WITH
INFRA-RED RADIATION

Fig 7. 100

RESULTS AND CONCLUSIONS

The results show that beef can be dehydrated quickly and efficiently by the use of infra-red radiation. The transfer of heat from the surface of the meat where the infra-red rays are converted into heat was found to be good. From the data in Table VII, it can be seen that there was only a 20°C temperature differential thru a three-eighths inch thickness of beef.

The quality of the beef obtained in these experiments was superior to that of the dehydrated beef produced by present commercial methods. There was no crusting, and only a slight change in color. There was no indication that the outer layers of beef were carbonized in any degree. The beef, after being dehydrated, could be placed in water for a few hours and restored to its original appearance and tenderness.

The cost of dehydrating beef by this method will no doubt be higher than the cost by present commercial methods, but the improvement in the flavor and quality would justify addition expense.

The time required for the dehydration by this method is considerably less than that required by any other process. In the process developed by Swift and Company (1), the meat is cooked for several hours prior to the dehydration. The time saved by using infra-red radiation for the dehydration would in part compensate for the slightly higher power costs of this method.

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V I T A

out

Wilbur Pirtle Adams, the son of Leslie F. Adams and Nova Nottingham Adams, was born on May 29, 1921. He received his elementary and secondary education in the public schools of Hardin County, Kentucky, graduating from Lynnvale High School at White Mills Kentucky in May, 1938.

Mr. Adams entered the University of Louisville in September, 1938, and received his degrees of Bachelor of Chemical Engineering and Master of Chemical Engineering in May, 1942, and May, 1943, respectively.

He was a member of Sigma Tau, a national honorary engineering fraternity, and of Theta Tau, a national professional engineering fraternity. He was elected scribe of the latter fraternity during his senior year and remained in that office until graduation.

I should like to take this opportunity to thank the Louisville Drying Machine Co., which sponsored this fellowship, and all those who assisted me with my research during the past year.