

A METHOD OF PREPARING FRUIT CONCENTRATES
FOR USE IN ENOLOGY

by

WILLIAM FRANCIS FILZ

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1949

APPROVED:

Professor of Food Technology

In Charge of Major

Head of Department of Food Technology

Chairman of School Graduate Committee

Dean of Graduate School

ms 59749

ACKNOWLEDGEMENTS

The writer greatly acknowledges the help of Mr. George Lorant in describing the evaporator used in the General Foods research laboratory which was a basis for the modified apparatus described herein.

Acknowledgements are also extended to Dr. Ho-Ya Yang for his suggestions and encouragement while conducting this investigation and to Mr. Kenneth Duggan for his generous and efficient assistance in photographing the apparatus.

TABLE OF CONTENTS

I. INTRODUCTION.....	1
II. APPARATUS	
Literature Survey.....	4
Details of Construction	
a. Constructing Heat Exchanger.....	8
b. Constructing the Liquid Circuit.....	15
c. The Vapor Condensing Train.....	17
Operational Data	
a. Boiler Performance.....	21
b. Performance of Condenser Train..	27
c. Overall effectiveness.....	29
III. PREPARATION OF CONCENTRATE	
Literature Survey.....	38
Preparation of Fresh Juice.....	51
Preparation of Concentrates.....	53
IV. FERMENTATION OF CONCENTRATES	
Pure Culture Preparation, Inoculation and Rates of Fermentation.....	55
V. SUMMARY AND CONCLUSION.....	67
VI. PROPOSALS FOR FUTURE WORK.....	70
BIBLIOGRAPHY.....	72

LIST OF TABLES

<u>Tables</u>	<u>Page</u>
I. Data on Evaporator and Its Operation Using Distilled Water.....	32
II. Concentration of Essence Fractions.....	35
III. Effect of Concentration on Fresh and Clarified Juices.....	54
IV. Rates of Fermentation of Clarified and Unclassified Musts.....	56
V. Rate of Fermentation of Apple Juice Using Apple Concentrate for Amelioration.....	59
VI. Rate of Fermentation of Apple Juice Using Sucrose for Amelioration.....	59
VII. Fermentation Rates of Four Strains of <u>Saccharomyces elipsoideus</u> on 30 Degree Brix Apple Concentrate.....	64

LIST OF FIGURES

<u>Figures</u>	<u>Page</u>
1. Heat Exchanger.....	14
2. Liquid-vapor Separator.....	16
3. Water Condensing Unit.....	18
4. Essence Recovery Unit.....	20
5. Heat Exchanger in Operation.....	24
6. Liquid-vapor Separator in Operation.....	26

SCALE DRAWING

Glass Recirculating Vacuum Evaporator.....	31
--	----

A METHOD OF PREPARING FRUIT CONCENTRATES FOR USE IN ENOLOGY

I. INTRODUCTION

A problem of major interest to the fruit grower and processor in the Pacific Northwest is to find more market outlets for fruit such as satisfactory methods of preparing fruit juice concentrates. Two factors have focused attention on the problem and they are (1) the demand for western grown fruit by eastern confectioners and jelly makers, and (2) the burdensome increase in freight rates on shipping this material to the east coast. Attempts at preparing concentrates have not met with much success in the past due mainly to the lack of proper equipment. The desirable volatile constituents were lost and the resulting product had scorched flavors and little aroma characteristic of the original product. This renewed interest in concentrates has been further spurred by recent advanced developments in methods for making concentrates (9, 3) and recovering the materials responsible for taste and aroma in fresh fruits (26).

These same problems have existed in attempting to prepare concentrates on a laboratory scale. There has been a definite need for a small evaporating unit to effectively concentrate a fruit juice and to recover

the volatile essence fractions of the juice. The construction of such an apparatus is one of the objectives of this investigation.

The techniques of preparing jellies and similar products from fruit juices and concentrates are well established and are now familiar knowledge. Another application of such concentrates is to the field of enology. Very little work has been done to improve the relatively weak natural flavor of some wines such as apple and other pome fruits now on the market. The use of a concentrate of these fruit juices instead of ameliorating with cane or beet sugar might well improve their flavor. This would be especially true if the volatile essence responsible for the characteristic flavor of the fruit could be separated during the concentrating process and returned to the wine after fermentation of the concentrate. The only research similar to this idea is discussed in a United States patent issued to William A. Rooker in April, 1947 (33'). His invention relates to an improved fermented juice product and the process for making such a product. In general, this invention comprises (1) expressing the juice from fruit, then distilling the aromatics from the juice and collecting them, next (2) subjecting the juice remaining after distillation of the aromatics to fermentation, and finally (3) recombining the aromatics distilled off

with the fermented juice, after fermentation has ceased. In this process only from one to five per cent of the volume of the unfermented fruit juice is distilled off since this amount is known to contain the major portion of the aromatics. This amount of distillation does not change the solids concentration a great deal. According to the inventor this process is applicable to the manufacture of cider, champagne, wines, and brandy. The above method is a process patent only and does not describe any equipment for performing the distillation and makes no mention of the use of concentrates in the fermentation process.

The objectives in this investigation then, are two-fold. First, to construct a laboratory-size evaporator for the manufacture of high quality concentrates and second, to study the fermentation of said concentrates with regard to speed of alcohol production and quality of the fermented product.

II. APPARATUS

Literature Survey

For this study of fruit concentrates and its application to enology, it was necessary to obtain a means of preparing concentrates which would resemble the fresh and natural product as closely as possible with regard to retention of color, flavor and aroma. The large size and high cost of existing evaporators made it desirable to construct an evaporator on a research or laboratory scale. To eliminate any possibility of off-flavors due to metallic contamination and to attain complete visibility in a piece of research apparatus, the author decided to construct the evaporator entirely of glass.

A review of the literature revealed very little information on the unit operation of evaporation on a laboratory scale. Prior to the development of part glass laboratory evaporators by Kemmerer (21), and by Mitchell and co-workers in 1944 (27) the most efficient laboratory evaporator was of the type described by Davis (12). This was the familiar setup consisting of a large Claisen flask used as the boiling flask and a second large distilling flask fitted to the side arm of the Claisen flask being used as the condensate receiver.

By means of a separatory funnel fresh liquid could be added to the boiling flask; by an additional tube sealed to the inside of the receiving flask and made to dip below the condensate level the condensate could be continuously removed. Boiling temperatures of 50 degrees Centigrade were obtained by using a water aspirator vacuum on the system. The amount of material that could be concentrated in one operation was limited by the capacity of the boiling flask due to the difficulty of continuously removing the concentrate. Due to the aforementioned limitation, the evaporative surface, the desire to trap off the more volatile fractions, and the speed or rate of evaporation this type of evaporator was abandoned.

Kemmerer constructed a laboratory evaporator used to recover or concentrate volumes of liquid that are too small for pilot-plant equipment but large enough to be very tedious with the usual laboratory distillation apparatus. This unit consisted essentially of three plain glass condensers coupled in parallel serving as the heating units, a splash bulb serving as a vapor liquid separator, and a copper surface condenser for solvent recovery. This unit was reported to have an evaporative capacity of 10 to 12 liters of water per hour under a vacuum of 25 millimeters and a temperature

of 40 to 50°C. and from this standpoint would have fulfilled the requirements for a small size evaporator. However, due to the difficulty in using steam under pressure and the metal condenser of small surface area it was decided not to construct one of this type.

An evaporator designed and constructed by Mitchell and co-workers seemed to be best suited to the problem. The discussion of their apparatus in the literature consisted only of the fluid circulating system with no information concerning condensation or fractionation of vapors. The boiler or heat exchanger consisted of five Pyrex tubes approximately 18" long and 3/8" O.D. (outside diameter). Four of the tubes were evenly spaced around the periphery of a balloon flask 2 1/2" in diameter and one in the center of the flask. The unit was encased in a 3" I.D. (inside diameter) metal jacket with a single steam inlet at the top and the condensate outlet at the bottom. The remainder of the unit consisted of a 8 1/2" diameter flask with a tangential inlet for the heated juice and a 4" flask above the larger one acting as a trap for entrained liquid and foam. One inch diameter Pyrex tubing completed the circulation system. An inlet for fresh liquid was located at the lowest point in the system just in front of the boiler. Although not shown in their drawing the authors stated

that a liquid draw-off could be located at any point in the liquid return line. For their apparatus the authors obtained an evaporation rate of 12.15 lb./hr. at a pressure of 103 mm. of mercury and a heat transfer coefficient of 142 Btu/SqFt/Hour/ $^{\circ}$ F. For these data the temperature of the circulating water was 126 $^{\circ}$ F.

This all-glass circulating unit was ideally suited for the problem at hand and it was decided to construct a unit with the afore mentioned type of circulating system.

Details of Construction

The apparatus was constructed entirely of Pyrex laboratory glass (Pyrex brand chemical glass No. 774 of the Corning Glass Works). When the worked areas are properly annealed, this glass is reasonably resistant to mechanical shock and quite resistant to thermal shock. The very low coefficient of thermal expansion, 32×10^{-7} inches between 19 and 350°C. accounts for the resistance to thermal shock. The mechanical strength of Pyrex, or of any glass, is dependent on the thoroughness of strain removal. Extreme care was taken during the annealing of each worked area in the apparatus. Even though this piece of equipment was not intended for operation at pressures greater than atmospheric, the pressures are of sufficient magnitude to warrant this extra care in fabrication.

a. Constructing the Heat Exchanger.

Basic and advanced operations in the manipulation of glass and the fabrication of glass equipment are adequately described elsewhere (14, 18, 35, 40). The construction of the heat exchanger was not described in any literature on glass blowing and involved details of sufficient importance to discuss herein. Eighteen pieces of 1/4" O.D. tubing were geometrically arranged in two concentric circles, the outer one being 2 1/2" in

in diameter. Two jigs were made of 2" wood stock with 1/4" holes bored completely through one jig and one half the distance through the other. A hole of smaller diameter was then drilled the rest of the way through each of the 18 holes. This left a collar to support the tubes and the smaller hole served as an entrance for a blowing tube. This jig served as the bottom support for the tubes and the other as a spacer farther up the length of the tubes. Due to the relatively low coefficient of heat transfer for standard wall Pyrex tubing a special thin wall stock of 0.020" thickness was employed. Two 250 m. Erlenmeyer flasks were used as headers and this presented the problem of sealing this very thin walled tubing to the relatively thick walled flask bottom. To overcome this difficulty 2" pieces of standard wall tubing were joined to each end of the thin wall lengths. This gave a total tube length of 20" with 16" of thin walled tubing as the effective heat exchange length.

For a temperature differential of about 80°C. on the boiler tubes a simple calculation shows the expansion to be about 0.005" for the 20" length. In order that the stress due to this elongation might be alleviated it was decided to give the tubes a slight offset or curve at the center. This would cause any expansion to be manifest in a direction other than parallel to

the axis of the bore of the tube. So that all the tubes would have the same degree of curvature a form was constructed of asbestos board. It consisted of one piece 20" long and 1/4" thick with the convex curve in the center and two pieces 20" long, 5/8" thick with the same degree of curvature in the center. The three pieces were screwed together with the thin piece in the center and about 1/4" below the level of the other two. This left a depression the size of the tubing and of the desired curve. The prepared tubes were laid on the form, one at a time and held in position by a rubber band at each end over the tube and the form. A brushy gas-oxygen flame was played over the entire curved area and as the glass softened it was pressed to the shape of the form by the tension of the rubber bands. The tubes thus formed were set in the jigs the latter being fastened to a ring stand for support. The curved areas of the tube were all turned in the same direction so as to keep the maximum diameter of the unit as near 2 1/2" as possible.

Even though a spherical shaped flask is the stronger under vacuum it was decided to use Erlenmeyer flasks for the headers because of the larger flat area on the bottoms and because extremely high pressures were not to be employed. An extension tip was made from brass tubing for a pre-mix gas-oxygen hand torch for reaching

down through the neck to the bottom of the flask. To supply fresh air to the flame and to remove the products of combustion two side arms were sealed opposite each other near the bottom of the flask and a stream of air blown through the flask. With the flask clamped in position over the prepared tubes the operation was as follows:

1. Heat the area in the bottom of the flask directly over the tube to be sealed on.
2. With a blunt carbon rod press the softened hot glass into contact with the tube.
3. With the blowing tube inserted in the hole of the jig containing the tube being worked, reheat the contact area and blow out a kidney.
4. Break away the excess glass and fire polish the joint; flare out the hole if necessary using a tapered carbon reamer.

This operation was repeated until all 16 tubes had been sealed through the bottom of the flask. During the operation a second torch was played on the flask around the worked area to insure uniform heating and reduce the possibility of strains developing. This process necessitated a helper who further assisted by changing the blowing tube in the bottom jig as new tubes were

sealed into the flask. At this point the whole area was heated to annealing temperature and cooled very slowly. The partially completed unit was removed from the jigs, inverted, and clamped on the ring stand. The other header flask with its two side arms was clamped into position and the operation just described was repeated. This time an extension consisting of a piece of two millimeter tubing six inches long was needed on the end of the blowing tube to reach through the flask and into the tube being worked on the opposite end. The side arms previously sealed on near the bottom of the flask were removed when the operations were completed.

The heat exchange unit at this point consisted of the two header flasks with the 16 tubes sealed between them. In order that advantage could be taken of the visibility in the heat exchanger the jacket for it had to be of glass also. This presented the problem of steam inlets. Inlet tubes could have been sealed to the side of the Pyrex jacket but this would probably have been a source of trouble due to the difficulty of annealing a piece of large diameter and the uneven heating caused by steam entering at these two points. To prevent breakage at this point it was decided to use two separate pieces of tubing for the jacket and connect them with a brass coupling at the center fixing the steam inlets

to the coupling. The outside diameter of the jacket tubing was 4". A piece of brass pipe 2" long was cut from stock 4" O.D. and 1/8" thick. A second ring was made from 1/16" brass sheet to a size of 4" I.D. and 3 1/2" long. The smaller ring was centered inside the larger one and soldered in place. Two 5/16" holes were drilled in the center of the length of the collar and on opposite sides. Two 2" lengths of 5/16" brass tubing were soldered into the holes thus forming the steam inlets in the collar. Then rubber gaskets were placed inside the collar on the shorter piece of brass pipe as a resting place for the glass tubing so as not to have the steam heated metal in direct contact with the glass. The 4" I.D. Pyrex tubing fit fairly snug in this collar but not close enough to be dangerous due to differences in expansion. A few turns of friction tape around the outside ring and onto the glass tubing made a good enough seal so that an aspirator vacuum could be pulled on the jacket. A wooden cradle was built for the jacket supporting it at the center and at each end. Heavy canvas webbing was used on the ends to fasten the large glass tubing securely to the cradles. Pieces of rubber tape were used as cushioning material. The complete unit may be seen in the accompanying photographs. The heat exchange unit was placed

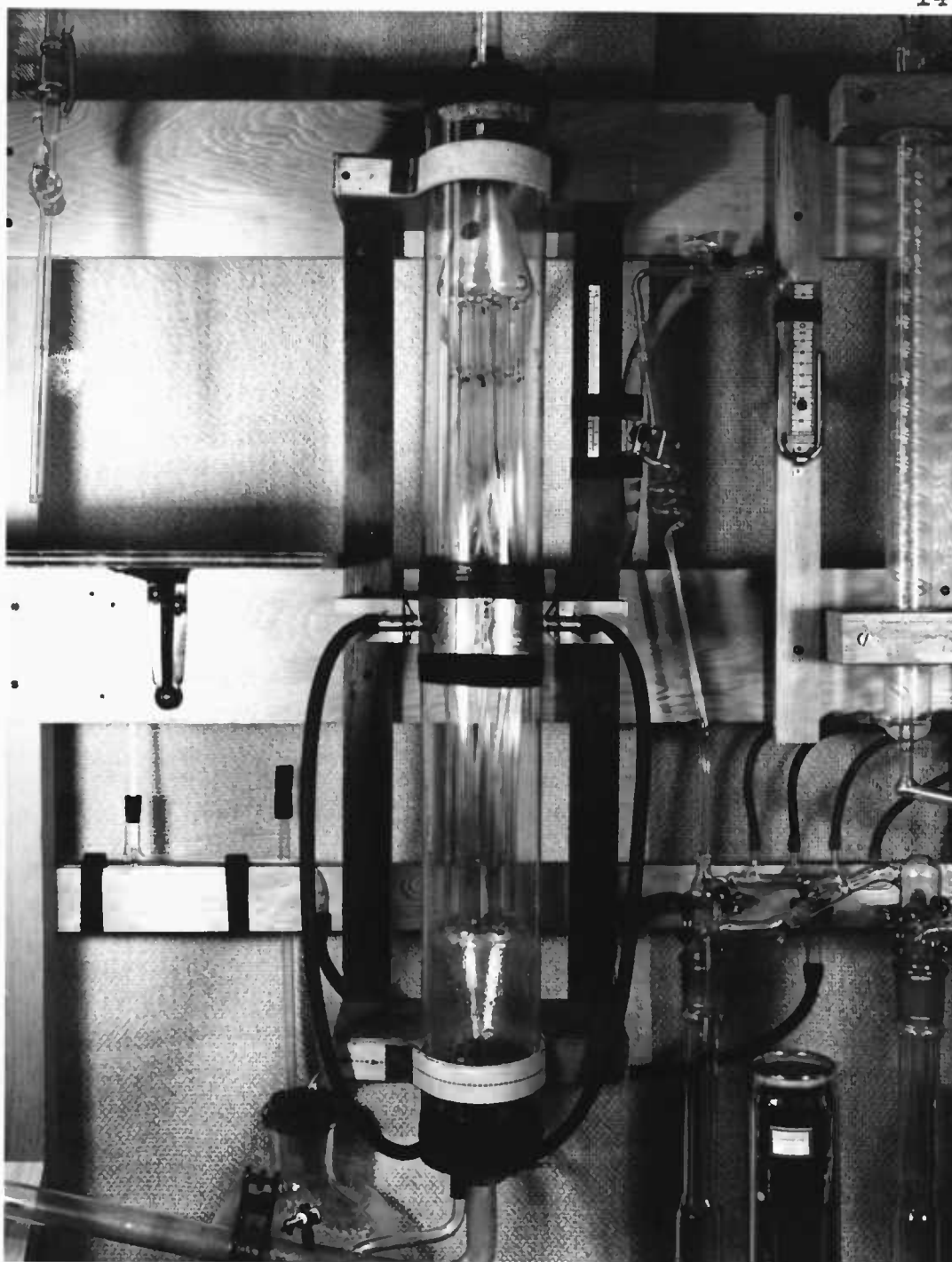


Figure 1. Heat Exchanger

inside the jacket and centered by #15 rubber stoppers bored to fit the necks of the header flasks. One inch hose clamps backed by leather gaskets were placed around the glass tubing extending beyond the rubber stoppers to hold the heat exchange unit firmly in place inside the jacket. Hose clamps were fixed tightly against the tops of the rubber stoppers further securing the stoppers in the ends of the jacket tubing.

b. Constructing the Liquid Circuit.

The liquid-vapor separator consisted of an 8" diameter balloon flask with standard taper fittings welded in the positions shown on the accompanying drawing. By using standard taper fittings the unit could be easily disassembled for cleaning and excessive strains due to ring seals eliminated. The inlet tube to the separator was an extension of the inside part of the standard taper fitting and reached to within $\frac{3}{8}$ " of the inner wall of the flask. Liquid entering at high velocity from the boiler was forced around the inside area of the flask providing ample surface for liquid-vapor separation and evaporative cooling. A trap was made from a 4" diameter balloon flask and fastened by means of a standard taper fitting to the top of the separator.

The remainder of the liquid circuit was completed using 1" O.D. tubing and ball and socket joints as shown

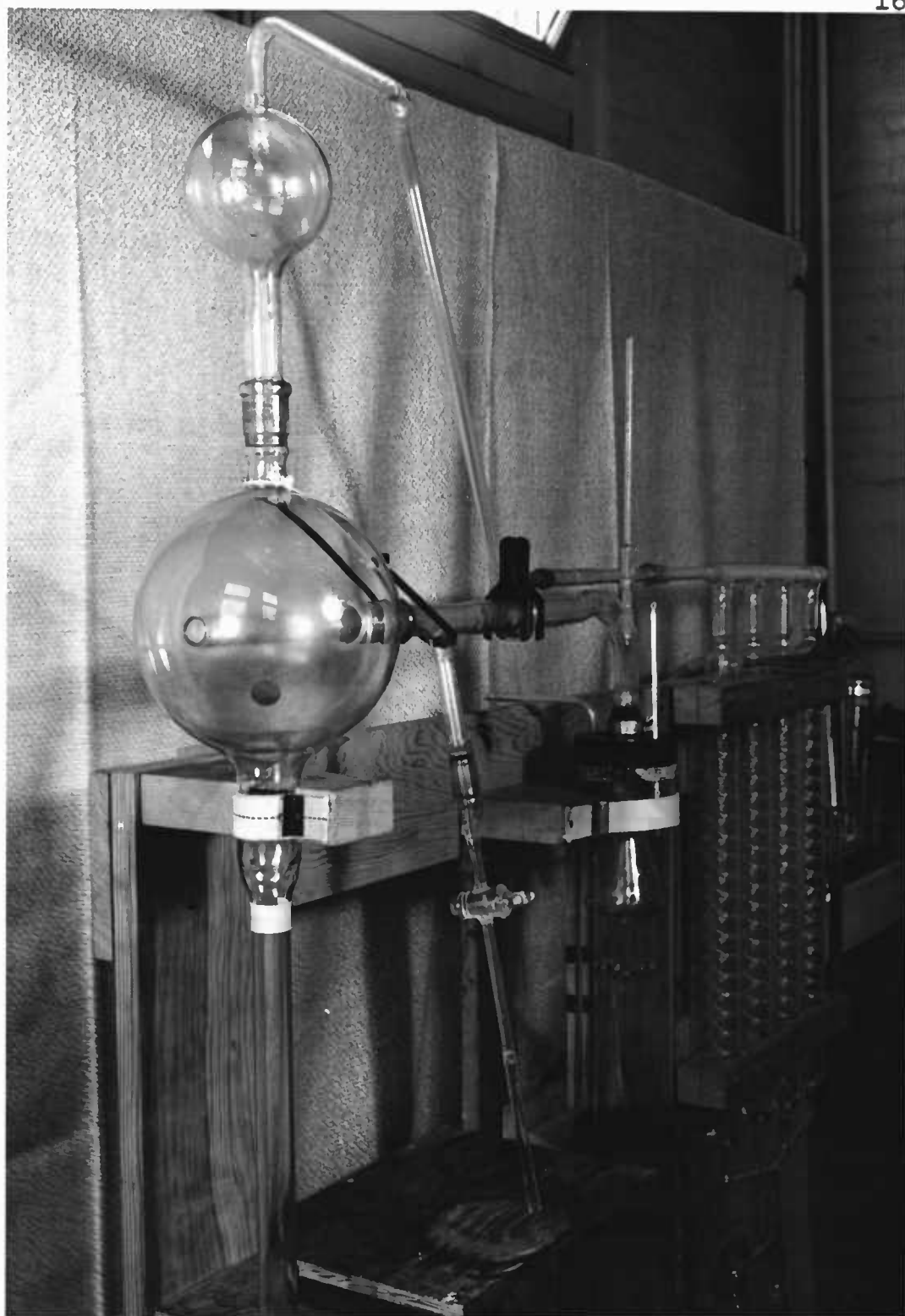


Figure 2. Liquid-vapor Separator

in the accompanying drawing. The ball and socket joints were helpful in overcoming alignment difficulties in mounting the equipment and made disassembling much easier. The liquid-vapor separator was held in place on a wooden cradle by webbing straps in a manner similar to the boiler jacket. The details of this mounting can be seen from the accompanying photographs and drawing.

c. The Vapor Condensing Train.

A slip joint in the vapor line from the separator trap to the bank of condensers helped take up vibrations and other shocks while the unit was in operation; this joint also made it possible to uncouple and remove the trap from the separator for cleaning. The slip joint was sealed by rubber tape.

The vapor condensing unit consisted of four commercial reflux condensers mounted in a special frame. Each condenser was clamped in two places with a sponge rubber cushion between the glass and the wood. The four units were coupled by a manifold of 3/4" tubing at the top and 1/2" tubing at the bottom. The manifolds were completed after the condensers were clamped securely in the frame. The condensing unit was coupled to the vapor line by means of standard taper. A second standard taper was welded to the bottom manifold in the center and at the lowest point to fit into the water

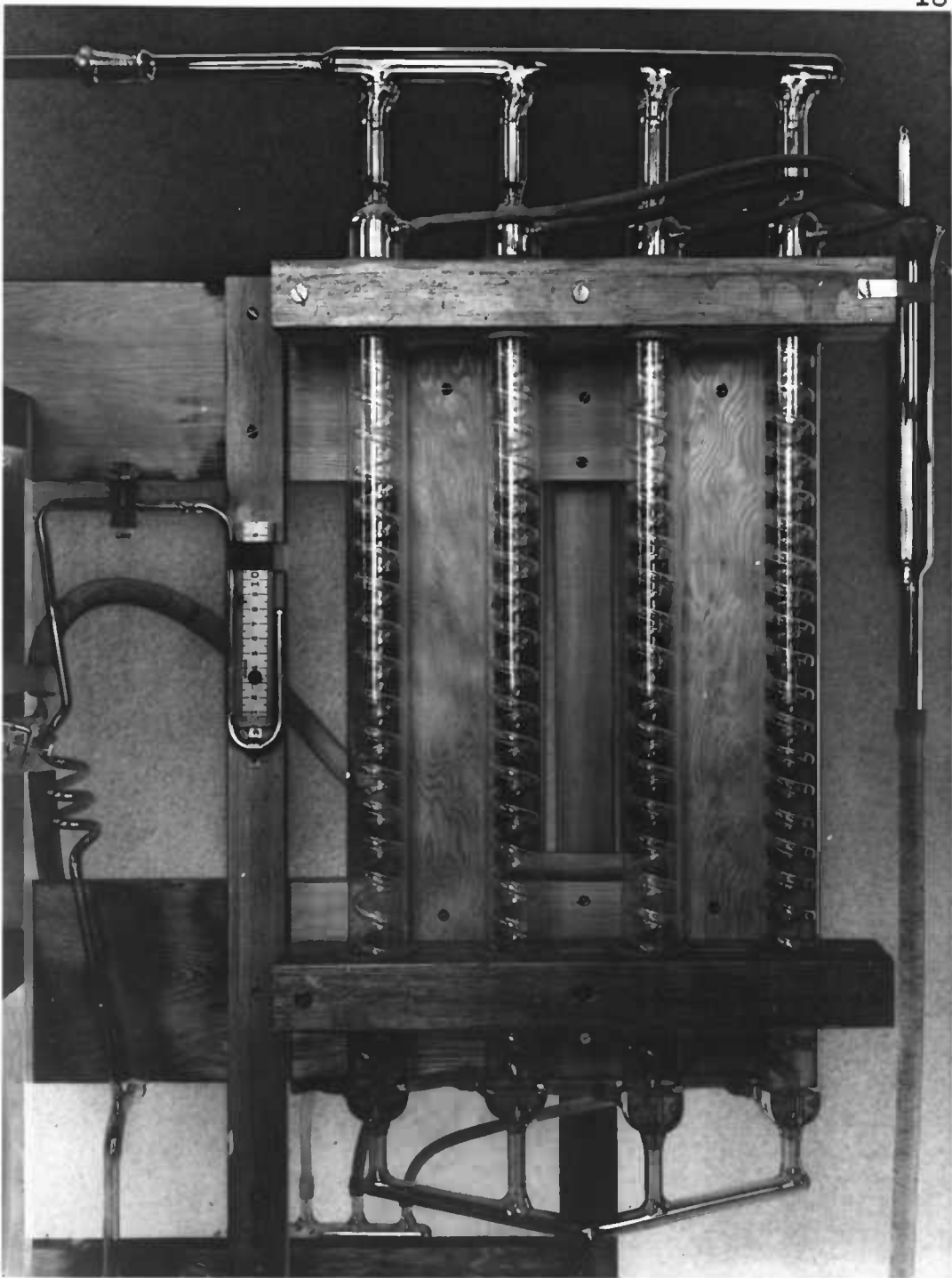


Figure 3. Water Condensing Unit

receiving flask. Directly above the taper a side tube sealed on led to the first trap. This side tube was protected from collecting any condensate by a by-pass. ring seal extending down into the water receiving flask. This receiver was an 800ml. Kjeldahl flask fitted with a standard taper. Two side arms were sealed into this flask in the position shown in the drawing to connect to an auxilliary water receiver.

The fractionating traps were of type four as rated by Sanderson (34). They were designed and constructed in this manner because this type offers minimum obstruction and can be easily taken apart to remove their contents without removal of the whole trap from the system. An outlet tube from the top of the second trap connected to the vacuum pump completed the system. A mercury manometer was inserted in the system through this outlet tube from the trap.

The details of mounting the parts of this apparatus certain points of construction, and the supporting framework can be obtained from the accompanying photographs. The dimensions of the unit may be obtained from the scale drawing.

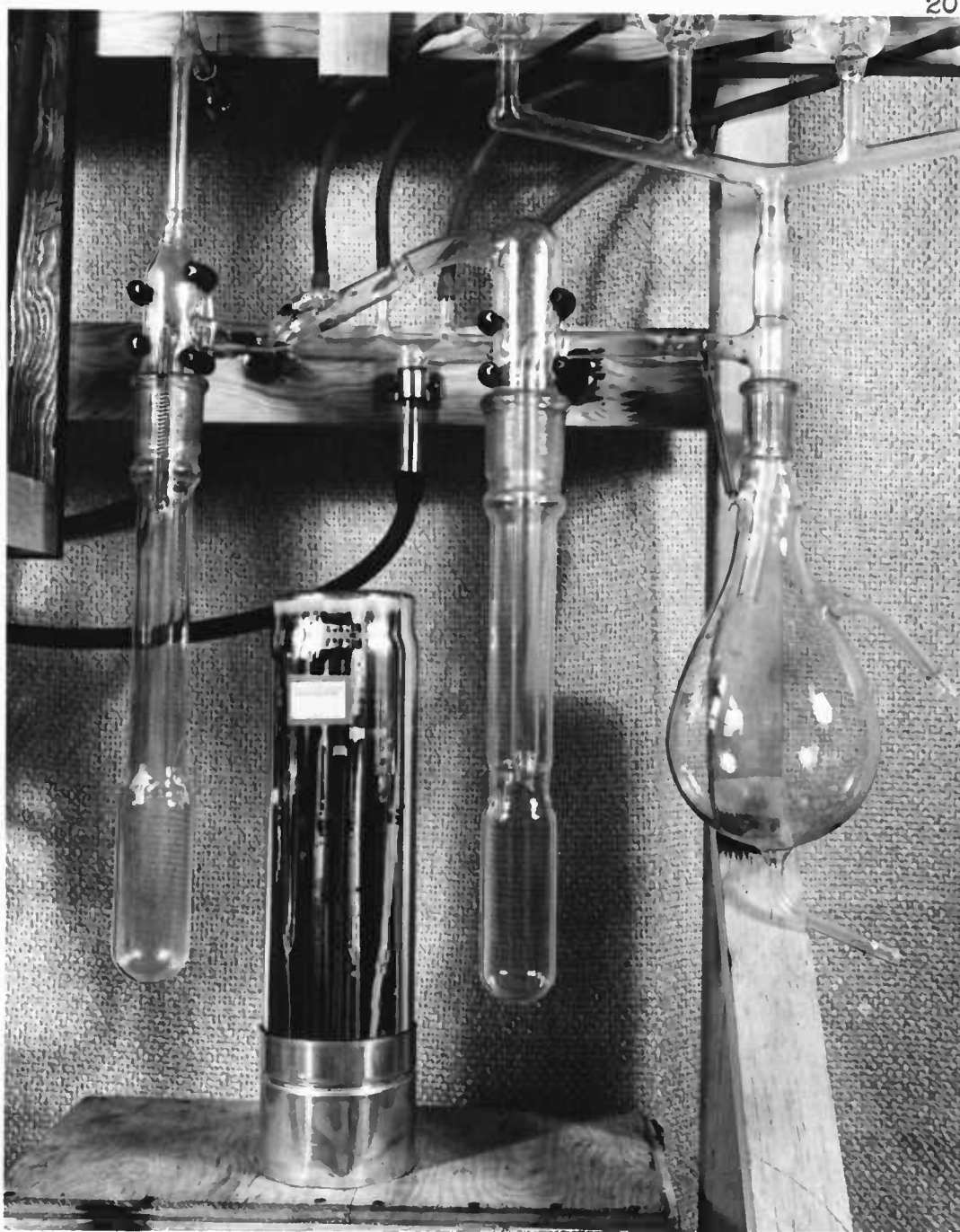


Figure 4. Essence Recovery Unit

Operational Data

a. Boiler Performance

In principle this laboratory model evaporator operates as do most any of the long tube natural circulating evaporators found in the chemical and food industries. The liquid in the heat exchanger tubes boils, and the vapor rising as froth forces slugs of liquid ahead of it at high velocity up the tubes and out into the liquid-vapor separator. As this process is repeated the liquor is rapidly circulated from heat exchanger to separator to return line to heat exchanger and so on over and over. Reavell (32) in a study on the concentration of fruit juices found that in the ordinary method of evaporation where a jacketed pan or where a calandria type pan is used, the temperature of the liquor at the bottom of the pan is higher than the temperature of the liquor at the top owing to the depth of the liquor; in addition to which there is the difficulty that the liquor is in contact with the heating surface, and with relatively little movement for quite a long time. For these reasons he lists the following principles to be carefully observed in concentrating a fruit juice: (1) the liquor must pass continuously through the heating zone; (2) the time of contact

be as low as possible. This evaporator meets all three of these requirements due to the high coefficient of heat transfer realized by the great velocity of the liquid over the heating surface. The character of the flow of liquid and vapor through the tubes insures a complete and constant wetting of the heat exchange surface. Actual boiling within the tubes begins at the position of the steam inlets. The length of the tubes in the lower half of the jacket below the steam inlets act as individual preheaters to a certain extent because the entire jacket is filled with steam.

An analysis of the flow of liquor through the individual boiler tubes is as follows. The level of the liquor in the bottom of the liquid-vapor separator flask is several inches higher than the bottom of the upper header flask and as a result there is a tendency for the boiler tubes to be full constantly. When the evaporator is first put into operation ebullition does take place equally and simultaneously in all the tubes. However after circulation begins the picture is entirely different. As the portion of liquid within the tube directly opposite the steam inlets is vaporized the liquid above this portion is forced ahead of the vapor. This leaves a sudden void in half of the boiler tube. Due to the afore mentioned difference in height of liquid

levels returning liquid immediately fills the void to the bottom of the upper header. This sudden surge of liquid does not become heated sufficiently to be vaporized and due to the pressure in the header caused by the presence of vapor and liquid from some of the other tubes the liquid is forced back down the tube. It is forced down about half the length of the tube. The difference in head again forces the liquid up the tube and as it passes through the super heated zone at the steam inlets it picks up sufficient heat to be vaporized. This constant pulsation takes place continuously and alternates among the 16 tubes so there is constant vaporization and rapid circulation. The pulsation takes place with such rapidity that the inner surfaces of the heat exchanger tubes are wetted and renewed so fast that no damage to the liquid can occur. The liquid and vapor pass over into the separator and contact the inner wall of the bowl with such velocity that its entire surface is covered with the liquid. At this point the vapor, including water and more volatile fractions, is separated from the liquid and the latter cooled by evaporative cooling. This cooling reduces the temperature sufficiently to prevent any boiling in the return line and increases the density just enough to affect the rapid circulation obtained.

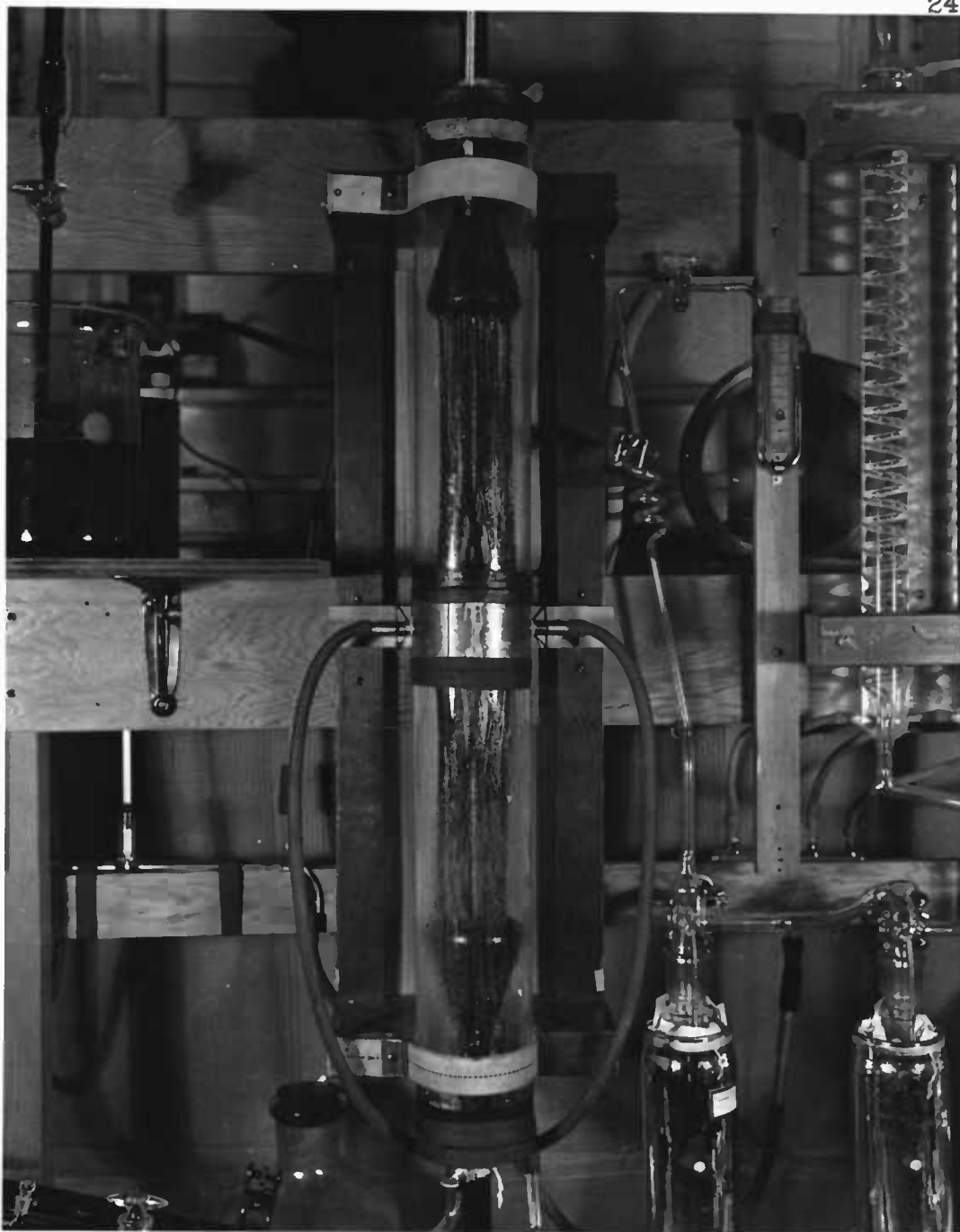


Figure 5. Heat Exchanger in Operation

To put the unit in operation a vacuum of between 3 to 5 mm. of mercury is pulled on the whole system at the pump connection point V on the drawing. The tap water to the condensing coils is turned on and the water aspirator is turned on to partially evacuate the boiler jacket. Dewar flasks or "Thermos" bottles are placed around the traps T_1 and T_2 which are packed with water ice and dry ice respectively. Fresh juice preheated to approximately 120°F . is let into the system at point I. The unit being partially evacuated permits the atmospheric pressure to force the juice into the system. The juice heated to 120°F . and subjected to a vacuum of about 8 mm. vaporizes in part and is completely deaerated. The unit is filled with juice to the level of the top of the heat exchanger tubes and the steam is turned on. Caution is necessary in the preliminary heating of the heat exchanger and jacket. The time required for this initial coming up period is about five minutes. Ebullition then begins in the manner described. The level of the liquid is now brought up to bottom of the separator bowl and kept there by periodic addition of fresh juice. As the concentration builds up within the circulating system some of the material can be removed periodically by a concentrate reservoir attached to points O and O'. In this manner

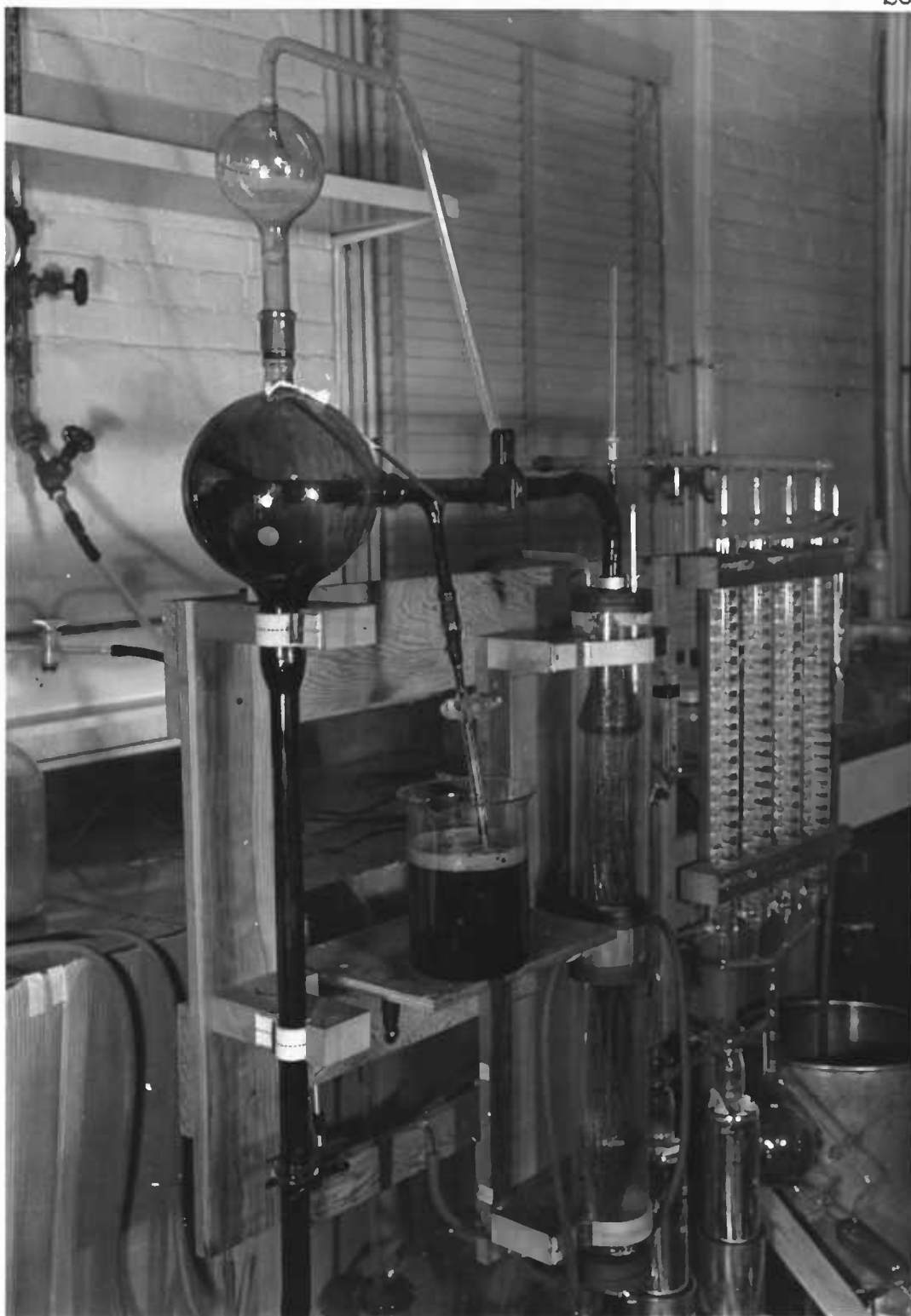


Figure 6. Liquid-vapor Separator in Operation

the concentration can be regulated.

b. Performance of the Condenser Train.

Due to the fact that the unit was to be made of glass, the many different boiling fractions in the juice and the difficulty of estimating fluid film heat transfer coefficients, no calculation was made as to the amount of condenser surface necessary for the unit. Therefore the existing condensing surface of the four spiral condensers was utilized by regulating rate of flow of the cooling water and thereby governing the temperature in the condensers. A temperature was soon determined that gave the optimum results with regard to speed of evaporation, completeness of water vapor condensation, and maximum essence fractionation. The water level in the receiver flask is maintained at about one-half the capacity of the flask to expose as large a surface as possible to the effects of the vacuum. The difference in vapor pressures of the essence fractions from the condensed water fraction makes its escape from the exposed liquid surface possible (34). This level is maintained by regulating a screw clamp on the pressure tubing connection from point W to the auxiliary receiving flask.

The remainder of the essence fractionating train consisted of the two traps as mentioned previously. They

were designed and constructed in such a manner as to provide a minimum gas velocity and a minimum of turbulence. The purpose of the water ice trap was to remove some of the water entrained as vapor by the other gases. This resulted in a much higher essence concentration than that attained by a single dry ice trap. This intermediate trap does increase the concentration of essence in the final trap, but as pointed out by Sanderson (34) "It is a common error to suppose that a condensable gas may easily be separated quantitatively from a relative non-condensable gas merely by passing the mixture through a zone having a temperature at which the vapor pressure of the condensable gas is negligible. Such a separation may be far from quantitative. There appear to be at least two possible explanations for this. First, the condensable material may be passing through the trap in such a manner that it does not become cooled to the temperature of the trap. Second, the condensable material may be cooled to the trap temperature but in such a physical state as to be entrained with the non-condensable gas."

Dry ice with a sublimation temperature of -78.5°C . was used for obtaining the lowest condensing temperature in the system. So that the dry ice would provide rapid thermal conduction through convection

currents, diethyl ether was used as a cooling medium. It has a very low vapor pressure at -78.5°C . and does not cause violent frothing and boiling over as do acetone and ethyl alcohol. During one operation period a third dry ice diethyl ether trap was inserted in the pressure tubing line from the last trap to the pump. At the end of a 35 minute run a slight fog had condensed in the trap but there were no drops of liquid in the bottom of the trap.

c. Overall Effectiveness

Table I shows average operational characteristics under optimum conditions as determined by experimentation.

The rate of evaporation and the resulting overall heat transfer coefficient is not as high as it should be due to the limiting factor of condensing surface. In operation using fruit juices the factors listed in Table I were nearly identical with those for distilled water. As a matter of fact, the unit operated more smoothly using fruit juice due to the lack of superheating and resulting bumping and surging as was encountered with distilled water. As the solids concentration of a fruit juice increased no increase in temperature was necessary until the concentration reached about 45 per cent at which time more heat was required to keep up the

rate of circulation.

Concentrates of apple juice with a per cent solids of as high as 70 were prepared in this unit. As observed by Charley, Hopkins, and Pollard (8) it is necessary to remove the pectin from fruit juices if a very high concentration is desired. With apple juice a concentration of 52 per cent solids was obtained with unclarified juice before partial gelling occurred in the unit. The 70 per cent concentration was reached with juice that had been clarified with Pectinol and filtered. The necessity of clarifying the juices prior to concentration is especially important with the cane fruits in general, raspberry in particular, a concentration of only 37 per cent could be reached with the unclarified juice before partial gelling took place. However, if the volatile essence is to be recovered from the juice it is best to concentrate it fresh and unclarified as the small particles of fruit flesh from the first pressing contain a great deal of these substances (26).

To test whether or not any harm was done the juice in the way of darkening and destruction to vitamins a lot of apple juice from a commercial concern that had been fortified with vitamin C at the rate of 32 mg. to four ounces was concentrated to 33 per cent solids

FOOD TECHNOLOGY DEPT.
OREGON STATE COLLEGE
CORVALLIS, OREGON

GLASS RECIRCULATING VACUUM EVAPORATOR

DRAWN BY WM. F. FILZ TRACED BY G. E. ROSS
FEBRUARY 15, 1948

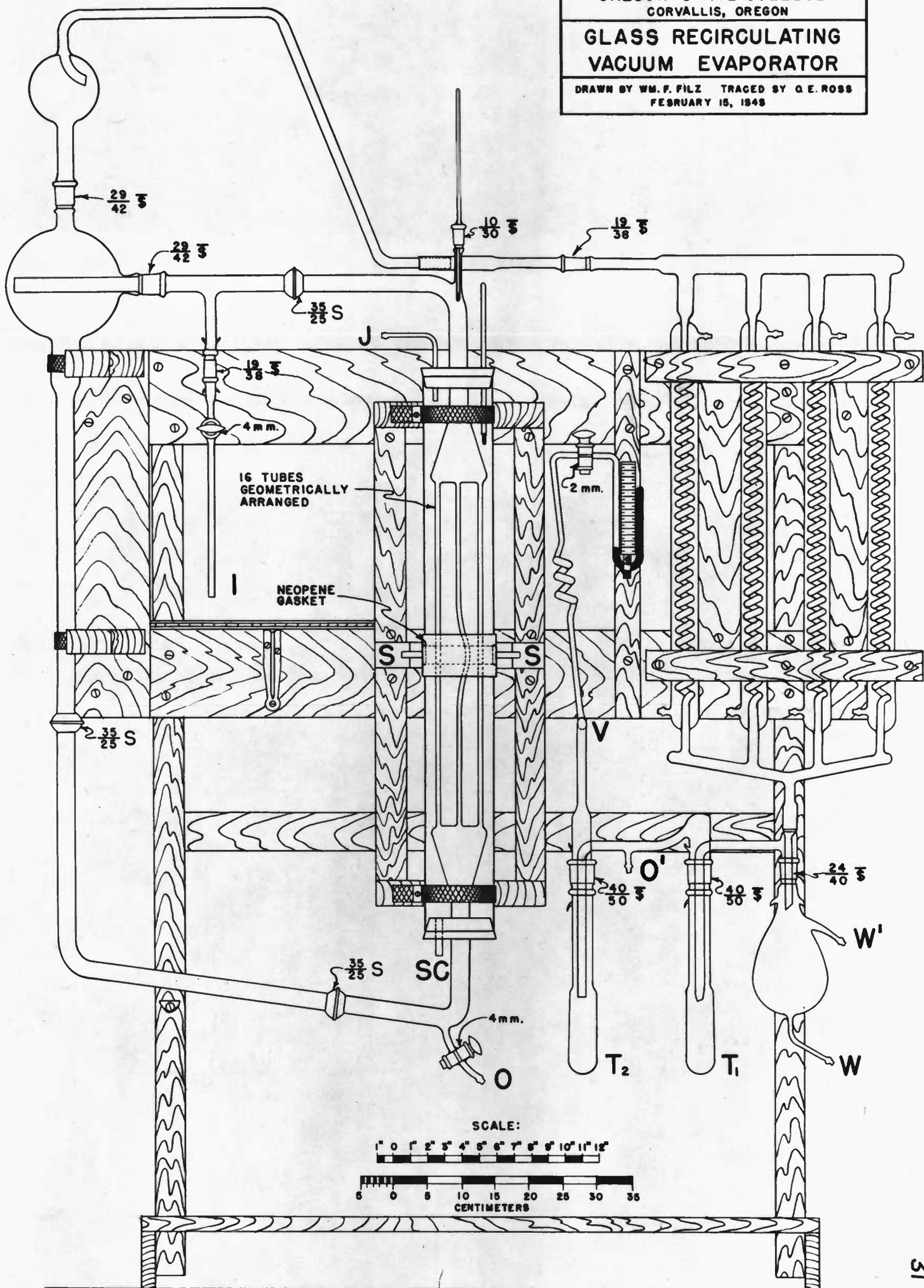


TABLE I

Data on Evaporator and Its Operation Using Distilled Water

<u>Mercury</u> <u>pressure</u> <u>in mm</u>	<u>Liquor</u> <u>temp</u> <u>in °F</u>	<u>Steam</u> <u>temp</u> <u>in °F</u>	<u>Temp in upper</u> <u>steam jacket</u> <u>in °F</u>	<u>T†</u> <u>°F</u>	<u>Water</u> <u>evaporated</u> <u>lb/hr</u>	<u>Evaporative</u> <u>surface</u> <u>ft²</u>	<u>Water</u> <u>evaporated</u> <u>lb/hr/ft²</u>	<u>Btu</u> <u>ft²/hr/</u> <u>°F**</u>
14-17*	118-122	206	154	86	10.9	1.245	8.75	104

Apparatus of Mitchell and Co-workers (27)

103	126	212	—	86	11.4	0.955	11.95	142
-----	-----	-----	---	----	------	-------	-------	-----

Operation of 12-liter flask on a steam cone (27)

97	123.8	212	—	88.2	10.35	1.880	5.5	66.2
----	-------	-----	---	------	-------	-------	-----	------

* Absolute.

† Difference in temperature between steam and liquid in heat exchanger.

** lb. water evaporated/hr/ft² surface x latent heat of steam at evaporating temp.
temp. of incoming steam - temp. circulating liquid

and 64 per cent solids. The solids concentration of the original juice was 13.5 per cent. Upon analysis for vitamin C the 33 per cent sample showed a concentration of 77 mg. per four ounces for a 98.4 per cent retention and the 64 per cent sample a concentration of 153 mg. per four ounces for a 98 per cent retention. These data indicate that there is no destruction of vitamin C in fruit juices prepared in this unit.

A sample of the same 64 per cent solids concentrate made from clarified and filtered commercial juice was diluted to 13.5 per cent solids and its color compared in matched 50 ml. Nessler tubes with a sample of fresh juice of 13.5 per cent solids. The colors were identical and it was impossible to distinguish the diluted concentrate from the fresh juice.

The degree of separation of the volatile essence from the fresh juice was difficult to determine because of the very small amount of the material originally contained in the fruit. Power and co-workers (31) who pioneered much of the work on the odorous constituents of the apple found that the amount of volatile product represents only about 0.0007 per cent of the entire fruit. Milleville (25) who recently devised a method for stripping the volatile essence from apple juice found that even at a 150 fold concentration the actual

essence concentration was only a fraction of one per cent. The fact that only two or three gallons of juice were to be concentrated at one time together with the very low concentration of the essence in the juice presented a problem of obtaining analytical data. Power and co-workers (31) found the volatile acids of the Ben Davis apple are chiefly formic, acetic, and caproic acids. They obtained a positive reaction for acetaldehyde and identified the aliphatic terpene alcohol geraniol in the McIntosh apple. They confirmed the belief that the odorous constituents of apples was partially due to amyl esters and disproved the then popular belief that amyl valerate was present in apples. Milleville (24) recently has stated that contrary to the belief of the prior art the volatile flavoring constituents are predominantly substances other than esters such as alcohols, aldehydes, ketones, ethers, and volatile acids.

Because of these recent investigations it was decided to use the aldehyde content of the distillate to give some indication of the volatile essence concentration although it is not likely that the analysis for any one of the flavor constituents would give a true index of flavor concentration because of fractional evaporation due to differences in vapor pressures.

The method of Joslyn and Comar (20) for the determination of acetaldehyde in wines was employed. The method was modified by making the concentration of iodine and thiosulfate 0.025 N instead of the recommended 0.05 N. The analyses were made on the aqueous solutions collected in the dry ice trap. The aldehyde content was calculated as acetaldehyde in all cases.

TABLE II

Concentration of Essence Fractions of Apple Juice

<u>Juice concentrated:</u>		<u>Dry ice Fraction:</u>		<u>Essence Recovery:</u>	
<u>Volume</u>	<u>Final %</u>	<u>Aldehydes</u>	<u>Volume</u>	<u>Inc over</u>	<u>Per cent</u>
<u>in gallons</u>	<u>solids</u>	<u>gm/100ml</u>	<u>in ml</u>	<u>fresh jc</u>	
3 (uc)	32	0.0020	68	4.0*	2.4
3 1/2 (uc)	31	0.0024	75	4.8*	2.7
2 3/4 (c)	70	0.0052	118	10.4*	11.8
3 (uc)	54	0.0060	105	12.0*	11.0

* Assuming a figure of 0.0005 per cent as the average essence concentration on fresh juice.

(uc) Unclearified and unfiltered juice
(c) Clarified and filtered juice

The water fraction from all of the concentration trials shown on Table II had a noticeable aroma of apple essence but the analytical method used was not sensitive enough to determine the aldehyde concentration in such a dilute solution. The fraction in the water ice trap also had an apple essence aroma; here again the volume of reagents used in the titration were quite small and

were thought not to be of sufficient accuracy to be considered.

Since, by the characteristic apple aroma there was indication of considerable retention of essence in the concentrates and in the water fractions it is evident that this apparatus is not designed for stripping the essence from the juice as is the unit designed by Milleville (26). It is more like the unit used by Charley (8) wherein the flavor retention in the essence enriched concentrate is essentially complete. The essence concentration was too low to start with so the basic assumptions were necessarily rather general and too small batches were concentrated to give a complete picture of this phase of the operation. The real test of the value of the essence fraction was evidenced by comparing the flavor and aroma of two separate samples of the same concentrate one of which had the essence fraction combined with it. It had a superior taste and aroma. This was more pronounced in higher concentrations such as 40 to 50 per cent solids.

Concentrates of apple, cherry, grape, loganberry, boysenberry, and raspberry juices were prepared in this evaporator. They ranged in concentration from 30 to 70 per cent solids and when combined with their respective essence fractions were remarkably like the

fresh product. In some cases it was difficult to discern the diluted concentrate from the fresh juice; in others there was a slight difference in flavor. This was especially noticeable in unclarified cane fruit juices.

III. PREPARATION OF CONCENTRATES

Literature Survey

a. Laboratory Investigations of Freezing and Vacuum Concentration.

Some of the earlier references to juice concentration methods were to those done by freezing (15,23). Cruess (40) and later Grove (47) used vacuum in conjunction with freezing concentration methods. Grove noted that juices with an acidity of less than 0.25 per cent became dark when concentrated. Those with a high acid content (greater than 0.7 per cent) tended to caramelize and become brown. He suggested that successful concentration necessitated removal of the pectin to prevent gelling, adjustment of the acid content of the juice to 0.12 per cent using a combination of calcium carbonate, potassium carbonate and potassium hydroxide and finally, the addition of 5 per cent sucrose and 5 per cent glucose to the final concentrate. The concentrate thus produced was considered a satisfactory substitute for molasses and was also recommended in the sweetening of ciders and the preparation of carbonated drinks. It had a pronounced cooked flavor.

In order to satisfy the demand for apple juice

concentrates with natural flavor present, Carpenter and Smith (4) investigated the use of a Pfaudler vacuum pan together with an ester impregnating unit. With this system, the concentrate was cooled and recirculated to condense and absorb the volatile flavors from the material that was undergoing subsequent concentration. The juice was first pressed, flash heated to 180°F., flash cooled and filtered. They studied the degree of impregnation obtained, the ester and aldehyde content of the syrups and their viscosity and character for bottling purposes. One of the difficulties encountered in the impregnation was the excessive dilution of the concentrate with the water that was condensed along with the esters. Mottern and Morris (28) suggested that this difficulty could be overcome by increasing the initial concentration and suitable control of the temperature of the material undergoing concentration.

Poore (30) investigated the production of concentrates from cull apples in Washington State. He employed both concentration by freezing and by vacuum. While the freezing method conserved a large proportion of the natural flavors, it was considered to be too expensive for practical use. He examined the composition of the volatile materials given off during vacuum concentration and found they contained amyl esters of

formic, acetic, and caproic acids, some aldehydes and a trace of geraniol. He noted that the concentrates formed a gel if they contained more than .55 to 65 per cent total solids. It was found necessary to sterilize a product of this concentration to avoid spoilage but the product was very convenient for use by bottling concerns.

Investigations in England of concentrated apple juice were reported by Charley (5) in 1937. The prepared concentrates were used in the manufacture of unfermented apple juice, and fermented cider. He reported that a cooked flavor characteristic of some concentrates did not detract from the quality of the product after fermentation.

Reavell (32) described the application of a rising-film evaporator to the concentration of juice. Concentration was accomplished in three stages and the volatile substances were automatically added back to the concentrate. The use of a rising-film evaporator was also studied by Charley (7) and the unit he used was of the Kestner recirculating type equipped to recover the ester fraction. He found that flavor changes took place if the apple juice was exposed to a temperature of 140°F. for an extended period of time. The changes in flavor, however, were not marked until the concentration neared completion. A high acid content tended to

give a "cooked" flavor to the concentrate. The reduction of the acidity was accomplished by adding potassium carbonate or calcium carbonate, although drastic reduction of the acid affected the flavor adversely.

He found that the volatile fraction stripped from the concentrate varied with the temperature and that while the distillate contained 0.57 per cent of volatiles when the coil outlet temperature was 125°F., the amount was only 0.10 per cent for a temperature of 107°F. Later (6) he found that the volume of distillate could be reduced by passing the distillate through the system a second time using a higher distillation temperature and a slow rate of flow. When the ester fraction was concentrated sufficiently and bottled it appeared to have an inhibitory effect on spoilage organisms. He noted that the ester content of a concentrate was substantially less after 14 months of storage than when first added.

Contrary to the view held by many, that fermentation of the juice helps to develop the aroma, he contended that the fermented juice lost its fresh apple flavor. The latter opinion is now accepted almost entirely. In his attempts to synthesize beverages he found that a very acceptable product could be obtained by mixing ester concentrate, malic acid, sugar and water in the correct proportions. He was able to concentrate

apple juice to a thick treacle having the same consistency as golden syrup and with a specific gravity of 1.485. He suggested that it could be used in the manufacture of jelly and also as a substitute for sugar. There were difficulties in the production and handling of treacle on a pilot plant scale owing to its stickiness and high viscosity. He suggested that the production be accomplished stepwise in that juice be continuously concentrated under vacuum to a specific gravity of 1.200 following which the partially-concentrated juice was evaporated batchwise under vacuum to a specific gravity of 1.425.

The production of treacle necessitated the use of pectinol-treated juice to prevent gelling. Charley found that neutralization, if carried out under properly controlled conditions was an adequate substitute for pectinol treatment. These studies showed also that high tannin content as well as high acid gave a concentrate with unpleasant flavor and that juices neutralized to an acid content of 0.15 per cent with potassium carbonate were unpleasant due to the presence of potassium salts.

During World War II, the Eastern Regional Research Laboratory (13) detailed a method for producing bland syrup from apple juice. This process was also

described by Mottern and Morris (28). The object of the process was to eliminate flavor, odor, color and gellification to give a bland syrup suitable for bakery, ice cream, soft drink and other food industries. The product was considered superior to corn and sorghum syrups, equal to maple syrup and somewhat inferior to invert syrup and honey. In addition to the food uses, its hygroscopic properties made it valuable as a humectant. It was considered too sweet for table use.

Weubert (29) studied the physical and chemical changes taking place in the concentration of juices and found that concentration by freezing retained nearly all of the aroma while vacuum concentrated juices without ester impregnation were almost devoid of aroma.

Willeville and Eskew (25) described a pilot plant process for recovering natural apple flavors by superheating the juice, flash vaporizing it at atmospheric pressure, mechanically separating the vapor from the unvaporized juice and fractionating the vapors to obtain a more concentrated flavor. They were able to produce ester concentrates with or without a cooked flavor to satisfy particular market requirements. The cost of production of the ester concentrate was estimated at 90 cents per gallon. Although most workers agree that 8 to 10 per cent of the juice volume must

be evaporated to recover the apple essence present, Wells (38) suggested that the bulk of flavoring materials could be recovered in the first three per cent of the distillate and that the alcohol content of this fraction was sufficiently low to escape the taxable limit.

Buck and Mottern (2) were successful in eliminating the bitter after taste in apple syrup by passing the syrup through a bed of an ion-exchange resin. The bitterness was said to be due to calcium oxalate formed during the liming of the juice. The ion-exchange treatment removed 80 to 90 per cent of the malic acid and also traces of arsenic that may have persisted from spray residues.

b. Recent Juice Concentration Patents.

Recent patented inventions for the concentration of fruit juices are for the most part along the same types as the methods just reviewed. A patent of February, 1948, issued to Malcolm (22) describes a method of concentrating fruit juices by freezing. The juice is precooled and deaerated then passed through successive freezing stations at gradually lower temperatures. At each step the frozen parts are removed and the lighter and denser of the frozen portions are separated. The denser parts are repassed through some of the freezing

stations and finally the resulting product is subjected to centrifuging. No data was given on maximum concentration obtainable by this method.

Holzcker (19) recently received a patent for concentrating fruit juices in which the juice is fed into a vacuum chamber which is subsequently evacuated and the juice subjected to quick freezing. Part of the water is thus evaporated and the rest frozen and removed as ice. The remaining slush is transferred to a centrifugal basket and broken down. Thus in a given example from an original 32 pounds of orange juice containing 12 per cent solids, three pounds of water were evaporated and 19 pounds of ice removed leaving approximately ten pounds of concentrated orange juice containing 36 per cent solids.

Cognizant of the fact that in the concentration of fruit juices and similar materials the destruction of heat sensitive compounds is avoided by minimizing the time of exposure to heat an apparatus was designed by Zahm (42). In his equipment the volatile esters and essential oils are recovered from the water vapor and restored to the concentrate. Evaporation takes place in vacuo from a thin, rapidly moving film. The vapors are partly condensed in a primary condenser. The more volatile portion is condensed in a secondary condenser

and mixed with the concentrate.

c. Recent Industrial Developments.

Vacuum Foods Corporation (3) have developed and are using a process whereby orange juice is concentrated in a vacuum evaporator, packaged in cans and frozen. It is not sterilized by heat due to the probably impairment of flavor. Several firms, including Vacuum Foods Corporation, have been marketing the frozen concentrate with considerable success. Vacuum Foods Corporation, however, operates its concentrating process at considerable higher vacuum and hence lower temperature than other processors. Their unit consists of two separate banks having a juice capacity of over 1000 gallons per hour. The concentrators are 13 columns 28 feet high by 30 inches in diameter. To supply the latent heat of evaporation the walls are jacketed with hot water that comes from the barometric condenser by way of the hot well. Each column has 200 square feet of evaporating surface and the vapor and juice leaving the columns are maintained at 50 to 55°F. The heating surface is considerably warmer, but is not hot enough to injure the flavor.

Juice is sprayed onto the heated walls of the interior of the columns in which a vacuum of 12 to 15 mm. of mercury is maintained. As the juice trickles

down the column it gives up a part of its water by evaporation. On reaching the bottom it is pumped to the top of the next column by small, motor driven centrifugal pumps and the procedure is repeated through the series of 13 columns. Though the evaporation is done in series, it is emphasized that this is not a 13-effect evaporator. If it were a multiple effect evaporator the first effects would necessarily be too hot for the juice and loss of flavor would result.

The vacuum of 12 to 15 mm. of mercury is maintained by high pressure steam booster ejectors and by auxiliary booster ejectors exhausting into barometric condensers. Coming from the concentrator the juice has been concentrated to about 50° Brix which represents about a five-fold concentration. During the boiling that has taken place in vacuo some of the delicate flavors of the orange have been carried away. This loss is overcome by combining fresh orange juice with the concentrate to bring it down to 42° Brix. One important feature of this method is the discovery that the high acidity of a concentrated juice serves to retard enzyme activity and thus prolongs the merchantable life.

The very latest and most revolutionary type of evaporator is the one designed by Cross (9). "The tremendous increase in efficiency and economy of operation

as well as the relatively low evaporating temperatures is made possible by the transfer of the latent heat of vaporization of the evaporated water to a second vapor of lower specific volume. This recovery of the heat required to vaporize the water is of paramount importance to the economy of the unit operation of evaporation. Many systems have been devised to affect this recovery, but their economic usefulness has been restricted by the high specific volume of water vapor at usual evaporation temperatures. The transfer of heat from water vapor to a secondary vapor affects an enormous reduction in volume. When water is evaporated at 60°F. its vapor has a volume of 1,208 cu.ft./lb. and contains 1,058 Btu of latent heat. If this vapor is condensed by the transfer of its heat to boiling anhydrous ammonia at 45°F., the net result will be one pound of water at 60°F., and two pounds of ammonia vapor at 45°F. The total volume of ammonia will be 7.2 cu. ft., with latent heat of 1,058 Btu. By accepting a loss of 15°F. in specific temperature, the volume of vapor to be compressed has been reduced from 1,208 (the volume of water vapor) to 7.2 cu. ft. It is obviously unsound to compress 1,208 cu. ft. of water vapor in order to salvage 1,058 Btu of heat. But the compression of 7.2 cu. ft. of ammonia with a rise in temperature from 45 to 103°F. to salvage

1,058 Btu is practical, even in large-scale operations. It can be carried out economically in fully developed commercial equipment of moderate size and cost, with the expenditure of only 60 Btu of mechanical energy."

"At the plant of Florida Citrus Cannery Cooperative, the pioneer commercial installation of the above type is used to concentrate orange juice from 11 to 55° Brix. Boiling takes place at 58°F. Ammonia is used as the secondary medium, with 103° high side temperature, 58°F. evaporation temperature, and 41°F. low side temperature. Water is evaporated from the orange juice at a rate of more than 4,000 lb/hr. Three stages of forced falling film evaporation are used, with pump recirculation in each stage. The three exchangers are of the shell and tube type, with the orange juice boiling inside the tubes and ammonia condensing within the shell outside the tubes. Water vapor is separated from the concentrated orange juice at the base of these exchangers, and is conducted to a fourth shell and tube exchanger. In this exchanger, the water vapor is condensed on the outside of the tubes by the boiling of liquid ammonia at 41°F. within the tubes. Orange juice enters the first evaporator, where it is concentrated to about 17° Brix. The partly concentrated product then overflows to the second evaporator, where additional water is removed, concentrating the juice to

approximately 30° Brix. The third evaporator completes the concentration. The juice then tests approximately 55° Brix. The concentrated product is removed continuously by a variable speed product pump. Concentration is controlled by modulating the flow of juice at the inlet and outlet. Vapors from the three evaporators are collected in the water vapor conductor pipe, and passed to the shell of the fourth exchanger. The liquid ammonia that was condensed in the evaporators is first passed through a supplemental condenser to remove surplus heat; then through an expansion valve to reduce its temperature by flashing, and finally flooded inside the vertical tubes of the refrigerated shell and tube exchanger. By a mutual exchange of latent heat, the liquid ammonia is vaporized at 41°F., and the water vapor is condensed at 58°F."

Preparation of Fresh Juice

In preparing a fruit juice concentrate for subsequent fermentation the limiting factor is the acid content of the fresh juice. Total acidity in a finished wine of over one per cent necessitates too much sugar for a balanced sugar-acid ratio and is more acid than the consumer is accustomed to. As demonstrated by Buck and Motern (28) it is possible to remove acidity from fruit juices by passing them through an ion exchange resin. This practice would probably add too much to the cost of the final product to make its application practical. The only other alternative is to select fruit with a low enough acid content that subsequent concentration to the desired per cent sugar will not raise the acidity beyond the maximum level.

The main factors effecting the amount of acid in the apple are the variety and the degree of maturity (39). Apples vary in acidity, calculated as malic acid, from 0.1 to 1.1 per cent. From the standpoint of essence content, Griffin and Co-workers (16) found that a blend of McIntosh, Red Delicious, Stayman, and Jonothan was most desirable. The acid content of these varieties varies from 0.16 per cent for the Red Delicious to 0.73 per cent for the Rhode Island Greening. For making wines of about 14 per cent alcohol the initial sugar content

should be about 30 per cent sugar. If a maximum of 0.9 per cent acid is set for the final concentrate this means that the average acid content of the fresh juice cannot be over 0.42 per cent. From the acidity of the varieties just listed it is evident that a juice with such an acid content could be prepared by proper blending.

When a fruit juice is concentrated every constituent that is non-volatile at the concentration temperature will be increased proportionately. This means that scrupulous care must be given in selection of the fruit and preparation of the juice. Tressler, Joslyn, and Marsh (37) give a standard procedure for accomplishing this operation. Any undesirable odors and flavors such as those from unsound fruit and unsanitary equipment and utensils will be picked up in the juice and their presence magnified in the final concentrate.

The apple juice used in these experiments was not prepared by the author and no accurate information is available as to the exact varieties used and the conditions under which it was prepared. The free run juice was frozen in 30 lb. tins and stored at 0°F. for a period of about three months. The acid content varied in the 30 lb. tins from 0.26 per cent to 0.61 per cent as malic acid. The solids content was between 13 and 14 in all lots tested. The juice of higher acid content

was blended with the juice of lower acid content before use. As the main object in preparing apple wine from the fruit concentrate is to determine whether a wine of better body, flavor and aroma results, a careful organoleptic analysis of the juice was made prior to concentration. Only that juice possessing a full apple flavor void of any off-flavor was used.

Preparation of Concentrates

The concentrates were prepared in the evaporator in the manner described in a previous section, Operational Data, of the apparatus on pages 21 to 37 of this thesis. The essence fractions were transferred to brown glass stoppered bottles and frozen until ready for use.

In the preliminary experiments two batches of juice were prepared from the same lot. To observe the effect of clarification on the fermentation of the juice concentrate one of the batches was treated with 0.1 per cent of the enzyme known as Pectinol A. The clarified juice was racked from the sediment but not filtered. An analysis of the fresh juice both clarified and unclarified showed similar results indicating little change as a result of enzymatic clarification. Table III shows a comparison of fresh juice and concentrate.

TABLE III

Effect of Concentration
on Fresh and Clarified Juices

		Per cent malic acid (by weight)	pH	Per cent solids
		<u> </u>	<u> </u>	<u> </u>
Fresh Juice:	Unclarified	0.261	3.7	14.0
	Clarified	0.258	3.7	14.0
Concentrate:	Unclarified	0.566	3.7	30.0
	Clarified	0.551	3.7	30.0

These data show that although the acid content was doubled, the pH remained constant due to natural buffer systems in the juice. This is an important point in favor of the use of concentrates for subsequent fermentation.

IV. FERMENTATION OF CONCENTRATES

Pure Culture Preparation, Inoculation and Rates of Fermentation

An active inoculum for these concentrates was prepared using the champagne strain of Saccharomyces elipsoideus. A tube culture of the yeast was used to inoculate 300 ml. of pasteurized juice. This juice incubated at 80°F. for two days had a Brix reading of 2.0. Then 300 ml. of the concentrate were added and allowed to incubate for two days at which time the Brix reading was 4.0. The inoculum was considered ready for use. Two such cultures were prepared.

The concentrates were pasteurized and sulfur dioxide added in the form of $K_2S_2O_5$ at the rate of 50 ppm. The cultures were added to the two batches and incubated at 81°F. Table IV on page 56 shows the rates of fermentation of the clarified and unclarified musts using the decrease in Brix reading as an index.

The following data shows the rate of fermentation to be considerably more rapid in the unclarified must. This information supports the work of Taverniér and Jacquin (36) who found that unclarified musts ferment much more actively to practical exhaustion of the fermentable sugars. They found that clarified musts

ferment much more slowly and that fermentation stops while there still remains a considerable proportion of sugar. They attribute this to the removal of a considerable proportion of the nitrogen required by the yeast as food.

TABLE IV
Rates of Fermentation
of Clarified and Unclassified Musts

Time in hours	Clarified juice Brix Reading	Unclassified juice Brix Reading
0	27.0	26.5
48	20.0	18.0
72	16.0	12.0
96	13.4	9.0
120*	11.4	8.0
168	9.6	7.4
192	8.0	6.6
240	6.6	5.8
Per cent alcohol.....	13.16	13.22
Per cent total acid as malic...	0.790	0.710

* 0.1% Pectinol A added at this point.

Bettlestone (1) in a study of osmosis and fermentation found that the osmotic effects of corresponding concentrations of different carbohydrates on yeast cells are identical and for dilute solutions of the carbohydrates and of alcohol the osmotic effects are proportional to the concentration. He found that for normal yeast cells, 10 to 12 per cent solutions of carbohydrate and 5 to 7 per cent solutions of alcohol

have equivalent osmotic effects. This relationship between the carbohydrate and alcohol is such that during fermentation, the conversion of sugars into alcohol causes no alternation of the osmotic conditions. In light of these observations the osmotic effect of these final concentrations of sugar and alcohol does not account for the cessation of fermentation in the wines. The reason may be a toxic effect on the yeast cells.

During the course of the fermentation the previously clarified must became very cloudy due to yeast cells and other suspended material. As noted in Table IV Pectinol A was added midway in the fermentation period. The unclarified must became quite clear with the addition of Pectinol A but the enzyme had very little if any effect on the cloudiness of the previously treated must. This leads one to assume that the clarifying action of such enzyme preparations depends upon the flocculated pectinous material to carry the suspended yeast cells down with it as it settles to the bottom of the container. The action of clarifying enzymes on fermented musts is nil if the musts have been clarified prior to fermentation.

When the essence fraction recovered from preparing the concentrate was added to the wine from these two trials and the per cent sugar brought up to about

7.5 with cane sugar the wine had a full bodied flavor and aroma except a slight bitterness was noted in both cases. This slight bitterness made a true evaluation of the flavor difficult. This bitterness was present in the wine before the essence was added.

Cruess (11) discusses the use of grape concentrate as a source of sugar for making fortified wines or for adding to the sugar content of grape must naturally low in fermentable sugars. It was thought desirable to try this method in the production of an apple wine. A concentrate of 62 per cent solids and 1.18 per cent malic acid was prepared from clarified apple juice. A volume of 2 1/2 liters of juice containing 14.5 per cent solids and 0.278 per cent malic acid was prepared and inoculated with 300 ml. of an active 48-hour-old culture of Saccharomyces elipsoideus champagne strain in a manner similar to that previously described. The volume of concentrate necessary to produce a wine of 14 per cent alcohol was added in two separate batches. The fermentation record is presented in Table V.

TABLE V

The Fermentation Rate of Apple Juice
Using Apple Concentrate for Amelioration

<u>Total Time in hours</u>	<u>Interval in hours</u>	<u>Total Vol in ml</u>	<u>Brix Reading</u>
0	0	2800	12.2
48	48		4.6
84	36		-1.0
*	--	2980	----
132	48		-1.5
*	--	3160	----
156†	24		1.5
204	48	3160	0.0

* 180 ml. of concentrate added at this time.

† 0.1% Pectinol A added at this time.

TABLE VI

The Fermentation Rate of Apple Juice
Using Sucrose for Amelioration

<u>Total Time in hours</u>	<u>Interval in hours</u>	<u>Brix Reading</u>
0	0	12.5
48	48	5.0
72	24	3.0
116*	24	1.0
140	24	6.5
188	48	4.0
212*	24	2.0
246	24	5.4
270	24	4.2
294	24	3.2
328†	24	2.0
352	24	1.2
376	24	-0.4
400	24	-0.5
424	24	-0.9

* 168 gm. of sucrose added after each of these read.

† 0.1% Pectinol added after this reading.

The supernant wine was racked from the lees, filtered using a diatomaceous earth filter aid, pasteurized and bottled. The per cent alcohol was 13.48 and the malic acid content 0.543 per cent. This wine with the Brix adjusted to 5.5 and the essence fraction equivalent to the volume of concentrate added back possessed a pleasing flavor characteristic of apple and was not quite as dark as the wine prepared entirely from the concentrate. Here again a slight bitterness was detected. As can be observed from Table V the rate of fermentation using the concentrate as a source of sugar is very rapid and goes well toward exhaustion of fermentable sugars.

Table VI shows the rate of fermentation for a control batch of wine made by the usual method of ameliorating with sucrose to obtain the desired alcohol content. A volume of 2 1/2 liters of juice of 14.5 per cent solids and 0.261 per cent malic acid were prepared and inoculated with an active culture of Saccharomyces elipsoideus in the usual manner and incubated at 81°F. The necessary sugar was added at the times indicated in the table. The final per cent alcohol was 13.93 and the acid content was 0.409 per cent expressed as malic. After racking, filtering, adjusting the Brix reading to 5.0, and pasteurizing,

the wine had a light straw color but had very little resemblance to apple in taste and aroma. The flavor was flat with very little character. The slight bitterness was also present in the control sample.

The concentration of the pigments in the wine made from the 30° Brix concentrate made it somewhat darker than the control sample made in the ordinary way. This deeper amber color was in no way objectionable but it seemed worthwhile to investigate the possibilities of using a decolorizing carbon to remove a portion of the pigments to lighten this color if possible. Both the vegetable charcoal 'Norite' and the animal charcoal known as bone char were tested. Separate samples of the concentrate were treated with 0.25 per cent of these two carbons. The concentrate and the carbon were heated to 140°F. and filtered both while hot and after cooling to 34°F. Upon comparing the filtrate with the original sample it was apparent that these materials had a negligible effect if any at all on the color of the product.

This same procedure was tried on samples of the wine prepared from the 30° Brix concentrate. In this case the change in color was also very slight but the sample treated with 'Norite' and filtered either hot or cold seemed a shade lighter than the control and the sample treated with bone char.

As mentioned before, this deeper color of wine made from concentrate as compared with ordinary wine is not objectionable and therefore the inability to remove these pigments is of little consequence.

In order that a more accurate evaluation of the flavor of the wine prepared from the concentrates could be made it became necessary to try to locate the cause for the bitterness present in all batches prepared thus far. The thawed juice had a pleasing flavor and no indication whatsoever of an off-flavor. The evaporator was kept clean at all times and all vessels used during the fermentation were cleaned thoroughly.

It is known that the champagne strain of the wine yeast does produce a slight bitterness characteristic of some types of champagne. With this in mind it was decided to check different strains of Saccharomyces ellipsoides for the flavors produced and for the rates, quality, and completeness of fermentation of 30° apple concentrate.

Four different strains were chosen for this investigation. They were Sauterne, Burgundy, California, and the same Champagne strain as used heretofore. Active cultures of these strains were prepared by inoculating 50 ml. of pasteurized juice with a tube culture of the yeast. After 36 hours at 61°F., 50 ml.

of the concentrate was added to the culture and incubated for a 24 hour period. Four 650 ml. volumes of concentrate (pasteurized 30° Brix of 0.904 per cent malic acid and containing approximately 50 ppm. SO₂) were inoculated with these four strains of yeast individually and incubated at 81°F. Table VII gives the rates of fermentation and the final analysis for the wines using the four different strains of yeast.

During the early part of the fermentation, the musts inoculated with the Champagne and Burgundy strains began to show definite signs of defecation. By the time 72 hours had elapsed these musts were practically clear. There was some foam on the surfaces and all the lees and practically all other formerly suspended material had settled to the bottom of the flasks. These two batches seemed sufficiently clear so as not to require the Pectinol enzyme for clarification but since the use of this material is so general it was decided to add it to all samples regardless of the apparent lack of need for it.

The musts inoculated with the California and Sauterne strains remained cloudy with no evidence of defecation throughout the fermentation process. As can be observed from Table VII, this definite clearing and settling of the lees and other insoluble material

TABLE VII

Fermentation Rates
of Four Strains of Saccharomyces ellipsoideus
on 30° Brix Apple Concentrate

<u>Total time</u> <u>in hours</u>	<u>Interval</u> <u>in hours</u>	<u>Burgundy</u> <u>°Brix</u>	<u>California</u> <u>°Brix</u>	<u>Champagne</u> <u>°Brix</u>	<u>Sauterne</u> <u>°Brix</u>
0	0	27.5	26.5	27.5	26.5
24	24	23.6	19.0	18.2	19.0
48	24	18.0	13.0	11.8	12.6
72	24	13.8	8.8	5.6	7.4
96*	24	7.6	7.0	3.0	5.0
120	24	4.0	5.6	2.8	2.8
144	24	1.4	4.6	2.8	1.6
168	24	0.6	4.0	2.8	1.0
X alcohol by volume.....		15.38	13.22	14.25	15.13
X total acids as malic.....		1.011	0.910	0.931	0.958
X volatile acids as acetic..		0.126	0.090	0.054	0.096

* 0.1% Pectinol A added to the musts at this time.

has no effect either on the rate of fermentation or on the amount of alcohol produced as compared with the samples in which there was no defecation.

This comparison of different strains of the wine yeast gave definite and conclusive evidence to the theory that the Champagne strain was the cause of the bitter flavor encountered in the previously prepared wines. This fact now leads one to believe that the bitterness is caused by the reaction of a metabolic product from the strain of yeast with some constituent inherent to the apple. As this constituent becomes more concentrated the resulting bitterness in the wine is also more pronounced. One may further conclude that this constituent is non-volatile as it was not removed in preparing the concentrate for fermentation.

The sugar acid ratio of these four batches of wine was adjusted to 9 - 1 using sucrose. The proportionate amount of the essence fraction recovered from the concentrating process was added to each sample. Approximations were made of the organoleptic qualities of the wine. Valid taste tests with reliable judges could not be employed because of the unavailability of experienced wine tasters and inadequacy of wine supplies to train a sufficient number of testers. Due to the dulling of taste bud sensitivity by alcohol

the taster of wine requires a great deal of training and experience to attain any degree of proficiency.

The general flavor of the wines made from concentrates was quite satisfactory. They had a more full bodied flavor than the control sample and their color was more intense. The adjusting of the sugar-acid ratio masked the bitterness produced in the wine fermented by the Champagne strain so that it was not noticeable. It was just as acceptable as the wine fermented by the other three strains. These results together with the fastest rate of alcohol production as noted in Table VII make the Champagne strain of Saccharomyces elipsoideus the yeast of choice in the fermentation of apple concentrates. These observations are substantiated by those of Yang (41) who found this strain the most desirable in the fermentation of apple juice.

V. SUMMARY AND CONCLUSIONS

This work has led to the construction of what is believed to be the first all-glass vacuum evaporator. This evaporator is rapid and efficient and possesses the other distinct advantages of a glass system such as: (1) ease of fabrication of intricate parts, (2) complete visibility of any phase of the operation, and (3) ease of cleaning. The disadvantage of being subject to damage by mechanical shock was overcome by careful annealing of all worked areas, construction of a rigid support, and careful mounting of all components.

The rate of heat transfer was found to be quite high but it was not at a maximum due to the limiting factor of water condensing surface. The use of an all glass heat exchanger proved very satisfactory once the problems of glass expansion were solved. The glass heat exchanger made it possible to observe the vaporization within the tubes and the fact that the flow of liquid and vapor is not continuous within each tube but alternates in a pulsating manner among the tubes.

Concentrates of apple, cherry, grape, loganberry, boysenberry, and raspberry juices were prepared in this evaporator. A solids content of as high as 70 per cent

was reached with clarified and filtered apple juice. It was found that cane fruit juices must be clarified with pectin hydrolyzing enzymes if a concentration higher than 35 to 40 per cent solids is desired in order to avoid gelling in the unit.

Fruit juice concentrates prepared in this unit are not adversely effected with regard to retention of natural qualities. The near 100 per cent retention of vitamin C and the fact that no darkening in color could be detected bear out this conclusion.

The concentrates prepared, the total of which when combined with the total volatile essence fraction and diluted to the original concentration of the fresh juice have a remarkable resemblance to the fresh juice.

The investigation of the fermentation of apple concentrates indicates that they may be successfully fermented to produce a wine of improved body and general flavor over wines prepared in the ordinary manner. Four different strains of the wine yeast were employed in fermenting the concentrates. They were: Champagne, Burgundy, Sauterne, and California strains. There was a definite difference in the rate of alcohol production and the quality of the fermented product for these different strains. The champagne strain of Saccharomyces elipseideus gives the best rate of alcohol

production and a low increase in acidity; but it does produce a definite bitterness not produced by the other strains. As the must to be fermented becomes more concentrated the bitterness in the fermented product also becomes more pronounced. It was found that upon adjusting the sugar-acid ratio of the wine fermented by this strain the bitterness was masked and a wine of pleasing flavor resulted.

Of the four strains of the wine yeast used in this experiment the product fermented by the champagne strain was rated as most desirable.

The rates of fermentation for concentrates were much more rapid than the rate for unconcentrated juice using sucrose for amelioration. The rate of fermentation using a 62 per cent solids apple concentrate as the source of sugar for alcohol was exceedingly rapid and produced a wine of good quality.

The fermentation of apple concentrates to produce an improved apple wine is entirely feasible provided the proper blend of apples is chosen in preparing the juice so that the final acidity will not be too high.

VI. PROPOSALS FOR FUTURE WORK

This glass vacuum evaporator with added condensing surface could be used for the concentration of heat labile materials other than fruit juices. Vitamin concentrates from materials in which they naturally occur could be prepared as well as other biological solutions. A by-pass should be installed in the return line from the liquid-vapor separator to the heat exchanger. This would permit trapping off of the liquid to check the progress of the concentration.

The possibility of removing some of the acid by ion-exchange should be investigated. An economic balance should be made to determine the cost of preparing concentrates for fermentation and compare this cost with that of using sucrose for amelioration and sweetening.

This method could well be applied to the production of wines from cherries, peaches, and plums — varieties which have an acid content low enough to permit concentration to the desired point. These fruits have a delicate flavor and if the materials responsible for the flavor could be retained during the concentration and that which was separated combined with the finished wine a superior product should result.

Another application of concentrates to enology

is in the preparation of a wine concentrate for use in cooking meats, poultry, and fish and for seasoning other dishes. This would mean that properly aged dry fruit wines would be concentrated to remove the alcohol, sweeted to the desired level and combined with any aromatic materials separated in the concentrating process. A highly flavored cooking liqueur would be obtained. The advantages of this preparation over ordinary wines used for cooking is that the latter in the case of fruit wines are too highly sweetened. In order to obtain the desired wine flavor the food is sweetened too much. The wine concentrate would be needed in smaller amounts and the objection of the sweetening effect would be overcome. An investigation of this idea has been undertaken and promising results are indicated.

BIBLIOGRAPHY

1. Beetlestone, N. C. Osmosis and fermentation. Journal of the Institute of Brewing. 36: 483-493, 1930.
2. Buck, R. E., and Mottern, H. H. Apple sirup by ion-exchange process. Industrial Engineering Chemistry (Industrial Edition) 37: 635-639, 1945.
3. Burton, Laurence V. High vacuum techniques utilized for drying orange juice. Food Industries 19: (5) 618-621, 1947.
4. Carpenter, C. C., and Smith, E. C. Apple juice concentrate. Industrial and Engineering Chemistry 26:449-454, 1934.
5. Charley, Vernon L. S. Fruit juices and syrups. Chemistry and Industry 15: 609-611, 1937.
6. Charley, Vernon L. S. Some investigations on the concentration and drying of fruit products. Chemistry and Industry 59: 823-825, 1940.
7. Charley, Vernon L. S. The commercial production of fruit syrups. Fruit Products Journal 17: 72, 1937.
8. Charley, Vernon L. S., Hopkins, D. P., and Pollard, A. A concentrated apple juice and treacle. Fruit Products Journal 21: 300-301 and 328-321, 1942.
9. Cross, Joseph A., and Gemmill, Arthur V. Revolutionary evaporator raises quality and lowers costs. Food Industries 20: (10) 1421-1423, 1948.
10. Cruess, William V. Commercial production of grape syrup. California Agricultural Experiment Station Bulletin 321, pp. 401-416, 1920.
11. Cruess, William V. The principles and practice of wine making. Avi Publishing Company, 1947, p. 239.

12. Davis, Benjamin L. Apparatus for continuous concentration of a solution under reduced pressure. Industrial and Engineering Chemistry (Analytical Edition) 14: (7) 548, 1942.
13. Eastern Regional Research Laboratory. New sweetness from apples; method for making it. Food Industries 14: 62-63, 1942.
14. Frary, Francis C., Taylor, Cyril S., and Edwards, Junius D. Laboratory Glass Blowing. Industrial Edition. McGraw-Hill Book Company, 1928, 1-80.
15. Gore, H. C. Apple sirup and concentrated cider; new products for utilizing surplus and cull apples. Department of Agriculture Yearbook, 1914, 227-229.
16. Griffin, E. L., Talley, F. B., and Heller, M. E. Comparison of essences from nine varieties of apples. Fruit Products Journal 27: 4-5, 1947.
17. Grove, O. Apple juice concentrates. Fruit Products Journal 13: 74-75 and 89, 1933.
18. Heldman, Julius D. Techniques of glass manipulation in scientific research. Prentice-Hall, Incorporated, 1946, 1-25.
19. Holzcker, Richard Apparatus and method of concentrating fruit juices. United States Patent Number 2,448,802. United States Patent Office Gazette 614: (1) 210, September 7, 1948.
20. Joslyn, Maynard A., and Comar, C. L., Determination of acetaldehyde in wines. Industrial and Engineering Chemistry (Analytical Edition) 10: 364-366, 1938.
21. Kemaerer, K. S. A rapid laboratory evaporator. Industrial and Engineering Chemistry 17: (7) 466, 1945.
22. Malcolm, Wade E. Concentrating fruit juices by freezing. United States Patent Number 2,436, 218. United States Patent Office Gazette 607: (3) 513, February 17, 1948.

23. McNair, J. B. Citrus Products, Part 1. Field Museum of Natural History Publication 236, Botanical Service, 6: (1) 121-128, 1926.
24. Milleville, Howard P. Present status of the manufacture and use of volatile fruit concentrates. Fruit Products Journal 27: (4) 99, December 1947.
25. Milleville, Howard P., and Eskew, Roderick K. Recovery and utilization of natural apple flavors. Fruit Products Journal 24: 48-51, 1944.
26. Milleville, Howard P., and Eskew, Roderick K., Recovery of volatile apple flavors in essence form. Western Canner and Packer, October, 1946, 51-54.
27. Mitchell, D. T., Sheldneck, and Dustin, James. Laboratory size glass circulating evaporator. Industrial and Engineering Chemistry (Analytical Edition) 16: (12) 538-540, 1944.
28. Mottern, H. H., and Morris, R. H. Bland apple syrup. Fruit Products Journal 23: 261-269, 1944.
29. Neubert, A. M. Effect of concentration on the composition and properties of rediluted juice. Fruit Products Journal 23: 166-169, 1944.
30. Poore, H. D. Production of apple juices, concentrates, and syrups. American Fruit Grower 55: 5-6, July, 1935.
31. Power, F. B., and Chestnut, V. R. The odorous constituents of apple emanation of acet-aldehyde from the ripe fruit. Journal of the American Chemical Society 42: 1509-1526, 1920.
32. Reavell, J. A. Recent work on the concentration of fruit juices and fruit drying. Chemistry and industry 15: 618-621, 1937.
33. Rooker, William A. A process of making fermented juice product. United States Patent Number 2,419,286. United States Patent Office Gazette 597: (4) 521, April 22, 1947.

34. Sanderson, H. A. Vacuum manipulation of volatile compounds. John Wiley and Sons, 1948, 3-93.
35. Strong, J. D. Procedures in experimental physios. Prentice-Hall Incorporated, 1945, 1-28.
36. Tavernier, J., and Jacquin, P. Influence of the partial elimination of nitrogenous matter in apple musts on the fermentation of cider; importance of defecation in cider making. *Chimie et Industrie* 56: 104-113, 1946.
37. Tressler, Donald K., Joslyn, Maynard A., and Marsh, George L. Fruit and vegetable juices. Avi Publishing Company, 1939, 356-399.
38. Wells, P. A. Apple essence of reduced alcohol content. *Fruit Products Journal* 27: 296, 1948.
39. Winton, Andrew L., and Winton, Kate Barber The structure and composition of Foods. John Wiley and Sons, Incorporated, 1935. 2: 565-584.
40. Wright, R. H. Laboratory glass blowing. Chemical Publishing Company Incorporated, 1943, 1-77.
41. Yang, Ho-Ya, The production of fruit wines in the Pacific Northwest. Paper presented before the 115th meeting of the American Chemical Society, March, 1949.
42. Zahm, George G. Concentrating liquids by evaporation. United States Patent Number 2,450,774. United States Patent Office Gazette, 615: (1) 209, October 5, 1948.