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<https://doi.org/10.18297/etd/1699>

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UNIVERSITY OF LOUISVILLE

THE UTILIZATION OF GRAPEFRUIT WASTE

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

Howard E. Bumsted

1940

THE UTILIZATION OF GRAPEFRUIT WASTE

Howard E. Bumsted

Approved by the Examining Committee:

Director

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May 21, 1940

FOREWORD

This investigation was a project in the Division of Industrial Research of the University of Louisville. It was carried on in the department of Chemical Engineering under the supervision of Dr. R. C. Ernst. The material in this thesis is of a confidential nature as it is covered by a contractual arrangement with the donor, the Louisville Drying Machinery Company. It is not to be released for publication or to be placed on the shelves of the library except with permission of the company and the approval of the director of the Division.

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ACKNOWLEDGEMENT

The author wishes to acknowledge the kind assistance and helpful guidance of Dr. R. C. Ernst, who directed this research.

ABSTRACT

This investigation was on the utilization of citrus wastes. The possibilities of fermentation of the waste to ethyl alcohol; vinegar; butyl alcohol, ethyl alcohol, and acetone; citric acid; and lactic acid were investigated. The extraction of pectin, citric acid, naringin, and the essential oils was considered as possible by-products along with the production of a breakfast food, organic fertilizers, activated carbon, and a carbon paint pigment.

The fermentation to vinegar, the production of organic fertilizers, activated carbon, and the carbon paint pigment were found to offer the best solutions to the problem.

The use of caustic and calcium chloride as a treating agent to replace calcium oxide was studied and found to make the waste pressable without an aging period.

INTRODUCTION

The disposal of wastes, produced during manufacturing processes, has become a major industrial problem.

This investigation involved the utilization of the waste produced during the juicing of citrus fruits. The fruit is cut in half and the juice expressed and canned. The waste consists of the rind, rag, and any wash water used during the process.

The waste, if untreated, rots and gives off a very offensive odor creating a general nuisance. Therefore, its disposal or utilization is of major importance to the citrus industry.

The author proposed to study the possible methods of utilization of this waste either by the extraction of by-products present in the waste or by converting the waste into suitable by-products.

PRESENT STATUS OF THE TREATMENT
OF CITRUS AND RELATED WASTES

PRESENT METHOD OF TREATMENT:

The waste, consisting of rag, peel, seeds, etc., received from the cannery has a moisture content of 85 to 88 per cent. It is first hammer-milled and then treated with a 10 per cent lime solution to give a product containing 0.30 per cent lime. After the waste is aged in bins for four hours, it is pressed to give a solid of approximately 70 per cent moisture; then it is sent to a rotary tube drier where the moisture is reduced to 10 per cent. The effluent or press liquid is at present merely flushed out on beds and solar evaporated, during which time it undergoes bacterial action.

In Texas this method of effluent disposal is prohibited by law as it attracts the fruit fly, which has done considerable damage to the orchards. The waste, therefore, must be sterilized and buried, greatly increasing the cost of the disposal operation.

SURVEY OF TREATMENT IN SIMILAR INDUSTRIES:

All industries involved in the canning of fruit or vegetables have the same type of waste problems. Wastes from canneries (10) are in general not adaptable to treatment in Imhoff tanks by anaerobic bacteria because the waste is not in a form that can be utilized by the bacteria. Trickling filters and evaporation of the effluent (2) have

not proved satisfactory. These filters become clogged with the solid content of the waste. Most fruit wastes are high in volatile organic compounds which distill out giving the distillate a B. O. D. (biochemical oxygen demand) which is nearly the same as the original waste.

The tomato canning industry (9) has already solved its waste disposal problem by the use of coagulation and settling tanks after treating the waste with sodium aluminate, ferrous sulfate, sodium carbonate, or other coagulants. The sludge is pumped to drying beds, and the liquid has a B. O. D. of 90 to 180, which is comparable to sewage, and can be run to the sewers.

The pineapple industry (1) has also resorted to the same type of disposal system. After it has settled, the deposit is pumped from below the sludge line directly to the fields where it is used as a fertilizer.

It is known that some attempts are being made to solve the citrus waste problem in the United States but as yet no suitable process has been established.

COMPOSITION OF WASTE

The solid consists of two parts--the rag and the peel. The rag is the material which separates the juice sections and also covers the fruit, lining the inside of the peel. The analysis given in Table I (5) was sufficient for the study and therefore no analysis was carried out by the author except to determine the seasonal change in sugar content.

Various compounds are present in the waste in smaller amounts. There are several terpenes, as linonene, pinene, and nerol; two aldehydes typical of citrus fruits, citronellol and citral; two carotnoids, carotene and d-cadinene. Octyl alcohol and octyl aldehydes are also present. Phloroglucinol, probably formed by the hydrolysis of naringin, is present in very small quantities. Glucose, mannose, fructose, raffinose, galactose, levulose, arabinose, and xylose are some of the simple sugars present, also a few complex sugars.

TABLE I
GRAPEFRUIT ANALYSIS

Material	Rag Per Cent	Peel Per Cent
Total Solids	15.61	16.71
Ash	0.75	0.74
Acid as Citric Acid	0.63	0.74
Volatile Oils (Steam Distilled)	0.00	0.43
Ethyl Ether Extract	0.16	0.28
Crude Fiber	1.44	1.71
Protein (N x 6.25)	1.06	1.13
Total Sugars (Invert)	6.30	6.35
Pentosans	0.44	0.83
Calcium Pectate	3.56	3.19
Naringin	0.10	0.40

EXPERIMENTAL STUDY OF WASTE

INTRODUCTION TO EXPERIMENTAL STUDY

The materials present in the waste as shown in Table I were studied carefully and possible products that could be produced were considered. Those that appeared to be economically feasible were studied experimentally.

Fermentation was the most evident solution because of the sugars present. Ethyl alcohol and vinegar fermentations were investigated experimentally. Other fermentations that were considered were butyl alcohol, ethyl alcohol, and acetone; citric acid; and lactic acid. Mr. N. W. Muller conducted the preliminary work on the fermentations and his work will be indicated by an asterisk.

Because of the cellulose and sugars present, the possibility of a breakfast food was investigated. Feeding experiments were conducted on rabbits to determine the detrimental effects of the waste, if any, on the rabbits.

The extraction of citric acid, pectin, essential oils, and naringin present in the waste was considered as possible by-products. In this work the determining factor was the economics of the process.

Since activated carbon is produced at present from several organic wastes the possibilities of its production were investigated. The use of the carbon as a paint pigment was studied in connection with the activation studies.

Modifications of the present process were studied because of patent difficulty experienced by the sponsor of the fellowship. This is under investigation at this time.

A detailed presentation of the experimental results are given in the following chapters.

FERMENTATION STUDIES

I. ALCOHOL AND VINEGAR FERMENTATIONS

After careful examination of Table I, it was evident that the utilization of the sugars present in the rag and peel might offer a satisfactory solution to the problem. The extraction of the sugars as a by-product did not seem satisfactory because a mixture of sugars would crystallize. Fermentation appeared to be the only method of sugar utilization.

The first waste from Florida consisted of four samples: one uncooked clear filtrate and one cooked clear filtrate; one uncooked cloudy filtrate and one cooked cloudy filtrate. On each of these samples the sugar content was determined. The per cent of unhydrolyzed sugars in the cooked clear filtrate was 4.93*. Another sample of cooked clear filtrate was hydrolyzed for 2 hours at 100 °C with 25 cubic centimeters of 0.10 normal hydrochloric acid and the percentage of sugars, determined by Benedict's method, was 14.88*.

When the clear uncooked filtrate was received, fermentation had started. The uncooked cloudy filtrate from the presses gave no signs of fermentation, contained 4.93* per cent of unhydrolyzed sugars and 17.2* per cent hydrolyzed sugars. Upon analysis the cooked cloudy filtrate showed 5.3* per cent of unhydrolyzed sugars and 17.0* per cent of hydrolyzed sugars. The Balling hydrometer readings were nearly identical in the four samples.

Because of the large amount of sugars present,

*Indicates Muller's Work

TABLE II
FERMENTATION DATA

Run	Condition of Run	Balling		Per Cent Alcohol by Vol.	Season of Crop
		Initial	Final		
1*	.10 % NaOH added Cooked at 15 lbs per sq in. 30 minutes	13.90	6.00	4.20	Early Spring
2*	No treatment	12.50	----	4.10	Early Spring
3*	Vacuum distilled to remove oils	-----	-----	4.00	Early Spring
4	Sterilized at 20 lbs per sq in 30 minutes	10.03	2.95	2.00	Early Summer
5	Sterilized at 20 lbs per sq in 30 minutes	10.03	3.00	2.00	Early Summer
6	Sterilized at 20 lbs per sq in 30 minutes	10.03	2.95	2.26	Early Summer
7	Natural Ferment- ation. No Yeast added.	10.03	----	0.90	Early Summer
8	Sterilized at 20 lbs per sq in 5 % yeast added	9.30	----	3.01	Early Summer
9	Sterilized at 20 lbs per sq in 5 % yeast added	----	----	1.20	Late Summer
10	Same as No. 9 but with 50 % water added.	----	----	1.10	Late Summer

* Indicates Muller's Work

the fermentations were started with a good grade of distiller's yeast. The data in Table II were obtained.

The yield in Run 10 was calculated on the basis of waste used and not on the amount of the mixture fermented. It was thought the low yield might be caused by some possible poisoning of the yeast. However, since the yields in 9 and 10 were so nearly the same it was evident that the yeast was not being poisoned.

A Benedict's analysis for reducing sugars was run, and the unhydrolyzed sugar content had dropped to 0.90 per cent. The lack of sugar explained the low alcohol yield indicating a seasonal variation of sugar content.

Since alcohol was not desired as a final product the first three runs were fermented to acetic acid. The yields in Table III were obtained.

TABLE III
ACETIC ACID YIELDS

Run	Per Cent Alcohol by Volume	Per Cent Acetic Acid by Weight
1*	4.20	3.00
2*	4.10	3.10
3*	4.00	2.90

*Indicates Muller's Work

Since commercial vinegar must contain at least 5 per cent acetic acid by weight it is evident from the data in Table III that the vinegar to be marketable would have to be distilled to produce the desired concentration.

From 20,000 pounds of waste the present treatment would yield 13,000 pounds of the press liquid and 7,000 pounds of the solid containing 70 per cent moisture. The solid is dried to 10 per cent moisture and is sold for \$22 a ton. The moist solid from 20,000 pounds of waste would give 2,330 pounds of feed valued at \$25.60.

Based on the maximum yield obtained in the experimental work the 13,000 pounds of press liquid would yield 970 gallons of 5 per cent vinegar which retails at present at \$0.40 a gallon when bottled. This method of disposal would give an additional income of \$388 per 20,000 pounds of original waste. Poore (6) estimates the cost of production of vinegar from waste oranges, containing 9.5 per cent sugars, to be \$0.10 per gallon. He was able to produce a vinegar comparable to the best cider vinegar. If the distilled product were of such a quality that it could be sold as acid vinegar (colorless) it would command a much higher price.

The foregoing would indicate that the waste could be fermented to vinegar. Because of the low yield the fermented material would have to be distilled, and the waste from the bottom of such a still would constitute another disposal problem; however, in plant operation it might be

possible to run this waste to an evaporator, then dry it, and sell it with the feed.

It is usually necessary to have a raw material of constant composition for a successful commercial fermentation. In the production of vinegar the waste must first be fermented to alcohol requiring from 48 to 72 hours and then run through a vinegar generator. This process would call for vats of sufficient size to hold four days production of press liquid.

Figure 1 is a proposed flow sheet of a fermentation plant. This method of disposal is a solution to the problem and would not involve large expenditures for new equipment. The economical problem involved is the market demand for vinegar.

Figure 1
FLOW SHEET OF FERMENTATION PROCESS

II. OTHER FERMENTATIONS

Lactic acid; citric acid; butyl alcohol, ethyl alcohol, and acetone; or any other fermentation requiring sugars as a raw material could be produced from this waste by use of the proper organisms and conditions. The bacteria used in the production of butyl alcohol, ethyl alcohol, and acetone are very susceptible to poisons and are easily killed by other bacteria, yeasts, and molds. Therefore, the waste would have to be sterilized or at least pasteurized to prevent damage to the butyl organisms.

The fermentation of citric acid requires from 20 to 30 days for completion. While the citric acid produced by fermentation could be added to that extracted from the waste, the time required for fermentation would make this method of disposal appear unsatisfactory at the present time.

These fermentations were not considered economically feasible at this time because of the costly control, the seasonal variation in sugar content, and the time required for fermentation.

CEREAL USES AND FEEDING TESTS

It was thought that a suitable breakfast cereal might be produced from the solid waste because of the sugar and cellulose content. The naringin content was high enough, however, to make the material disagreeable to the taste.

The naringin present in the grapefruit gives the fruit its characteristic taste. The naringin content of fruit varies with the season, an average value for the juice being about 0.06 per cent. The bitter taste of naringin can be detected when one part is dissolved in 50,000 parts of water. When the pH of the liquid waste is increased the color changes, and this reaction is probably caused by the naringin since in alkaline solutions it gives an intense yellowish red color. A complete discussion of the properties of naringin is given by Poore (5).

It was found that the naringin would be removed by extraction with ethyl alcohol. After the removal of naringin the material was dried and then toasted. Then some sweet oil of orange was allowed to diffuse through the cereal to give it a pleasant flavor. The product had a pleasant taste but was difficult to chew. To overcome this difficulty a tenderizing process would have to be developed.

Feeding tests in connection with this work were conducted to determine the food value of the material and the effect of naringin on rabbits. Six rabbits were pur-

TABLE IV
DATA ON FEEDING TESTS

Rabbit No.	1	2	3	4	5	6
Diet	A	A	Control	Control	B	B
Color	White	Grey	Grey	Black	Black	Black
Initial Weight	3.813	3.750	3.625	3.625	3.875	3.625
Final Weight	5.687	5.563	5.128	5.625	6.750	5.563
Gain in Weight	1.875	1.812	1.563	2.000	2.875	1.938
<u>Gain in Weight</u> <u>Initial Weight</u>	.492	.480	.431	.553	.742	.535
Dressed Weight	2.983	2.983	2.375	3.000	3.125	2.500
<u>Dressed Weight</u> <u>Live Weight</u>	.517	.528	.457	.534	.463	.450
Condition of Liver, Heart, and Lungs	Good	Good	Good	Good	Good	Good
Feed consumed	15.70	16.37	15.50	16.60	18.05	16.15
<u>Gain in weight</u> <u>Feed Consumed</u>	.119	.111	.101	.120	.160	.120
<u>Dressed weight</u> <u>Feed Consumed</u>	.187	.180	.153	.181	.174	.155

Diet A--75 % Purina Rabbit Chow and 25 % unextracted waste
Diet B--25 % Purina Rabbit Chow and 25 % Extracted Waste
Control--100 % Purina Rabbit Chow

chased, divided into three groups of two rabbits each, and fed on three different diets.

Diet "A" consisted of 75 per cent of the Purina Complete Rabbit Chow mixed with 26 per cent of the dried feed as received from the Florida plant. Diet "B" consisted of 75 per cent of the chow and 25 per cent of the alcohol extracted dried feed which was free from naringin.

The third group was fed on the chow alone. The tests lasted from November 22, 1939, to January 19, 1940. The rabbits were fed every day and weighed every second day. The data in Table IV were obtained. Averages of the data are presented in Table V.

TABLE V
AVERAGE RESULTS OF FEEDING TESTS

Rabbit No.	1 & 2	3 & 4	5 & 6
Gain in Weight	1.843	1.178	2.312
<u>Gain in Weight</u> <u>Initial Weight</u>	.486	.492	.639
<u>Dressed Weight</u> <u>Live Weight</u>	.522	.495	.456
<u>Gain in Weight</u> <u>Feed Consumed</u>	.115	.110	.140
<u>Dressed Weight</u> <u>Feed Consumed</u>	.184	.167	.165

From the data in Table V it is apparent that the

waste has a better food value than the corresponding amount of the chow. Rabbit No. 5 on Diet "B" showed the greatest gain in weight. It is also apparent that the naringin had no ill effects since the rabbits were all in good health and the meat was not tainted with any foreign taste.

OTHER BY-PRODUCTS

SOLVENT EXTRACTION:

The extraction of oils has become a major industry in the last few years. The oils are used for perfumes and flavoring extracts. Such oils are now produced from lemon and orange peels. From Table I the volatile oils are 0.43 per cent of the peel.

Extractions were made using various solvents such as ethyl alcohol, benzene, carbon tetrachloride, acetone, and toluene. The oils were removed in all cases, but in treating with ethyl alcohol all the naringin was removed. The amount of oils present was so small that recovery was not considered economically practicable because of the limited present market.

STEAM DISTILLATION:

Since the oils could be separated by steam distillation it was decided to try that method of oil removal. Other organic compounds present in the rind would also distill out with the steam.

The material was distilled with 40 pounds per square inch steam. Again the oils and terpenes distilled out, but the distillate was very dilute and all efforts at concentration failed. The colloidal suspension formed by these oils in water was very difficult to break.

NARINGIN EXTRACTION:

The naringin present in the fruit represents another possible by-product. While it is present in small quantities its extraction might prove economically feasible.

The method of Poore (5) for the extraction of naringin from grapefruit residue was used. However, since there is no appreciable market for naringin, its extraction was not considered economically important. If naringin should have therapeutic value, thus creating a market, its extraction would not affect any of the other treatments.

CITRIC ACID RECOVERY:

Citric acid is used in large amounts in the beverage and preserving industries. The citric acid content of the grapefruit is very small, and at present nearly all the citric acid is produced from lemon waste and cull lemons. Because of the small amount present in this waste the expense of recovery would not be justified. If the citric acid were recovered a waste disposal problem would still remain. Therefore, it was decided that the recovery of citric acid was not feasible at this time and the investigation was discontinued.

PECTIN RECOVERY:

Pectin is a complex organic compound found in all fruits. It has the power of setting as a heavy gelatinous mass when boiled with acids or treated with alkalies. The preserving industries use large quantities of pectin which is produced from lemon and apple wastes.

The grapefruit residue contains less than five per cent calcium pectate. Again, as in the citric acid recovery a waste material would result and constitute another waste disposal problem.

This investigation was dropped because it did not appear feasible at this time because of the low percentage pectin in the waste and because it did not offer a total disposal treatment.

FURFURAL PRODUCTION:

Furfural is produced from pentosans which are present in the waste in small quantities. While this was true the production of furfural was attempted. The first run was made on the effluent and gave a yield of 0.166 per cent. The second run was made on a mixture of the solid and liquid giving a yield of 0.266 per cent by weight. This study was discontinued because of the low yields.

ORGANIC PHOSPHATES

For several years the producers of fertilizers have been looking for a cheap organic phosphate to use in place of phosphate rock as a fertilizer. The phosphate rock and triple super phosphate are so insoluble that frequently they do not reach the lower roots of the plants. It is thought that an organic phosphate would be more soluble and work farther into the soil (8).

Since this waste contains sugars and cellulose such a phosphate might be produced from it. The phosphoric acid would act as a cleaving agent and would cleave the cellulose down to sugars and react with them to form soluble phosphates. The waste in the untreated state rots, and because it gives off disagreeable odors and attracts large numbers of flies, it creates a general nuisance.

Phosphoric acid was added to the waste in amounts varying from 5 to 20 per cent by weight. The resulting mixtures were aged at room temperature for three weeks. The soluble materials were then determined by washing with water and drying. This process was repeated until the weight became constant. From this procedure the data in Table VI were obtained.

Sample 1 rotted and gave off a very disagreeable odor. Sample 2 showed a slight tendency to mold but did not rot. The other samples did not rot or show any signs of mold growth. If this material were to be produced in a commercial plant the drying would have to be done at

low temperature to prevent charring of the material. From the data in Table VI it would appear that 15 per cent phosphoric acid gave nearly complete hydrolysis since there is no appreciable increase in the soluble content in the 20 per cent sample. The analysis of soluble material will be repeated after a long period of further aging.

TABLE VI
SOLUBLE MATERIAL IN ORGANIC PHOSPHATES

Sample	Per Cent H_3PO_4 by Weight	Per Cent P_2O_5 by Weight	Per Cent Sol- uble Material
1	00	00	79.55
2	5	3.68	80.77
3	10	7.45	82.88
4	15	11.32	84.25
5	20	15.42	84.95

This fertilizer was investigated with the idea of a cheap domestic humus or one that could be used in refertilization of the grapefruit orchards. At present, plants are under experimental growing conditions to test this phosphatic fertilizer. To supply the nitrogen required tobacco dust was added. Then to cut down the strength of the material it was mixed with sand. The final mixture contained 25 per cent tobacco dust, 25 per cent of the phosphate material, and 50 per cent

sand. The experiments have not been in progress long enough to draw any conclusions. Fertilizer production represents a method of total disposal.

ACTIVATED CARBON

Because of the organic nature of the solid it was thought that activated carbon might be prepared from this waste. Activated carbon is rapidly becoming an important chemical, and its uses are wide and varied. Since this would offer a method of total disposal it was investigated.

At present activated carbon is produced from several wastes such as the sulfite waste from the paper industry. It is also produced from sawdust, poor grade coals, kelp (11), and other vegetable materials. A. N. Rao and S. N. Gundu Rao (7) have produced a highly activated carbon from bagasse and N. C. Chokkanna and B. T. Narayanan (3) have also prepared a good carbon from paddy husks. Although there are numerous articles in scientific literature on activated carbon very little information is given about its preparation.

Two methods of production of activated carbon are commonly in use at the present time. One is the use of a chemical activating agent. Such agents are phosphoric acid, sulfuric acid, caustic soda, and the chlorides of zinc and calcium. These agents are usually mixed with the material before carbonizing, and if they do not distill out during the activation they can be washed out of the carbon later and recovered. This process does not involve a large loss in weight of the carbon.

The other important method of activation is by gases. Here the activating gas is passed through the hot

carbon. These gases may be steam, hydrogen, chlorine, oxygen, or carbon dioxide. In this method of activation the loss of carbon may be very high. Fieldner, Hall, and Galloway (4) found that with steam activation the loss in the carbon may be as high as 70 per cent. In their experiments they used a silica tube and passed the gases through the carbon at 920 °C. In plant operation silica tubes would be too expensive, and if iron retorts were used the steam would break down to produce with the carbon, a producer gas, decreasing the amount of carbon.

Very little information is available concerning the actual theory of activated carbon. Some believe the activity is the result of selective oxidation while others believe that it is caused by the large surface area of the carbon.

Another method which should work from a theoretical viewpoint is the treatment of the carbon with solvents. The carbon produced by carbonizing the material without any activating agent is believed to contain some high molecular weight hydrocarbons absorbed in the capillaries of the carbon. It should be possible to produce an activated carbon by treatment with solvents to dissolve these hydrocarbons. This method has never been successful in actual practice.

In the production of kelpchar the kelp is dried and then heated slowly to allow the gases to escape with

a minimum of cracking. After this process the carbon is held at temperatures varying from 900 to 1,000 °C for several hours, producing a highly activated carbon. Since no activating agent is required it is believed by Zerban and Freeland (11) that the salts present in kelp are sufficient to produce the desired activation.

Activated carbons have been produced by mixing the material with kieselguhr or some other diatomaceous earth and then carbonizing. This process would add an impurity to the carbon produced. The infusorial earth is supposed to supply a large surface for the deposition of the carbon and thus give a very large surface area.

Preliminary experiments with the grapefruit carbon showed that it had some adsorptive power toward iodine solutions. To give a rapid method of measuring the activity of the carbon the adsorption of iodine was measured against a standard carbon. Nuchar "C" was the carbon used for this purpose. A value of 1 indicates a carbon of the same activity as the standard and a value under 1, or carbon of lower activity than Nuchar "C".

After careful consideration it was decided to use zinc chloride as the activating agent. Several runs were made using varying amounts of the activating agent. The temperature was maintained at approximately 920 °C which was the optimum temperature found by Fieldner, Hall, and Galloway. The carbon was tested and the results in

Table VII were obtained.

The material was placed in a large iron cylinder with caps on both ends and with an outlet for the carbonization gases. The cylinder was then placed in an electric furnace. The first five runs were made in a furnace which was too small to give even heating to all parts of the cylinder. Runs 7, 8, 9, and 10 were made in a larger furnace which gave a more even heating and the quality of the carbon improved.

TABLE VII
ACTIVATED CARBON DATA

Sample	Per Cent ZnCl_2	Activity
1	2	.276
2	15	.539
3	20	.735
4	25	.817
5	30	.903
6	20	.928
7	20	.931
8	25	1.150
9	25	.935
10	20	1.000

Since it is nearly impossible to keep the moist solid waste from decomposing because of the natural molds

and yeast the material used in Run 1, 2, 3, 4, 5, 6, and 7 consisted of 30 per cent of the dried solid and 70 per cent of the effluent. The yields of carbon based on the solid material averaged 45 per cent by weight. In other words, 100 grams of dried solid feed and 233 grams of the press liquid would yield 45 grams of carbon.

Run 8 was made using fresh waste that had been limed and the press liquid evaporated to a heavy syrup. This syrup was then mixed in the proper proportions with the moist solid and carbonized. The yield in this case was 4.34 per cent of the waste charged.

Run 9 and 10 were made using a freshly prepared waste which had not been limed. The fruit was juiced and the waste ground, then mixed with the zinc chloride and carbonized. Run 9 yielded a carbon with an activity of .935 and gave a yield of 4.4 per cent of the waste charged. Run 10 yielded a carbon with an activity of 1.00 and gave a yield of 4.93 per cent of the waste charged. The yields of Runs 8, 9, and 10, all made on fresh waste, averaged 4.42 per cent.

The current price of activated carbon varies between \$0.10 and \$1.50 a pound depending upon the quality. Muchar "C" has a market price of \$0.85 per kilogram or \$0.39 per pound. In large quantities it would sell for a lower price. Assuming \$0.30 a pound as an average value, 20,000 pounds of waste would yield 884 pounds of carbon selling for \$265.20. Zinc chloride costs \$0.04 per pound

but can be reclaimed from the acid wash.

One run was made by carbonizing the waste, adding the activating agent, and then heating to the activating temperature. The carbon produced was not highly activated, but more experimental work may show that this method would yield a suitable carbon with less of the activating agent.

Since any continuous process is better than a batch process, properties of various metals were investigated to see whether any would withstand the temperature believed necessary for activation. A suitable metal would have to retain its rigidity at a minimum of 1,000 °C since the inner tube of the drum would be in direct contact with the flame. No metal, produced commercially at the present time, has this property, but several metals will remain rigid at 700 °C. During the carbonizing the weight is reduced greatly, and a drum designed to handle the material at the inlet would be much too large at the outlet. It was suggested, therefore, that a continuous process be used for carbonization and a batch operation for activation. Figures 2 and 3 give proposed flow sheets for carbon production.

All equipment, with the possible exception of the primary carbonizing furnace and activating furnace, are built on a commercial basis at the present time. The carbonizing section of the drum must be air tight to prevent loss of the carbon by oxidation, yet allowance must

Figure 2

ACTIVATED CARBON FLOW SHEET

Figure 3
ACTIVATED CARBON FLOW SHEET

be made for the removal of the gases given off during the carbonization. Some work is being done on the design of the necessary equipment.

The gases given off contain some tar and a material resembling a pyroligneous acid from which useful by-products may be recovered. The fixed gases will burn and can be utilized as a fuel.

This method of disposal shows promise and studies in this direction should be continued. More experimental work is necessary, however, to determine the optimum temperature, the best activating agent, and the optimum per cent of the activating agent.

CARBON FOR PAINT PIGMENT

Furing the activation studies some of the carbon had not been activated was turned over to a local paint company for testing. This carbon was the direct product of the carbonization and had not been treated in any manner to remove the ash. The carbon was ground to 120 mesh.

The report from the paint company indicated that this carbon would produce a medium grade black pigment. It did not have a high tinting power, but this was probably caused by the large particles. The sample absorbed 27 grams of oil per hundred grams of pigment compared to 27 for drop black and 72 for lamp black. The gloss of the sample was nearly the same as lamp black.

It was estimated that a pigment of this quality after it had been washed and finely ground would sell for \$0.05 per pound. On the basis of a yield of 5 per cent by weight, 20,000 pounds of waste would yield 1,000 pounds of pigment worth \$50. At present 20,000 pounds of waste would yield 2,330 pounds of feed worth only \$25.60.

This would indicate a possible solution of the problem and would merit more experimentation as it represents a means of total disposal.

MODIFICATIONS OF PRESENT PROCESS

At present in Florida the disposal or utilization of the liquid effluent of the waste is the main problem since the solid waste, when dried, finds a ready market as a cattle feed. It might prove feasible to evaporate this liquid in a multiple effect evaporator until the bottoms became a heavy syrup. This syrup might be run back to the drier and dried with the feed. This procedure would increase the sugar content of the feed because all the carbohydrates would remain in the syrup, and they would be added to the dried feed.

In the present process the waste is treated with lime to make the material pressable. However, to complete this treatment the waste and lime mixture must be aged for four hours. It was desirable to find a substitute for the calcium oxide treatment.

Magnesium oxide, magnesium carbonate, calcium carbonate, calcium chloride, sodium chloride, sodium carbonate, sodium hydroxide, sulfuric acid, hydrochloric acid, and acetic acid were tried as possible treating agents. The acids had no appreciable effect while the magnesium salts had the same effect as calcium salts and required an aging time. The sodium salts also required an aging period and did not seem to free the water but did harden the material. Soda ash was the most effective of the sodium salts.

Mixtures of the salts were then tried. It was

found that if the material was made alkaline with caustic or soda ash and then calcium chloride added the change from a slimy to a pressable material was nearly instantaneous.

Preliminary experiments have indicated that the amount of caustic necessary varies from run to run. The minimum appears to be about 0.2 per cent and the maximum is 0.35 per cent. Within five minutes after the addition of the calcium chloride the waste becomes pressible.

This method of treatment shows promising results and gives a continuous process, eliminating the aging period. It would be advisable to try this work in semi-plant equipment before full scale operations are attempted.

SUMMARY

The investigation consisted of a study of the utilization of grapefruit waste. Fermentations, with special emphasis on alcohol and vinegar; extraction of the oils and naringin; steam distillation of the oils and terpenes; possible by-products, such as citric acid and pectin; organic phosphates for fertilizers; carbon for pigments; and activated carbon were studied as possible utilizations of this waste.

Certain modifications of the present process were also studied. It was found that magnesium salts can be substituted for calcium salts as treating agents and that if the waste is made alkaline before the addition of calcium chloride, the reaction is nearly instantaneous.

The press liquid was fermented to alcohol which in turn was converted to acetic acid. Based on the highest yield obtained during the experimental work 970 gallons of vinegar and 2,330 pounds of feed were obtained as a product from 20,000 pounds of the waste. Since vinegar sells at \$0.40 a gallon this would give an additional income of \$388.

The organic fertilizer shows promising results, but nothing definite can be said yet since experimental results have not been completed.

The carbon studies have been divided into two divisions--black pigments and activated carbon. A medium grade pigment can be produced from this waste. On the basis of a 5 per cent yield, 20,000 pounds of waste would

Figure 1
DIAGRAMATIC SUMMARY

give 1,000 pounds of carbon valued at \$50.00.

In the activated carbon studies, a yield of 4.42 per cent was obtained. Thus, 20,000 pounds of waste would yield 884 pounds of activated carbon. Based on a selling price of \$0.30 per pound this carbon would be valued at \$265.20.

The extraction of the oils present was not considered feasible because of the low yields and the difficulty of separation. The other fermentations were discontinued because of low yields, rigid control necessary, and the long periods of fermentation required. At present the by-products that could be produced either have no appreciable market value, or are supplied more cheaply from some other source.

Figure 4 is a diagrammatic summary of the work showing the different methods of utilization and the estimated value of the product from each treatment.

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FELLOWSHIP ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation for the fellowship assistance given by the Louisville Drying Machinery Company and the helpful advice of Mr. A. W. Lissauer.

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