AN ABSTRACT OF THESIS OF

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in Food Science and Technology presented on January 22,1981

Title: STUDIES ON THE RECOVERY OF CONCENTRATE PEAR ESSENCE FROM RIPE BARTLETT PEARS

Abstract approved: D.V. Beavers

Previously, it has not been possible to obtain a concentrated ripe Bartlett pear essence. From studies of Bartlett pear aroma characteristics, it was found that methyl and ethyl decadienoates are the components contributing to the characteristic ripe Bartlett pear aroma. It was also found that only perfume-like aroma products, lacking in typical Bartlett pear aroma, could be obtained in the early pear essence recovery trials. Thus, a laboratory scale fruit essence recovery unit was designed and built to study the difficulties in pear essence recovery.

Water was first used to calibrate the unit, then, apple juice was applied as a testing model to establish the basic essence recovery effectiveness of the unit. It was found that the high heat provided by the reboiler, would drive the high-boiling, low-volatile pear aroma components upward to the fractionating column top where they could be recovered

as overhead product. The high-boiling compounds were found in the reboiler discharge water in the low-heat tests.

A good, strong and characteristic ripe Bartlett pear essence was obtained in the high-heat pear essence recovery test. A concept of separating low-boiling alcohols from high-boiling esters, to avoid the interference from low-boiling alcohols in the concentrating high-boiling esters, was substantiated through developing a two-stage essence recovery unit. Characteristic Bartlett pear essence of 100 fold was produced successfully in the two-stage test. Along with the organoleptic evaluation, the essence product was also analyzed by GC-MS and UV spectrometry to confirm the presence of "decadienoates" -- characteristic Bartlett pear aroma components. This is the first time that a typical and good quality ripe Bartlett pear essence of 100 fold has been recovered.

Studies on the Recovery of Concentrate Pear Essence from Ripe Bartlett Pears

by

Mei-Chen Miaw

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of science

Completed April 1981

Commencement June 1981

APPROVED:

Associate Professor of Food Science and Technology
in charge of major

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Date thesis is presented April 27, 1981

Typed by Mei-Chen Miaw

ACKNOWLEDGEMENT

I wish to express my sincere gratitude and appreciation to my major professor, Mr. Darrell V. Beavers for his guidence and assistance during the period of study and preparation of this thesis.

My sincere appreciation is also extended to Mr. Howard Milleville for his valuable ideas and suggestions.

I would like to express my sincere gratitude to my parents and my family for their continuous support and encouragement during all these years.

I would also like to extend my appreciation to Mr. M.T. Wang, for this would not come true without his help.

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INTRODUCTION

An aroma recovery process removes volatile aroma from foods and concentrates it to a useful aroma-rich product. In 1944, an apple essence recovery unit was first designed and built by Milleville and Eskew. Following the success of apple essence production, the same or slightly modified unit was applied to recover aromas from other fruit juices such as orange, blackberry, cherry, strawberry, etc. As a result, a new juice processing field was opened and developed.

Bartlett pear is one of the major fruits harvested in the Northwest area. In 1978, almost 20,000 tons of green pears were processed to make concentrated pear juice in the States of Washington and Oregon. The processed pear juice is used as the base or portion of mixed fruit juice drinks, such as pear and apple, or pear and grape juice concentrate which are now big sellers in fruit wines, and fruits canned in fruit juices. No straight pear juice is consumed at the present time. Due to the difficulties in pressing ripe pears, juice filtration, and clarification, very little commercial concentrate pear juice has been made from ripe pears.

There are some research groups working on those physical-chemical properties of ripe pear juice, and some

progress has been achieved. When the manufacture of good quality of concentrated pear juice from ripe pears is developed, the recovery of good concentrated pear essence must be considered. More than ten years ago, research work on pear aroma was conducted at the University of California at Davis. Ripe Bartlett pear juice was processed through a flavor recovery unit to obtain single fold pear aroma solution. The composition of Bartlett pear aroma was then analyzed and it was found that the ten-carbon "decadienoates" were the dominant compounds contributing to the characteristic Bartlett pear aroma. Since then, no further work has been done on Bartlett pear essence recovery. A pilot-plant scale fruit essence recovery unit was built several years ago by Beavers and Milleville for the recovery of pear essence with 100 fold concentration. The product obtained from their test was a perfume-like essence with a strong fruity aroma, but which lacked the characteristics of Bartlett pear flavor. When water was used to wash the unit after the test, they accidentally found that the wash water had a strong and typical Bartlett pear aroma. It showed that the typical characteristic Bartlett pear aroma components stayed somewhere inside the unit, probably in the distillation column, and did not reach the top outlet of the column. Therefore, it was concluded that there existed some factors which were the obstacles preventing pear essence recovery. A lab-scale continuous essence recovery unit was

designed and built to study the proper operating conditions and to overcome the difficulties in Bartlett pear essence recovery.

LITERATURE REVIEW

ESSENCE RECOVERY FROM FRUIT JUICES

In the early days of the juice concentrating industry, during the preparation of commercial fruit juice concentrate, the volatile flavoring constituents of fresh juice, which gives the natural bouquet, were lost. A "cut-back" method, in which the original strength juice was added to the concentrated juice, was customarily applied to make up the deficiency of aroma in the products. Dilution of concentrated juice was the main disadvantage of the cut-back method, as well as the high cost of the final product (Moore, 1954). The numerous processes developed to recover fresh fruit aroma were not completely successful in the early stages of the development of the art, because some of the more volatile components were lost, or the initial fresh flavor was inadvertently altered in the course of recovery. Mottern (1937) described a process of extracting fruit juice volatiles in an enriched solution.

A method of recovering and concentrating the fresh aroma of apple juice was developed by Milleville and Eskew (1944). Four steps of processes were included: (1) superheating the juice to 320°F in 3 seconds, (2) flash vaporizing 10% of the

superheated juice at atmospheric pressure, (3) mechanically separating the vapors from evaporized juice, and (4) fractionating the vapors to obtain a more concentrated aroma product with strengths between 100 and 150 fold. A supplement (1945) to Milleville's paper indicated that a single pass rapid evaporator, for which only 30 psig of steam was needed instead of 120 psig of steam, was superior to a superheater. The most important advantages of this evaporating method were a decrease of fouling on the heating surface by the juice and reduction of steam pressure required.

Following the success of apple flavor recovery, the pilot plant experiments on recovery of aromas from orange juice were studied by Milleville et al. (1954). They found that vaporization of 10 to 15 percent of orange juice, processed in a single-pass evaporator, removed all of the organoleptically detectable volatile flavors. The volatile flavors of orange juice, when condensed, consisted of an oil phase and a water phase. It was found that under atmospheric pressure operation, the aromas in the water phase could be concentrated up to about one hundred fold without any significant changes in their character or flavor loss with the exception of orange juice.

Thus far, the recovery of fresh flavor constituents without modification depended not only on a rapid vaporization, but also on the stability of volatiles at 212°F, when separated from juice. Considering the heat stability

of orange juice, it was suggested that the essences recovered could be of improved quality if the processes were conducted under vacuum to lower the operating temperature. An essence-sealed air scrubber was developed to avoid loss of volatiles in noncondensible gases. The stripped juice from the separator could be further flash-vaporized under vacuum and concentrated without development of a cooked flavor. Griffin et al. (1949) applied the orange essence vacuum recovery unit, (with a capacity of 10 gallons per hour) to other fruit juices --grape, strawberry, peach, blackberry, youngberry, huckleberry and rhubarb. Satisfactory results were obtained for all tests, except for grape juice -- something was missing in the final product.

Dimick et al. (1951) set up one laboratory scale continuous vacuum flash evaporator for removal of flavor constituents from fruit purees and juices. The apparatus was also useful for thermal inactivation of enzymes, for making juice and puree concentrates, and for deaerating liquids. The material was heated to 90°C or above to obtain a superheated effect and rapid boiling of juice under 5mm Hg pressure. Using a small pilot plant unit, model systems of water containing several different levels of volatile organic compounds, were used to estimate the efficiency of removal (Phillips, et al.1951). This ultra-rapid processing unit could give complete removal of volatiles and also pasteurize the juice with much less heat damage. In 1952, a similar

process was developed by the Eastern Regional Research Laboratory. They reported that recovery of aromas from jam kettles and vacuum pans during manufacture of jams and preserves was satisfactory.

Moor (1954) successfully recovered and concentrated flavor and aroma from Keyston's grape juice. Flash evaporation of juice, essence stripping and essence concentration procedures were all employed under atmospheric pressure. A juice concentrating unit was connected with an essence recovery unit, with water removal from fruit juices at atmospheric pressure. In one single step, most of the water, which constituted up to 89.4% by volume of a 10°Brix juice, was removed by rapid vaporization without fouling on the heating surface, making a 72°Brix concentrated juice. Stripped aroma was concentrated in fractionating column.

The early Milleville and Eskew processes required boiling the feed juice at atmospheric pressure, which in some cases damaged both the stripped juice and the essence. Smith and Cornwell (1963) developed a low temperature processing system, in which the volatile flavors were removed in a nitrogen stripping column. Byer and Lang (1964) described a process in which the essence was recovered at reduced pressure in a multiple-effect evaporator. Roger and Turkot (1965) published research results of fractionating column designing. The early designs (Milleville and Eskew, 1944) showed the vapors entering the reboiler without a stripping

section, and the tower was simply an enriching column. Later designs showed a progressively longer stripping section (Eskew et al., 1950; Redfield and Eskew, 1953; Claffey et al., 1958) on the column. Roger and Turkot reported that feeding the tower with liquid at its boiling point instead of vapor and supplying all of the heat of vaporization from the reboiler could give a higher efficiency for stripping volatiles from juices. They also indicated that a multiple-effect evaporator could be employed to utilize the latent heat from aroma-laden vapors to conserve the available steam supply.

Bomben et al. (1966) introduced the WURVAC (western utilization research vacuum aroma column) unit which used a vacuum to obtain desirable low temperatures, and a unique unit to absorb volatile materials in any suitable solvent by use of a liquid-sealed vacuum. Later on, Bomben et al. (1966) described a modified WURVAC system which was smaller in size and which contained changes in the design of the column. Orange essence recovered by WURVAC units were evaluated by Mannheim et al. (1967). Organoleptic and GLC analysis showed that the products containing "aroma solution" were at least equal to or more like fresh orange juice than products made by the commercial cut-back method. Bomben et al. (1969) remodified a WURVAC unit to produce aroma concentrates suitable for addition to dehydrated food. A stream of non-condensible gases was introduced into the column to

strip volatile aromas from 100 fold essence under a diaphragm vacuum pump instead of a liquid-sealed vacuum pump. The aroma concentrates were obtained by compressing the gas-volatile mixture and feeding it into cold traps where the volatiles were condensed at atmospheric pressure. This method provided essences of 1,000 fold or greater without reextraction.

FRACTIONAL DISTILLATION SYSTEM

Distillation is a method used to separate components having different boiling points in a mixture (Daniels and Alberty, 1974). It is widely applied in the petroleum industry to manufacture oil products. Theoretically, any two liquids which have different vapor pressures or boiling points at a given pressure, can be separated by fractional distillation (Carney, 1949). This process depends on the distribution of the substances between gas and liquid phases; each phase has a different composition. The boiling point/composition diagram (Fig. 1) of a simple binary solution can be used to explain the effect. When this binary solution is partially vaporized at T_1, the more volatile component A is concentrated in the vapor phase, and the equilibrium vapor. This vapor with composition b can be condensed by lowering the temperature along line bc. The vapor formed by partially vaporizing the condensate will have the composition corresponding to d. Therefore, the vapor phase is still further enriched in the component A. This process of vaporization and condensation may be repeated many times, with the result that a vapor fraction of pure component A is obtained.

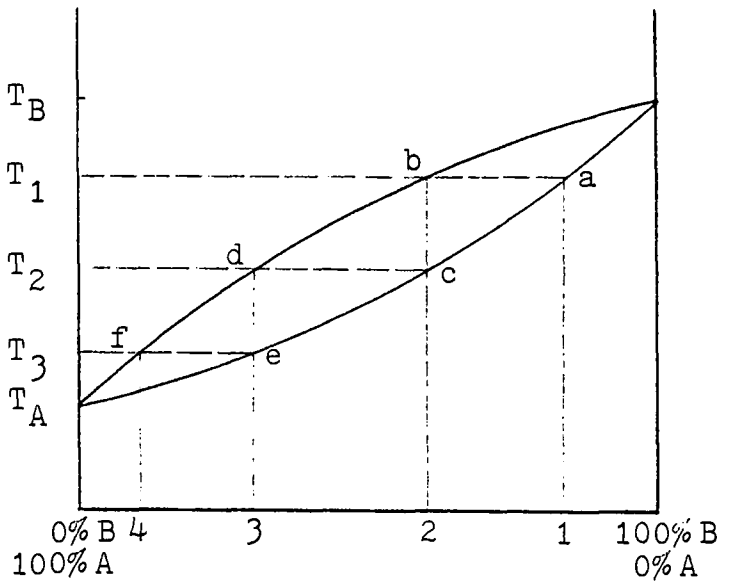


Figure 1. Boiling Point/Composition Diagram

However, instead of applying such a complicated sequence in the separation operation, it is preferable to carry out the same process in a fractionating column. The vapors leave the reboiler at the base of the column, travel up through the column and pass out the top where they are condensed. Part of the condensate is returned to top of the column as liquid reflux. As the vapors pass through the column, they contact the liquid phase traveling downward. Some of the more volatile components of the liquid phase are vaporized and enter the gas phase. This results in some of the less volatile components of the gas phase condensing into the liquid phase. This mass transfer takes place throughout the

column and produces a separation of components. In order to promote contact between two phases so that mass transfer may occur, the column is built up with bubble plates or packing materials to disperse both the gas phase and the liquid phase. A bubble-plate column is shown in Fig. 2.

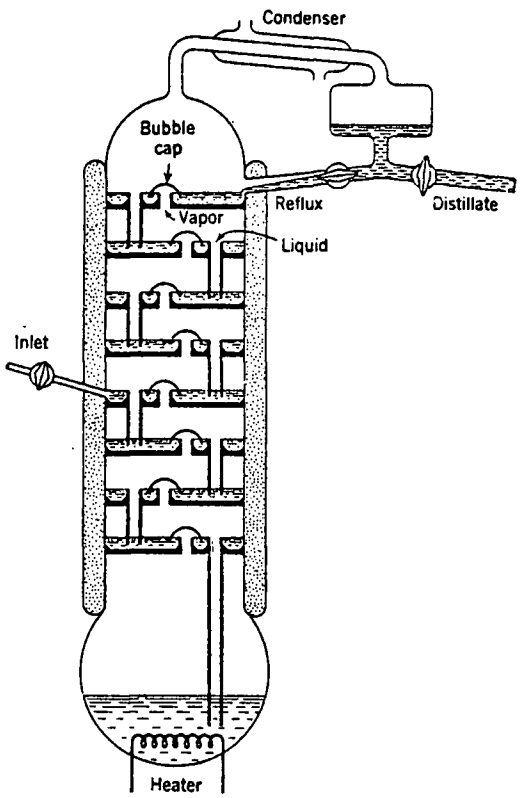


Figure 2. Bubble-cap Fractionating Column

Each bubble plate section is equivalent to a single still, and the liquid on the upper plate is equivalent to a condenser. Vapors leaving each plate are in equilibrium with the liquid on the plate, then pass upward through the bubble caps, where they are partially condensed. Part of the resulting solution is vaporized again and is condensed in the next higher layer, while part of the liquid overflows and runs down the tube to the next lower plate. In this manner, there exists a continuous flow of recondensed liquid returning to the reboiler at the bottom. In the essence distillation column system, this liquid returning to the bottom is water, and the vaporized/condensed liquid moving up to the top contains the concentrated aromas. The whole system attains a steady state in which the composition of the solution on each plate remains unchanged as long as the composition of feed-in material remains unchanged. The same theory can be applied to the packed column, and additionally, a packed column is able to provide a larger surface area for intimate vapor and liquid contact. When selecting the column type, one must consider the ease of construction, cost efficiency of the commercially constructed unit, and generality of usefulness (Carney, 1949). The most efficient type of fractionating column, when the pressure drop is not so important, is the bubble-plate column. However, it is not usually considered in the category of laboratory use because of the difficulty of construction and alterability. Also, a large quan-

tity of material is held up as liquid on the plates, thus reducing the efficiency of this type of column for small-scale laboratory fractionation, despite the advantage of its high throughput (amount of material passing through the column top in a unit time). Therefore, an easily-constructed, packed column is commonly used in the laboratory. A closely spaced packing may cause a continuous change in direction of the flow of liquid and vapor and results in maximum contact with a good throughput. Raschig rings are generally used for packing. They may be made of rolled or cast metals, porcelain, stoneware, glass, carbon and rubber, etc. Saddle packing is designed to reduce pressure drop in the column. The minimum liquid flow rate for the packed column is determined by the flow required to obtain adequate wetting of the packing. The packed column also has a relatively narrow satisfactory operating range of liquid flows and vapor flows. The most efficient operating effect occurs close to the flooding point.

CHARACTERISTICS OF AROMAS

Senses of color, texture, taste, odor and even sound are all parts of the flavor profile (Teranishi *et al.*, 1971). The definition of flavor as proposed by Hall (1968) is: "Flavor is the sensation produced by a material taken in the mouth perceived principally by the sense of taste and smell, and also by the general pain, tactile and temperature

receptors in the mouth. Flavor also denotes the sum of the characteristics of the material which produced that sensation." Material contributing to the odor response are the aroma compounds contained in food. The general characeristics of food aromas can be summarized as follows: (1) aromas produce a response in the human odor sense organ, (2) aromas are present at very low concentration in food, and (3) aromas are all organic compounds (Bomben et al., 1973).

Food aromas are usually a mixture of hundreds of compounds of widely varying molecular structure, boiling points, and solubilities. Esters, ethers, alcohols, aldehydes, ketones, hydrocarbons, amines and mercaptans are all types of compounds contributing to food aromas. Aroma molecules are produced in the normal metabolism of growing plants, by the action of enzymes on flavor precursors, or by chemical action of oxidation-reduction during cooking. The mechanism of aroma production is exceeding complex and only vaguely understood (Bomben et al., 1969). Hewitt et al. (1956) published a research paper on flavor formation. Flavor precursors were discussed in this report in which the precursors could be enzymatically changed to flavor compounds. During food processing, the enzymes catalyzing those chemical reactions were denatured by heat and lost their catalyticability. Some non-volatile heat stable compounds present in foods would survive processing and among these will be the flavor precursors. White mustard seed containing active

enzymes when added to dehydrated watercress and cabbage restored the characteristic aromas.

When compared to water, all aroma compounds have rather high molecular weight. Comparing the homologous series of compounds, the vapor pressure will decrease with an increase in molecular weight. Many of the aroma compounds also have long alkyl chains, which provide a repulsive force between aroma molecules and surrounding water molecules of the solution. This intermolecular force is described by a quantity called the "activity coefficient". The vapor pressure along with the activity coefficient will determine the volatility of a compound, which is the degree of how readily the compound escapes from a food (Bomben et al., 1973). A compound such as octanol (bp. 194°C) is more volatile in an aqueous solution than is ethyl alcohol (bp. 78°C). In general, the homologous series of compounds, when dissolved in water, will show an increase of volatility with increasing molecular weight (Butler et al., 1935; Buttery et al., 1969). Therefore, in the course of aroma recovery, volatilities of constituents which contribute to significant food flavor and aroma are important, when considering the efficiency of the process. Within a homologous series, the relative volatility increases as the hydrocarbon chain is lengthened. A decrease in vapor pressure is more than compensated for by an increase in the activity coefficient. As a result, in a dilute aqueous system, high-boiling compounds are more volatile

than low-boiling compounds.

The term "essence" is used to describe "the concentrated aroma solution", which is desirable in practical industrial utilization. The accepted method of defining essence concentration is by the term "fold". This is the volumetric ratio of liquid feed and essence obtained. Basically, essence is composed of 92 to 95% water, even when it is in the concentrated form; 5 to 8% alcohols (methyl and ethyl alcohol), and some tenth of a percentage unit to ppm of the typical aroma contributing constituents, such as aldehydes, ketones, esters, etc. The aroma recovery process removes the volatile aromas from foods and concentrates it to the essence.

In the aroma removal steps, the aroma is transferred from food to a second phase. This second phase can be a gas, liquid or solid (Bomben et al., 1973). No matter how the second phase is formed, separation of any aroma compound from another food component can be achieved if the ratio of concentrations of these compounds is different in two phases (in terms of the separation factor). The separation can be reached at a single stage if the separation factor is large. If the separation factor approaches unity, then it will need several equilibrium stages to achieve the complete separation. The separation factors for the compounds in apple juice are much higher than that for methyl anthranilate (the dominant compound which contributes to Concord grape

aroma), and consequently they are easily concentrated at the top of the column over a wide range of operating conditions (Bomben et al., 1969).

Considering the stability of food flavors, the major factors causing off-flavors in foods are oxidation and microbial deterioration. Heat and light also play a part in the formation of off-flavor (Keppler, 1977). An investigation on storage stability of frozen citrus concentrate indicated that storage temperature greatly affects the rate of chemical and physical change in stored concentrate (DuBois et al., 1951). No significant changes were noted during 11 months storage at $0^{\circ}F$ or below. Kew et al (1962) made a similar report of concentrated citrus juice stability.
Blair et al. (1952) pointed out that the off-flavor which developed in canned orange juice is due to some of the substances produced by chemical interaction of the terpenes contained in the peel-oil with the acid juice.

CHEMICAL PROPERTIES OF PEAR ESSENCE

The chemical and physical properties of Bartlett pears of different degrees of ripeness were investigated to establish the relationship between the maturity of fresh pears before canning and the acceptance of the finished products (Leonard et al., 1954). Claypool et al. (1958) reported that Bartlett pears from different growing areas differ greatly in content of acid, soluble solids, volatile, and

reducing substances. The ripening temperature and firmness at canning are important to the flavor of the canned products. A considerable amount of attention has been directed to the gross composition of pear fruits and various workers have studied the specific groups of compounds that are present. Harley and Fisher (1927) were able to demonstrate the presence of acetaldehyde among volatiles, and Tindale et al. (1938) followed the alcohol and acetaldehyde content of Bartlett pears during ripening. They observed a continuous increase in the alcohol content, and reported that acetaldehyde increased during cold storage and subsequent ripening, then reached the maximum at core breakdown. Antoniani et al. (1954) conducted maturity studies on both pears and apples, and reported that the amount and ratios of 2, 3 butylene glycol and acetoin varied during the ripening process. Antoniani and Serini (1955), and Serini (1956) reported similar observations. Luh et al. (1955) announced that as pears ripened at 20°C, methyl alcohol, total carbonyl compounds, acetyl methyl carbinol, diacetyl, and esters content gradually increased. Mehlitz and Matzik (1950) identified formic and acetic acids by paper chromatographic studies of the volatile acids of several pear varieties, but did not include Bartlett pears. In the conventional pear puree process, volatiles were driven off into the atmosphere with the result that the puree produced, was almost totally lacking in flavor.

On the basis of matching gas chromatographic retentions, Drawert (1962) identified ethyl formate, methyl acetate, ethyl acetate, ethanol, isopropanol, 2-butanol, 2-methyl propanal, n-butanol pentanol, 3-methyl butanol, n-hexanol, and other esters in pears. Lim (1963) utilized the same method in following the production of the low-boiling volatiles from Bartlett pears and other fruits during the ripening process. He identified ethylene, acetaldehyde, and six normal acetates from methyl to hexyl acetate in Bartlett pears. Jennings et al. (1960) gave attention to the volatiles which are ultimately responsible for the characteristic pear aroma. By processing fresh ripe pears in a specially designed closed system, a dilute aqueous aroma solution with typical desirable aroma of Bartlett pears was recovered. The extracts of aroma solution were fractionated by gas chromatography into 32 fractions. Each of these was submitted to a trained aroma panel, and five of them appeared to contribute significantly to the desirable pear flavor, while four possessed atypical and undesirable aromas. Jennings (1961) and Jennings and Creveling (1963) established that the typical aroma of Bartlett pears was due to esters and studied the hydrolysis products of pear aroma by gas chromatographic separations, infrared and ultroviolet spectroscopy of individual fractions. They reported that the hydrolysates consisted of acetic, propionic, butyric, caproic, caprylic, nonanoic, and 2,4-decadienoic acids; ethyl,

n-propyl, and n-hexyl alcohols.

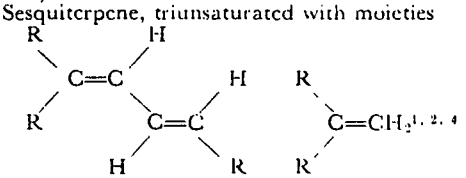
Regarding sensory evaluation, aroma compounds from natural sources can frequently be divided into two separate classes (Jennings, 1964). One class consists of natural components of the substance that individually possess aromas suggestive of, and differentiating that substance, might be termed "character impact compounds". The other class might be termed "contributory flavor compounds". These could be defined as natural compounds of the substance that contribute fruitiness, bouquet or fullness but do not suggest the particular fruit or product source. In further studies of volatile esters of Bartlett pears (Jennings and Serenants, 1964 A), Bartlett pear essence was separated by gas chromatography without losing its desirable aroma characteristics. It was determined that the methyl ester of trans-2:cis-4 decadienoic acid was a "character impact compound", and hexyl acetate was identified as a "contributory flavor compound" of Bartlett pear.

Heinz et al. (1964) studied the relation of instrumental and sensory techniques as methods evaluating the intensity of pear aroma. A satisfactory method was developed, utilizing ultra violate spectroscopy. The 2,4-decadienoate concentration was determined by measuring the absorption intensities of aqueous pear samples at 263-267 mμ. The results of these measurements were shown to correlate well with the aroma intensities. Heinz et al. (1965)

followed the production of these decadienoate esters during the ripening of Bartlett pears, and found that the rate of development reached a maximum immediately following the climacteric point. The individual compound of pear aroma was identified by using techniques including retention data, infrared, ultraviolate, nuclear magnetic resonance, and mass spectroscopy, melting point and formation of appropriate derivatives (Heinz and Jennings, 1966). Components of Bartlett pear essence which were identified, are listed in Table 1.

Light and oxygen may cause the cleavage of cis bonds of the trans:2-cis:4-decadienoate esters in the essence to form 4-oxy trans butenoate esters and hexanal (Jennings, 1967). Even though oxidized, this essence still possessed characteristically desirable pear aromas. There is very little information available about storage stability of pear essence. Leonard et al. (1976) indicated that canned pear puree with pear essence added back, was stored at 68°F and 34°F for one year. No significant change occurred in either stored temperature sample.

Table 1. Volatile Components of Bartlett Pear

Methyl acetate[1]	Ethyl *cis:* 4-decenoate[2, 5, 6]
Ethyl acetate[1, 2]	Methyl *trans:* 2-*cis:* 4-decadienoate[1, 2, 4]
Ethanol[1]	Methyl 3-hydroxy octanoate[2, 3, 6]
Propyl acetate[1]	Ethyl *trans:* 2-decenoate[1, 2]
Propanol[1]	Sesquiterpene, triunsaturated with moieties
Butyl acetate[1, 2]	
Hexanol[1, 6]	
Butanol[1, 2]	
Amyl acetate[1, 2]	
Pentanol[1, 2]	
Hexyl acetate[1, 2]	
Hexanal[1, 2]	
Cis-hexenyl acetate[2]	Methyl *cis:* 2-*trans:* 4-decadienoate[2, 7]
Heptyl acetate[1, 2]	Methyl *trans:* 2-*trans:* 4-decadienoate[2, 7]
Methyl octanoate[1]	Ethyl *trans:* 2-*cis:* 4-decadienoate[1, 2, 4, 7]
Methyl 4-oxy *trans* butenoate[2, 4, 5, 6]	Ethyl 3-hydroxy octanoate[2, 3]
n-Heptanol[1]	Ethyl dodecanoate[1]
Ethyl octanoate[1, 2]	Ethyl *cis:* 6-dodecenoate
Ethyl 4-oxy *trans* butenoate[2, 4, 6]	Ethyl *trans:* 2-*trans:* 4-decadienoate[2, 7]
Octyl acetate[1, 2]	Propyl *trans:* 2-*trans:* 4-decadienoate[2, 7]
Methyl *trans:* 2-octenoate[2]	Ethyl *trnns:* 2-dodecenoate[1, 2]
n-octanol[1, 2]	Ethyl *trnns:* 2-*cis:* 6-dodecadienoate[1, 2]
Ethyl *trans:* 2-octenoate[1, 2]	Butyl *trnns:* 2-*cis:* 4-decadienoate[2, 7]
Methyl decanoate[1, 2]	Methyl *cis:* 8-tetradecenoate[2]
Methyl *cis:* 4-decenoate[1, 2, 6, 7]	Ethyl tetradecenoate[1]
Ethyl decanoate[1, 2]	Ethyl *cis:* 8-tetradecenoate[2]

[1] Retention data.
[2] Infrared spectral data.
[3] Mass spectral data.
[4] Ultraviolet spectral data.
[5] Melting points.
[6] Derivatives.
[7] Synthesis.

ANALYSIS

The fundamental steps in analysis are separation, detection and identification. Early investigators studying aroma components were seriously handicaped because the methodology then available was not adaptable to the isolation and identification of extremely small amounts of volatile components. The development of the gas chromatograph has given the flavor chemist a significant tool in dealing with the small amount and complex composition of aroma samples. Actually, gas chromatography is nothing more than a method for separation of a chemical mixture into individual fractions. A single chromatographic separation infrequently results in fractions composed of a single compound. It is, therefore, important to collect each fraction and to re-chromatograph it so that a definitely isolated component can be achieved. The retention time of separation can give an indication of possible compounds, but it cannot be a dependable criterion for identification of each isolated compound. Dissimilar retentions can establish that two compounds are not identical. Similar retentions only indicate that a difference between two compounds have not yet been demonstrated. For definitive characterization studies, it is highly desirable to collect and re-chromatograph each individual fraction before finally subjecting the individual components to further identification. Teranishi *et al.* (1965) described a simple device for

collection of 0.5 to 5 and 5 to 100 milligrams of gas chromatographically purified material as oxygenated terpenes. The collected single compound can be further analyzed by mass spectrometry, infrared spectroscopy and NMR spectrometry to obtain final identifications (Jennings, 1963, 1964 and 1966).

A major problem in investigation of chemical components is the preparation of an aroma sample suitable for gas chromatographic separation. It is desirable that the concentrated sample represent, qualitatively and quantitatively, the volatiles originally present, without the production of additional compounds. The injected sample must contain enough of each individual component to activate the detector. Ideally, each chromatographic component should exist, as it passes through the column, as a concentrated mass occupying as short a length of column as possible. The injected sample must be small with relation to the volume of the carrier gas flowing into the column, and this small sample must be concentrated enough to give measurable peaks on a chart.

Direct injection of headspace vapor is the simplest way to introduce samples, (Jennings, 1965; Bussett et al., 1963; Jennings et al., 1962; Teranishi et al., 1963; Mendelsohn et al., 1966), but it is limited by the fact that in order to obtain detectable quantities of dilute vapor components, one must use such a massive quantity of vapor that the injection requires a considerable period of time, and the separated

components are, as a result, so diluted by carrier gas that they may escape detection.

Concentrated extracts of steam distillates are frequently satisfactory. Jennings (1967) utilized a deaerator effluent from a large commercial cannery that processes fresh fruits into purees. A large scale continuous liquid-liquid extractor, and charcoal absorption methods have been used by Heinz (1966). Both types of essences possessed the desirable aroma and their chromatograms are almost identical. Jennings and Nursten (1967) also developed a charcoal absorption method that permitted the concentrating of volatiles from very large vapor samples and their elution for chromatographic analysis. Ten percent Triton X-305 on Gas Chrom Q, 10% Carbowax 20M on Gas Paxk F or 20% Apiezon L on Chromosorb W have been suggested by Jennings (1967) to obtain the most satisfactory GC separation of the volatiles composing pear essence. However, none of these completely resolve this complex mixture.

The colorimetric method developed by Hill (1946, 1947), based on the conversion of esters to hydroxamic acids which formed a red complex with ferric ion, has been adapted for the estimation of volatile esters (Luh, 1955). The absorption spectra of the ferric hydroxamate complex show a maximum absorption at 520 mμ.

The further investigation reported by Thompson (1950) has led to a satisfactory procedure for esters derived from

acids with a unbranched chain of two to ten carbon atoms and esters of isobutyric and isovaleric acids. It had been established by Jennings (1961) that one of the major acids occuring in pear essence hydrolysates was a c-10 unsaturated acid that hydrogenated to yield n-capric acid. Jennings and Creveling (1963) reported an ultraviolet absorption curve for n-capric acid with a maximum at 260 mμ, Crossby and Hilditch (1949) reported a very similar curve for deca-2, 4-dienoic acid. Jennings, Creveling and Heinz (1964) reported the triconjugated system of the trans:2,cis:4-decadienoates isomers, which were the character impact compounds of Bartlett pear, exhibited maximum absorbances at 263 mμ. Heinz et al. (1964) have found that the dominant aroma compounds of ripe Bartlett pears (decadienoates) have maximum absorptions at 263-267 mμ, and used this method as a direct determination of typical aroma compounds in pear maturity studies (Heinz, Creveling and Jennings, 1965).

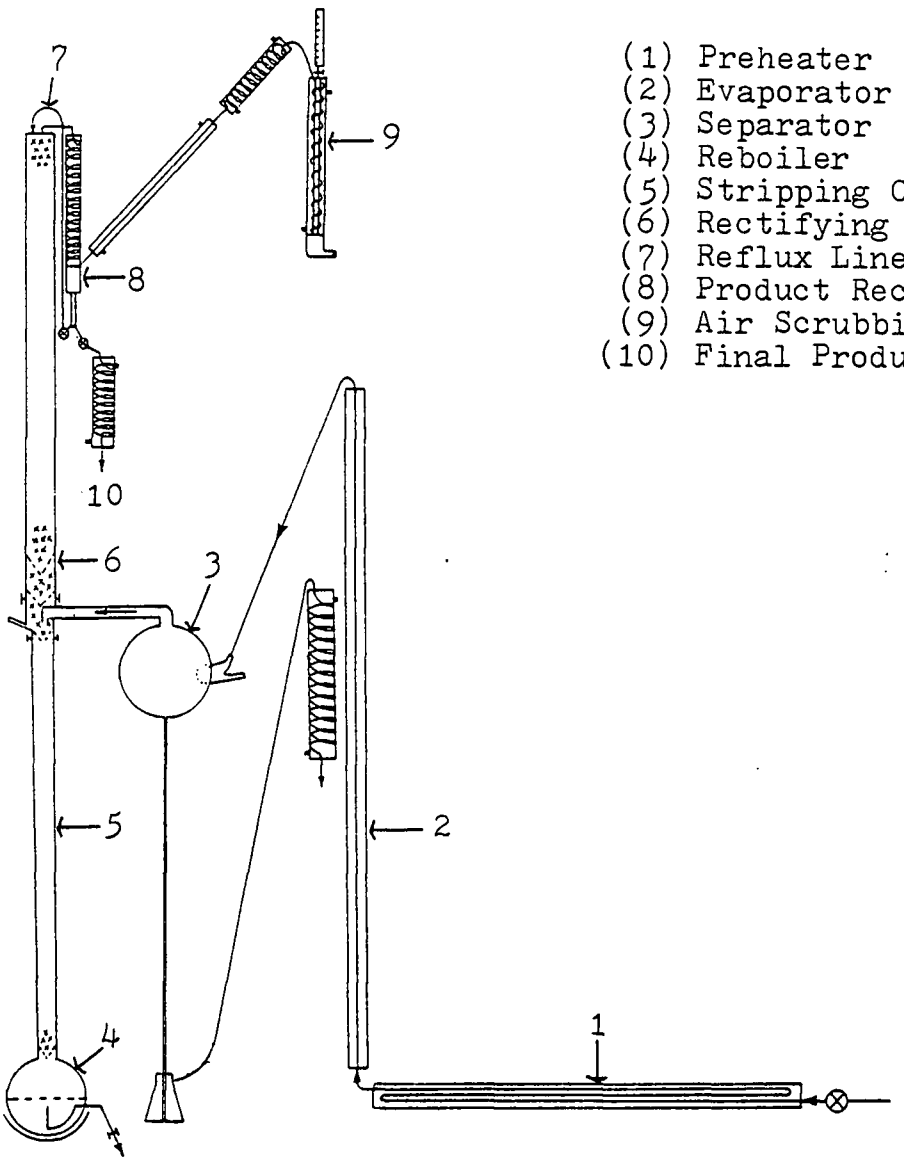
CONSTRUCTION AND DESCRIPTION OF UNIT

Milleville conducted a study entitled "Pilot Plant for Concentrating Fruit Juice and Recovering Volatile Flavors" in 1977. Based on this report, a laboratory-scale, atmospheric pressure continuous essence recovery unit with a capacity of 4,000-7,500 ml per hour was designed and built as shown in Figure 3. This unit includes (1) juice preheater, (2) partial juice evaporator, (3) fractional distillation system, and (4) vent-gas scrubbing system.

Juice Preheater and Juice Evaporator

A piece of two inch O.D./36 inch long stainless steel column was used as a steam jacket for the preheater. A nine feet long stainless steel tubing of 1/8 inch O.D. was arranged with two turns inside the preheater steam jacket as shown in Figure 4. The evaporator consisted of a piece of five feet long stainless steel tubing with a 3/8 inch O.D. inserted inside a stainless steel steam jacket five feet long and 1½ inches O.D. as shown in Figure 4.

The operating conditions were estimated in advance. Based on the estimated data, the sizes of preheater and evaporator were calculated and constructed.



(1) Preheater
(2) Evaporator
(3) Separator
(4) Reboiler
(5) Stripping Column
(6) Rectifying Column
(7) Reflux Line
(8) Product Receiver
(9) Air Scrubbing Tower
(10) Final Product

Figure 3. One-Stage Essence Recovery Unit

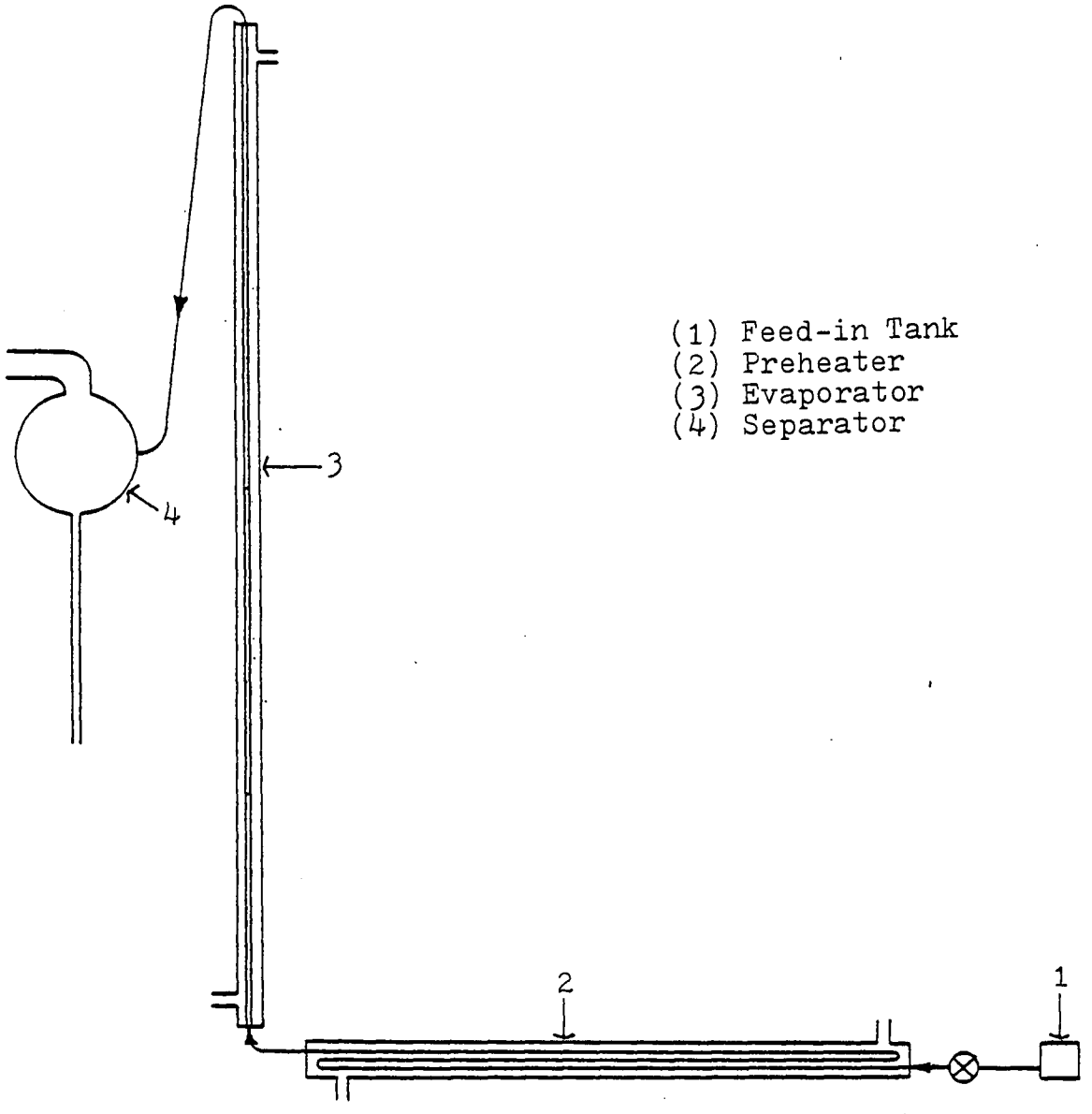
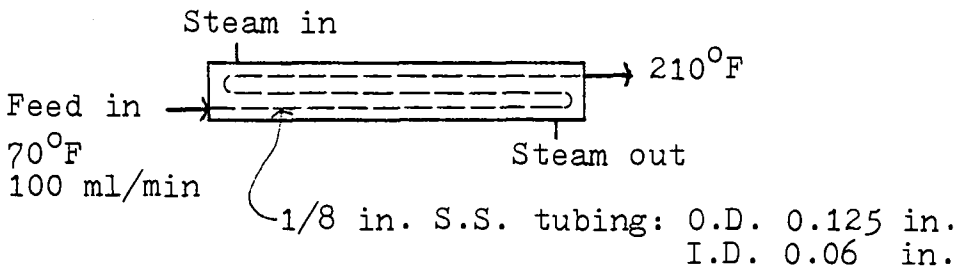


Figure 4. Preheater and Evaporator

Heat Exchange Calculation

I. Preheater



1 gallon = 8.3 lb = 3,785 ml

100 ml/min = 13.22 lb/hr

steam at 1 psig = 214°F

steam at 5 psig = 230°F

$Q = mC_p \Delta T$

$= 13.22$ lb/hr x 1.0 Btu/lb-°F x (210-70)°F

$= 1{,}850.8$ Btu/hr

Assume: Surface transfer coefficient of condensing steam is $h_o = 1{,}000$ Btu/ft^2-hr-°F (Henderson and Perry, 1966, P. 232)

Surface transfer coefficient of water in pipe is $h_i = 930$ Btu/ft^2-hr-°F (Henderson and Perry, 1966, P. 232)

L = thickness of tubing = 0.065 in

K = 12.4 Btu/hr-ft^2-°F/ft (Henderson and Perry, 1966, P. 231)

$$U = \frac{1}{\frac{1}{h_o} + \frac{L}{K} + \frac{A_o}{h_i A_i}} = \frac{1}{\frac{1}{1,000} + \frac{0.065/12}{12.4} + \frac{(0.125)^2}{930(0.06)^2}}$$

$$= 163.84 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F}$$

(A) When 1.0 psig of steam is used, assume one fluid constant temperature.

$$\Delta Tm = \frac{(210-70)^\circ F}{\ln \frac{(214-70)^\circ F}{(214-210)^\circ F}} = 39.07^\circ F$$

$$Q = UA\,\Delta Tm$$

$$1,850.8 = 163.84 \times A \times 39.07$$

$$A = 0.289 \text{ ft}^2 = \pi \times D \times L = \pi \times 0.01 \text{ ft} \times L$$

$$L = 9.20 \text{ ft}$$

(B) When 5.0 psig of steam is used, assume one fluid constant temperature.

$$\Delta Tm = \frac{(210-70)^\circ F}{\ln \frac{(230-70)^\circ F}{(230-210)^\circ F}}$$

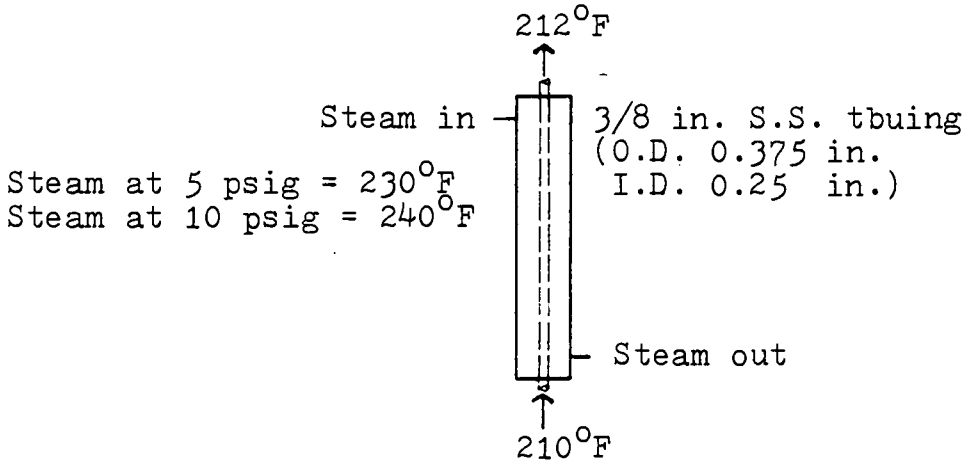
$$Q = UA\,\Delta Tm$$

$$1,850.8 = 163.84 \times A \times 67.32$$

$$A = 0.1678 \text{ ft}^2 = \pi DL$$

$$L = 5.34 \text{ ft}$$

II. Evaporator



Assume 30% of vaporization rate by mass

13.22 lb/hr x 30% = 3.966 lb/hr

latent heat of vaporization = 960 Btu/lb

$Q = mC_p \Delta T$

$= 13.22 \times 1 \times 1 \times (212-210) + 3.966 \times 960$

$= 3,833.8$ Btu/hr

h_o = 1,000 Btu/ft^2-hr-^{o}F (Henderson and Perry, 1966, P. 232)

h_i = 930 Btu/ft^2-hr-^{o}F (Henderson and Perry, 1966, P. 232)

L = thickness of tubing = 0.0625 in

K = 12.4 Btu/hr-ft^2-^{o}F/ft (Henderson and Perry, 1966, P. 231)

$$U = \frac{1}{\frac{1}{h_o} + \frac{L}{K} + \frac{A_o}{h_i A_i}} = \frac{1}{\frac{1}{1,000} + \frac{0.0625/12}{12.4} + \frac{(0.375)^2}{930(0.25)^2}}$$

$$= 260.46 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F}$$

(A) When 5.0 psig is used, assume one fluid constant temperature.

$$\Delta Tm = \frac{(212-210)^\circ F}{\ln \frac{(230-210)^\circ F}{(230-212)^\circ F}} = 18.98^\circ F$$

$$Q = UA\,\Delta Tm$$

$$3,833.8 = 260.46 \times A \times 18.98$$

$$A = 0.775 \text{ ft}^2 = \pi DL$$

$$L = 7.89 \text{ ft}$$

(B) When 10.0 psig of steam is used, assume one fluid constant temperature.

$$\Delta Tm = \frac{(212-210)^\circ F}{\ln \frac{(240-210)^\circ F}{(240-212)^\circ F}}$$

$$Q = UA\,\Delta Tm$$

$$3,833.8 = 260.46 \times A \times 28.98$$

$$A = 0.508 \text{ ft}^2 = \pi DL$$

$$L = 5.17 \text{ ft}$$

It is concluded, from the above calculations, that if 100 ml/min of feed-in rate with 30% of vaporization rate is used in the operation, the lengths of preheater and evaporator are determined as following:

Table 2. Determined Size of Preheater and evaporator

Steam Pressure	1.0 psig	5.0 psig	10.0 psig
Preheater	9.20 ft	5.34 ft	--
Evaporator	--	7.89 ft	5.17 ft

Therefore, nine feet of preheater and five feet of evaporator tubing were used for this unit in order to obtain the needed heat transfer.

VAPOR-LIQUID SEPARATOR

One three-liter round glass flask with a horizontal-tangential inlet was used as a separator, as shown in Figure 5. This was connected with the evaporator by a piece of 1/8 in. O.D. tygon tubing. Leaving the evaporator, the mixture of vapor and juice flashes into the separator. As a result, a whirling motion is produced inside the flask when the mixture enters tangentially. A centrifugal motion is produced which separates the vapor from the liquid. The separated vapor goes into the fractionating column from the top outlet of flask, and the separated liquid drains from the flask through the bottom opening. A small amount of pressure is formed inside the flask by flashing the mixture into the separator, and therefore, some vapor will rush out of the bottom of the flask along with the liquid. In order to prevent this, a water sealed barometric leg was constructed so as to ensure a closed system.

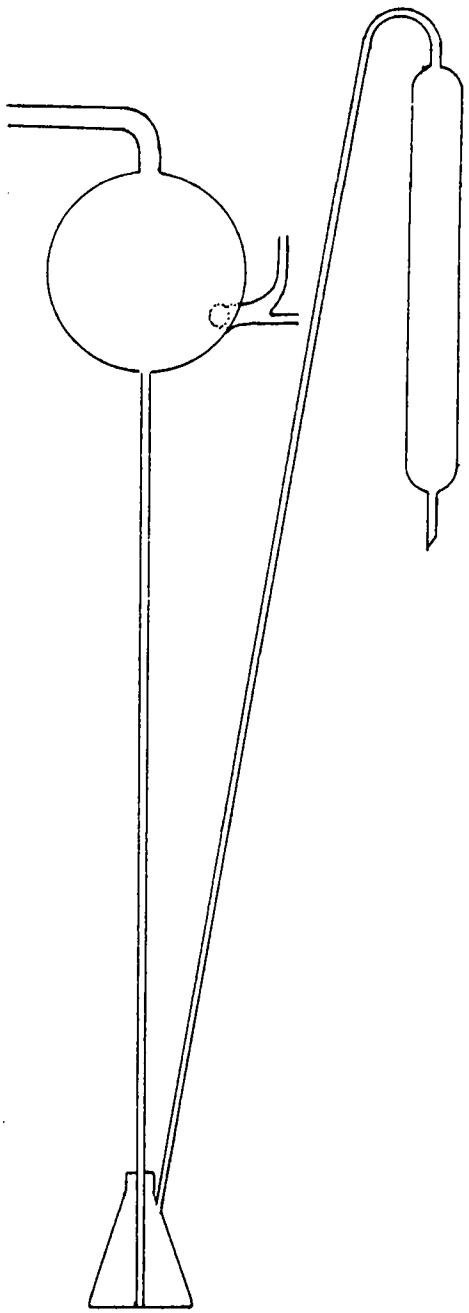


Figure 5. Vapor-Liquid Separator

FRACTIONAL DISTILLATION SYSTEM

Two sections of glass columns packed with curved ½ inch x ¼ inch porcelain saddles were connected together as the fractionating column. The upper part, beyond the feed, is 40 inches long with two inches I.D.. This is known as the rectifying section. The column below the feed is 36 inches long with 1½ inches I.D.. This is the stripping section. A one-liter round glass flask connected to the bottom of the stripping column acts as the reboiler, and a hot plate generates heat to boil the water in the reboiler, as shown in Figure 6. Vapors enter the fractionating system through the feed-in side arm between the stripping and rectifying sections. Most of the entering vapor will be condensed and drip downward in the column. The heat provided by boiling water in the reboiler will revaporize the condensate to strip the volatiles. A siphon tube attached inside the reboiler is used to regulate the water level in the reboiler. Several funnel shaped metal screens inserted in the column are used as packing support and to reposition and center the condensed vapors (liquid) which flow downward along the column wall. Vapors containing aroma components escape from the top outlet of the rectifying section and enter the condenser. Since the feeding vapors are 30% of the original juice feed, they contain mostly water: 3-6% noncondensible gases (dissolved gases in the juice), and only trace amount

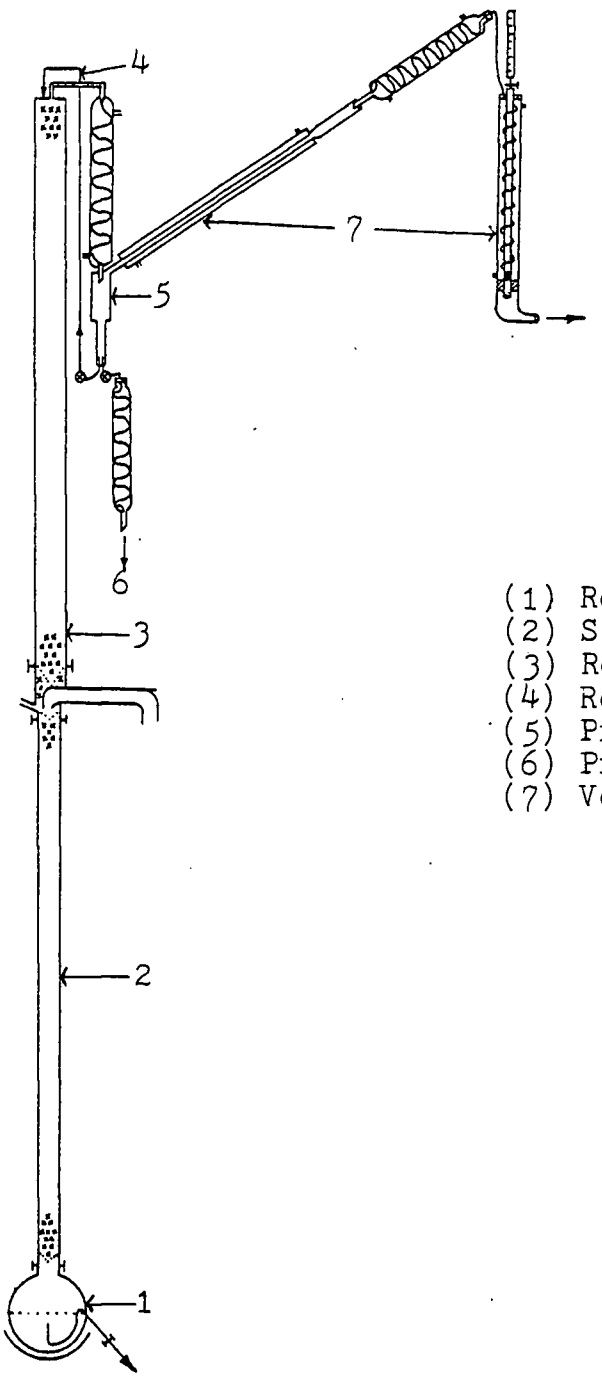


Figure 6. Fractional Distillation System

of volatiles. An FMI lab pump is used to feed the condensed vapor (liquid) back into the top of the fractionating system in order to produce a further concentrating effect. In a commercial essence recovery unit, the condenser is usually located away from the column with the reflux returned through a U-tube, as shown in Figure 7. This helps to prevent vapors from the column by-passing the condensate. When a small diameter reflux tube is used for the laboratory-scale unit, the tube will be "airbound" and the flow stops. Therefore, it is essential to have a pump returning the reflux to the column. The condenser can then be placed alongside of the column to save headroom. Returning the reflux cold can increase the fractionating efficiency of the column, but decrease the capacity and the thermal efficiency of the column. The most efficient procedure, especially for the small laboratory system, is to barely condense the vapor, and to return the hot liquid to the top of the column.

Another FMI lab pump is used to pump the condensate in the receiver to the product condenser for cooling, and then into the final product receiver. The product pump rate is set at one-hundredth of the juice feed-in rate to obtain a 100 fold essence. To reiterate, "fold" only indicates the volume ratio between the original juice feed and the final product.

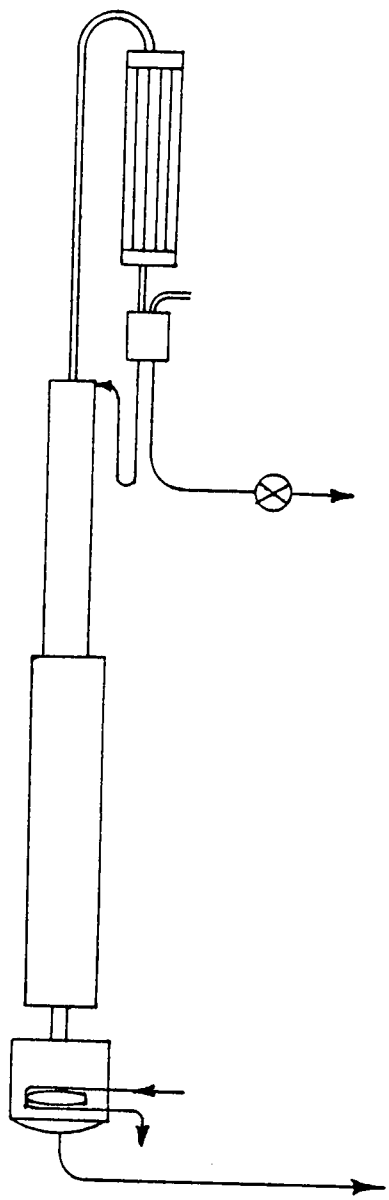


Figure 7. Reflux Feed-Back Set

VENT-GAS RECOVERY SYSTEM

Noncondensible gases (usually 3 to 6% by volume of juice, which is dissolved in the juice) include oxygen, nitrogen, and carbon dioxide which will be removed from the juice along with the volatiles and will eventually be vented from the system. The condensate in the receiver is hot, so some low-boiling volatiles will not be condensed and they will escape with the noncondensible gases. To prevent this loss, these vapors are condensed in a multi-stage system and the condensate is added to the hot liquid reflux from the first condenser. A straight condenser connected to the receiver is used as the first "vapor trap". This condenser condenses most of the volatile vapors. The second condenser (a coil condenser) in series further condenses any remaining vapor, and then, the escaping vent gases go through a 1/8 inch O.D. plastic tubing to the third condenser, as shown in Figure 8. The third condenser in the series is comprised of a 1/8 inch O.D. stainless steel tube coiled around the air scrubbing tower and inserted into a glass water jacket. Distilled water drips at the rate of one drop/30 seconds into the glass bead packed air scrubbing tower to catch any volatiles which remain in the noncondensible gases. The final condensate and the washing water are collected in a small receiver. This collected washing liquid is combined with the product from the fractional distillation to make the final full-flavor essence.

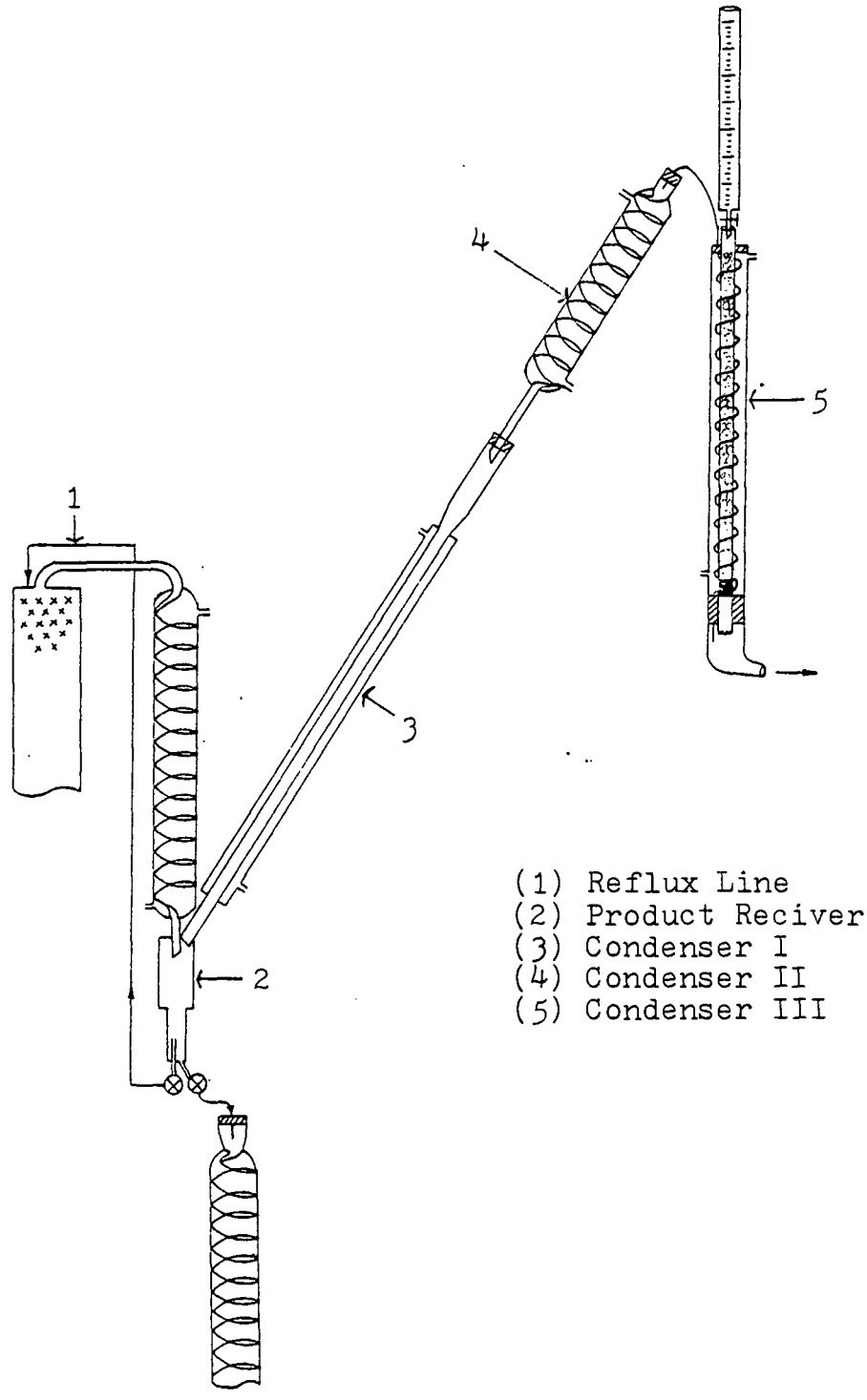


Figure 8. Vent-Gas Recovery Set

EXPERIMENTAL

GENERAL OPERATING PROCEDURES FOR THE ESSENCE RECOVERY UNIT

The equipment used for all of the fruit essence recovery tests is shown in Figure 3. To start the operation, first fill the reboiler half full with distilled water, and turn on the burner to heat up the water. It takes about half an hour to heat up the stripping section of fractionating column by generated vapors from the reboiler. Turn on cooling water at maximum flow for all condensers except the reflux condenser. Cooling water in the reflux condenser should be just enough to condense the vapor but not enough to cool the condensate and thereby not decrease the fractionating efficiency. Turn on the steam for preheater and evaporator at required steam pressure to give desirable heating and vaporizing effects. Start the feed-in pump which is set at a predetermined flow rate. Tap water is pumped into the system for about one hour to wet the fractionating column, and let the whole unit reach a steady state. The reflux pump is turned on to return the hot condensate in the receiver back to the fractionating column. After the unit has reached steady state and is stable, switch the feed material from tap water to the testing juice, drain off the condensed water in the receiver when juice is fed into the unit to eliminate the dilution caused by the existing water in the receiver. Distilled water is

dripped into the air scrubbing tower at one drop/30 seconds rate to catch any aroma compound leaving with venting gases. A few drops of sample is collected every 15 minutes from a feed-back "T" connection after the testing juice enters the system. Several mls of reboiler discharge water were gathered every 30 minutes to check the completeness of aroma stripping in the stripping section. When the whole system reaches steady state, individually collect the discharged water from the reboiler and "stripped" juice from the separator for a timed period. From the volume measured for a given time, the actual feed-in rate and vaporization rate can be obtained. The total volume of both collections will be the feed-in rate. The amount of discharged water from reboiler equals the amount of vapor entering the fractionating column. After 2½ to 3 hours of running the juice, turn on the product pump at 1/100 of the feed-in rate.

Sixteen thermocouples were inserted in the unit at sixteen different positions to detect the temperature. Ten of them were inside the rectifying section of the fractionating column to monitor the temperatures at each position, as shown in Figure 9. All of the thermocouples were connected to a multi-channel recorder and the temperatures were recorded.

For shutting down the unit, switch feed from juice to tap water for at least two hours to wash the unit. Keep all operations the same, except when turning off the feed-

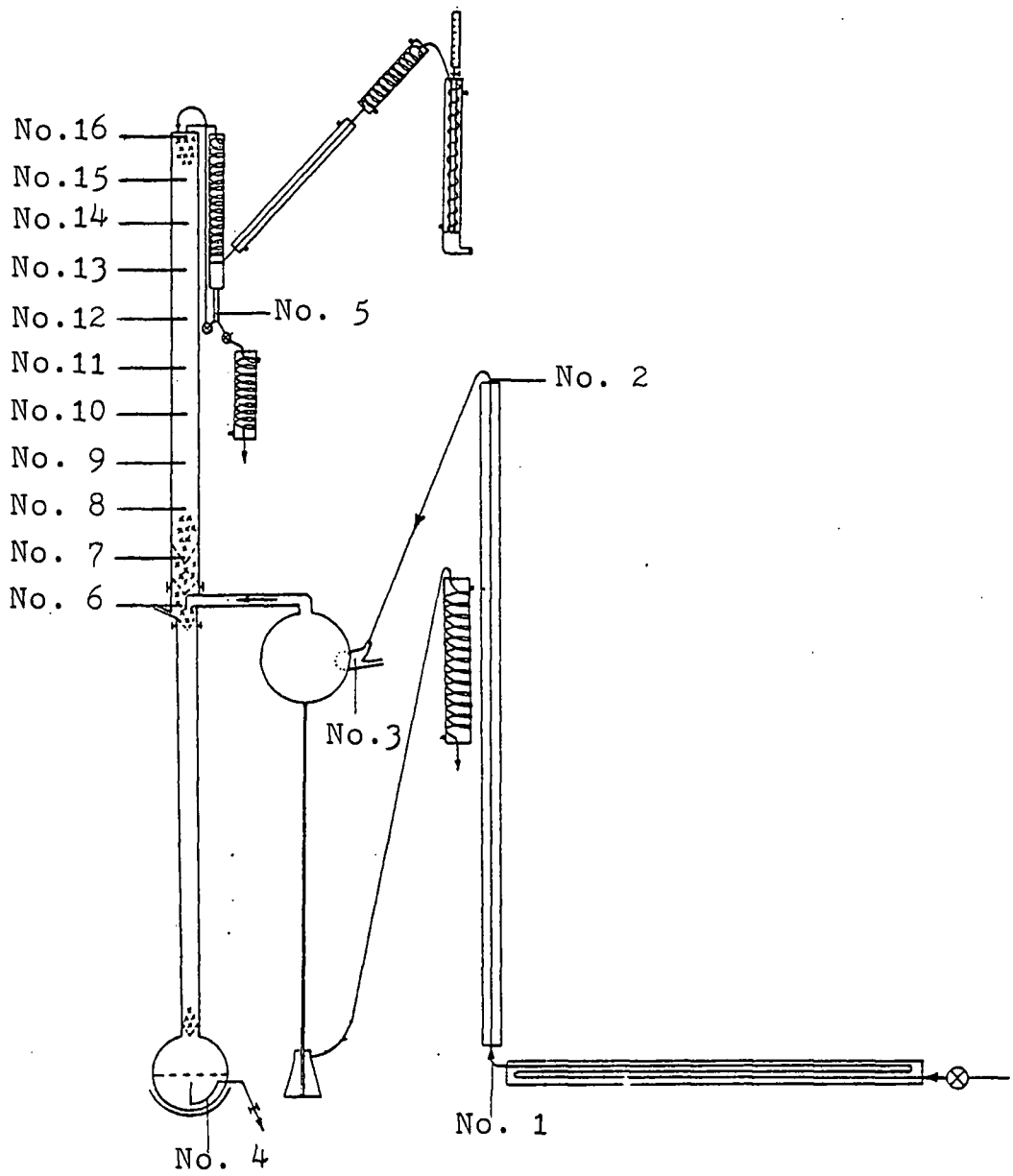


Figure 9. Thermocouple Positions

back reflux pump. Turn off the steam stream after hot water washing. Then, let cold water continuously enter the heat-exchange section for half an hour to cool the unit. One liter of 30% sodium hydroxide solution was pumped into the heat-exchange part to digest the fouling on the pipe walls. The steam was turned on to heat the solution, the solution was held in the pipe and separator flask for 30 minutes, drained and clean water was pumped thru the unit again to rinse out any residual sodium hydroxide in the unit.

PART I EQUIPMENT CALIBRATION

Calibration with Water

Tap water was used as testing model to calibrate the essence recovery unit as shown in Figure 3. According to the data obtained during the operation, heat exchange efficiency of preheater and evaporator and heating capacity of reboiler could be calculated. The operating conditions set in this water model test are listed below:

Table 3. Operating Conditions of Water Test

Feed-in Rate	5,600 ml/hr
Steam Pressure of Preheater	1.0 psig
Steam Pressure of Evaporator	7.5 psig
Vaporization Rate	30%
Reboiler Heater	300 watts

Calibration with Apple Juice

Fresh, ripe, 1977 harvested golden delicious apples were washed, crushed and pressed to produce fresh, unclear and unfiltered apple juice. Prior to the pear juice test, apple juice was used as testing material to determine the effectiveness of the unit. Operating conditions were set as follows:

Table 4. Operating Conditions of Apple Juice Test

Feed-in Rate	5,600 ml/hr
Steam Pressure of Preheater	1.0 psig
Steam Pressure of Evaporator	7.5 psig
Partial Vaporization Rate	29%
Reboiler Heater	134-192 watts

PART II ONE-STAGE PEAR ESSENCE RECOVERY TESTS

One thousand pounds of ripe, fresh, whole Bartlett pears were washed, crushed and pressed to produce pure pear juice of Brix 11.6°. Plastic buckets of approximate three gallon volume each were used as containers for pear juice, and all the juice buckets were stored at -40°F. Juice was taken out and thawed at room temperature before testing. Any large pieces of residual pulp was removed by straining through a cloth before the juice was pumped into the unit.

Pretest

The operating conditions are listed below:

Table 5. Operating Conditions of Pretest

Feed-in Rate	6,600 ml/hr
Steam Pressure of Preheater	2.6 psig
Steam Pressure of Evaporator	8.5 psig
Partial Vaporization Rate	30%
Beboiler Heater	300 watts

Twenty-three samples were collected from feed-back line "T" connection. Thirty minutes after the beginning of the juice run, sample collection of the product was started.

Low Heat Tests

Two tests were conducted to detect the temperature variance in the rectifying section. Operating conditions are shown in the table below:

Table 6. Operating Conditions of Low Heat Tests

	Test I	Test II
Feed-in Rate	5,800 ml/hr	5,800 ml/hr
Steam Pressure of Preheater	1.0 psig	1.0 psig
Steam Pressure of Evaporator	7.5 psig	6.0 psig
Partial Vaporization Rate	32%	25%
Reboiler Heater	118.8 watts	138 watts
Operating Period	2 hours	4 hours

Product pump was not started during the whole two hours of running in Test I. In the second test, product was collected after three hours of running.

High Heat Test

Table 7. Operating Conditions of High Heat Test

Feed-in Rate	6,000 ml/hr
Steam Pressure of Preheater	1.0 psig
Steam Pressure of Evaporator	5.0 psig
Partial Vaporization Rate	25%
Reboiler Heater	532 watts

One inch thick glass wool with alumimun foil cover was used as insulation material to wrap the fractionating column and separator to avoid heat loss. Product was collected after 2½ hours of the juice running during the whole four hours operation.

Pear Essence Recovery

Table 8. Operating Conditions of Pear Essence Recovery

Feed-in Rate	5,800 ml/hr
Steam Pressure of Preheater	1.0 psig
Steam Pressure of Evaporator	5.0 psig
Partial Vaporization Rate	25%
Reboiler Heater	850 watts

Started the operation with tap water for five hours to

wash the whole unit, then, switched the feed to pear juice. Product was collected after 2-3/4 hours of running the juice during the whole five hours of operation.

Two-Step Split Essence Recovery Test

Low heat was set for reboiler in this test to allow the high boiling pear aroma compounds to drain with the discharge water from reboiler. All of the discharge water was collected from the first step test. Then, the collected discharge water was used as feed material for the second step process. Operating conditions for two tests are listed below:

Table 9. Operating Conditions of Two-Step Split Test

	Step I	Step II
Feed-in Rate	5,800 ml/hr	5,800 ml/hr
Steam Pressure of Preheater	2.0 psig	1.0-2.0 psig
Steam Pressure of Evaporator	8.0 psig	10-12 psig
Partial Vaporization Rate	30%	38%-40%
Reboiler Heater	208 watts	850 watts

In the Step I process, after three hours of running the juice, started collecting the column top condensate as product #1. The whole Step I process was 15 hours long, and 4.5 gallons of discharge water was collected. In the Step II process, product #2 was collected at 4 ml/min rate after one hour of running.

PART III TWO-STAGE PEAR ESSENCE RECOVERY TEST

Material

Fresh ripe, whole Bartlett pears were processed thru the same steps mentioned in PART II material section. The juice was full of fresh, typical ripe Bartlett pear aroma and had Brix of 11.2°.

Equipment

The two-stage essence recovery equipment was composed of two basic units, as shown in Figure 10. The first unit was the same one used in previous tests, the second unit included an evaporator which was six feet long steam jacket of two in. O.D. with a piece of 3/8 inch O.D. stainless steel tubing inserted inside, and another fractionating distillation system which was the same size as the first one. The size of evaporator II was determined in advance, according to the estimated operating conditions.

Table 10. Estimated Operating Conditions for Evaporator Size Determination

Feed-in Rate	1,800 ml/hr
Feed-in Temperature	212°F
Vaporization Rate	1,800 ml/hr (100%)
Vapor-Out Temperature	215°F

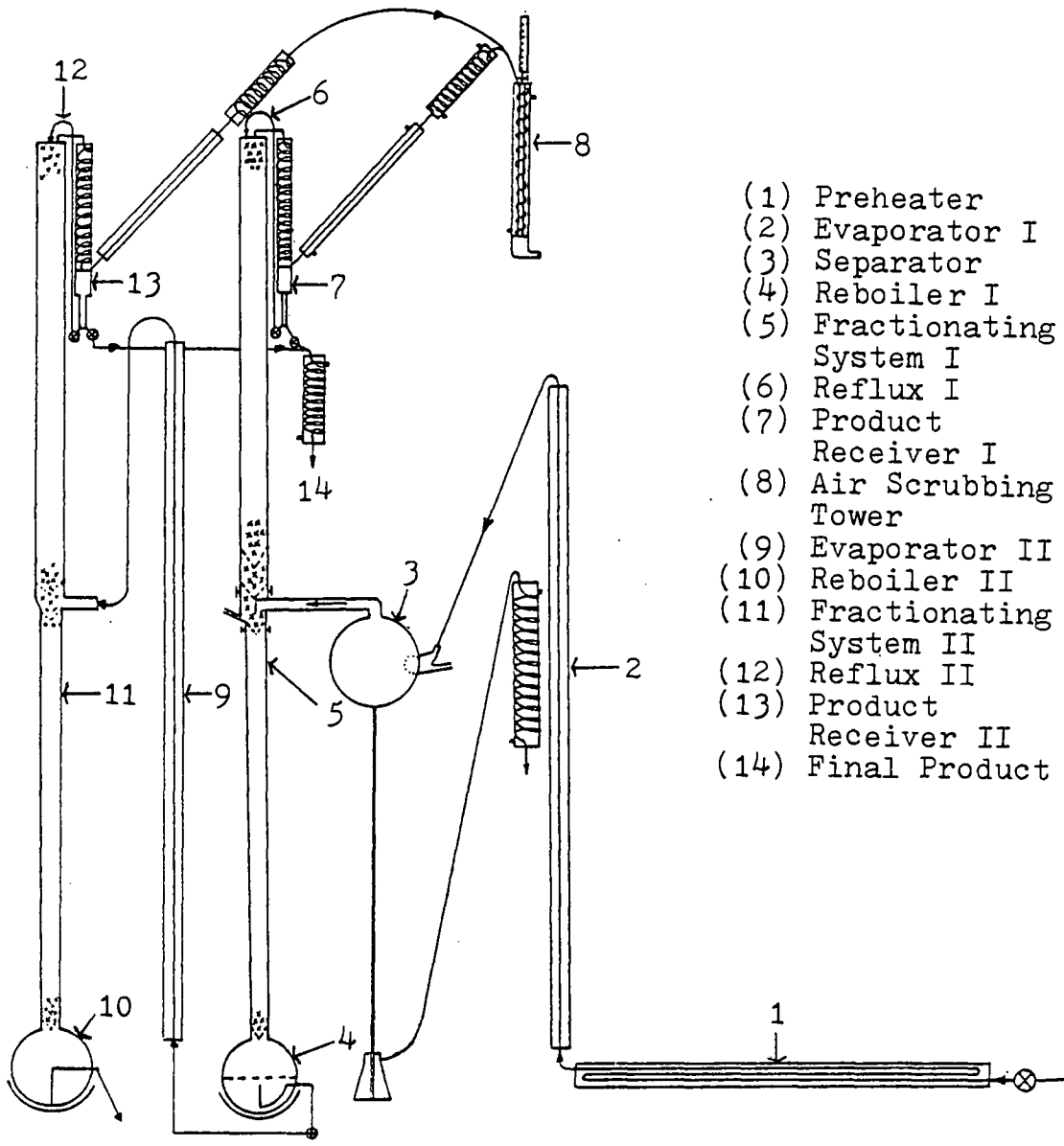


Figure 10. Two-Stage Essence Recovery Unit

Steam in at 10 psig = 240°F

Steam in at 5 psig = 230°F

Latent heat = 960 Btu/lb

$Q = mC_p \Delta T = (960 \times 3.96) + 3.96 \times (215-212)$

$= 3,813.48$ Btu/hr

L = thickness of tubing = 0.0625 inch

K = 12.4 Btu/hr-ft^2-°F/ft (Henderson and Perry, 1966, P. 231)

h_o = Surface transfer coefficient of condensing steam = 1,000 Btu/ft^2-hr-°F (Henderson and Perry, 1966, P. 232)

h_i = Surface transfer coefficient of water in pipe = 1,300 Btu/ft^2-hr-°F (Henderson and Perry, 1966, P. 232)

$$U = \frac{1}{\frac{1}{h_o} + \frac{L}{K} + \frac{A_o}{h_i A_i}} \qquad A_o/A_i = 2.25$$

$$= \frac{1}{\frac{1}{1,000} + \frac{0.0625/12}{12.4} + \frac{2.25}{1,300}}$$

$= 317.38$

(A) If 10 psig of steam is applied:

$$\Delta Tm = \frac{(215-212)^\circ F}{\ln \frac{(240-212)^\circ F}{(240-215)^\circ F}} = 26.47^\circ F$$

$Q = UA \Delta Tm$

$3,813.48 = 317.38 \times A \times 26.47$

$A = 0.454$ ft^2 $= \pi DL$

$L = 4.62$ ft

(B) If 5 psig of steam is applied:

$$\Delta Tm = \frac{(215-212)^{\circ}F}{\ln \frac{(230-212)^{\circ}F}{(230-215)^{\circ}F}} = 16.45^{\circ}F$$

$$Q = UA\,\Delta Tm$$

$$3,813.48 = 317.83 \times A \times 16.45$$

$$A = 0.73 \text{ ft}^2$$

$$L = 7.44 \text{ ft}$$

Therefore, it was determined that the length of evaporator II should be six feet in length in order to meet the alternative steam pressures.

A FMI laboratory pump was used to pump the reboiler I discharge liquid into the evaporator II. The vapor then entered the fractionating distillation system II for concentration. The reflux set and the condenser arrangement were the same as used in the first unit. When passing through two condensers, the uncondensed vapor went to the air-scrubbing tower of the first unit through a piece of 1/8 inch O.D. tygon tubing. Another product pump was set to pump the condensate in the receiver III to the product cooler.

Procedures

The beginning steps described in PART I, general operating section were applied to start the two-stage

operation. Operation conditions were set as follows:

Table 11. Operating Conditions of Two-Stage Test

Juice Feed-in Rate	6,000 ml/hr
Preheater Steam Pressure	1.5 psig
Evaporator I steam Pressure	9.0 psig
Reboiler I Heater	92 watts
Evaporator II Steam Pressure	12.5 psig
Reboiler II Heater	756 watts

Water was first fed into the unit for two hours to allow the whole system to reach constant steady state. Thirty percent of primary juice feed was vaporized by the evaporator I, and, the vapors then entered the first fractionating distillation system. The reboiler I heater was adjusted to provide 92 watts of heat which was high enough to drive the low-boiling components of pear aroma upward to the column top, and it was low enough to allow the high-boiling components to drip downward into the reboiler. The overflow liquid of reboiler I was pumped into the evaporator II to be totally vaporized. The high-boiling component rich vapors thus entered the fractionating distillation system II to achieve a further concentrating effect. The heater of reboiler II was adjusted to give 756 watts of heat which was high enough to drive the high-boiling compounds out of the column top. Several mls of discharge liquid from reboiler I were collected every 30 minutes to

check the presence of pear aroma. A few drops of sample were collected every 15 minutes from reflux II feed-back line, each of that collections was preevaluated to determine the existence of high-boiling pear aroma compounds in the condensate of receiver III. After 2-3/4 hours of running the juice, both product pumps were started. The product pump I was set at 0.7 ml/min rate, and the product pump II was set at 0.3 ml/min rate to match the required ratio between feed-in rate and product-out rate.

PART IV IDENTIFICATION OF BARTLETT PEAR ESSENCE

GC-MS ANALYSIS

Material and Method

The pear essence product obtained in "Pear Essence Recovery Test" was used as the sample. Thirty mls of concentrated essence (100 fold) was saturated with reagent grade anhydrous sodium sulfate, and was then extracted twice with a 30 ml portion of reagent grade ethyl ether for each extraction. The extract was removed to a concentration tube and ether was evaporized under a stream of nitrogen. The final product was a non-clear liquid possessing very strong and typical ripe Bartlett pear aroma.

Varian Aerograph 1,400 gas chromatography with ionization detector interfaced to a Finnigan Series 1,015C automated mass spectrometer equipped with a digital data

system was applied for analysis. Two tenth µl of sample was injected into the 500 feet x 0.03 inch I.D. stainless steel capillary column coated with nonpolar SF-96. The column was first heated at 70°C for 5 minutes, then, programmed to the maximum of 160°C by increasing the temperature 2°C/min. Injection temperature was 185°C, carrier gas was nitrogen of 15 ml/min flow rate.

Ultraviolet Spectroscopy

The pear essence and reboiler II discharge water obtained from the two-stage pear essence recovery test were used as samples in this test. The solvent, (reagent grade n-pentane), was purified by passing it slowly through a column packed with silica gel. The purified solvent was found to be free of absorption maxima from 320 to 220 mµ. A 25 ml portion of pear essence sample was transferred to a 250 ml separatory funnel and 25 ml of purified n-pentane was added, the flask was stoppered and mixed thoroughly. The pentane layer was then transferred to a cuvette for ultraviolet determination. The same procedures were applied for the reboiler II discharge water sample preparation. A Perkin-Elmer spectrophotometer 550 was used to measure the absorbance from 320 to 220 mµ.

RESULTS AND DISCUSSION

PART I CALIBRATION OF EQUIPMENT

Calibration with Water

Water was used as testing model to calibrate the unit. The practical operating data obtained in this test could be used to evaluate the design of the unit. From the recorded temperature,

Table 12. Detected Temperature in Water Test

Thermo-Couple Nos.	1	2	3	4	5	6	16
Temperature ^{o}F	210	215	214	217.5	120-140	214.5	214

it showed that the water was preheated to the exactly expected temperature of 210^{o}F. The water was partially vaporized at 215^{o}F which indicated that some back pressure was built up inside the evaporator. The one degree lower temperature at No.3 thermocouple was due to heat loss thru the tygon tubing which connected evaporator and separator. Vapor entering the fractionating system was at 214.5^{o}F which meant that the reboiler provided enough heat to keep the vapor from undesirable condensation. The half degree decrease at column top outlet was due to heat loss. An unexpected high temperature of 217^{o}F was detected in the reboiler. so there was higher than one atmosphere pressure in the whole system. This essence recovery unit was estimated to

operate under atmospheric pressure, but the combination of feed-in pump, product pump and barometric leg made it a partial closed system. Heating and vaporization inside the system, and the back pressure as the result of resistance in the two columns caused a higher than atmospheric pressure in the column and the resultant higher temperature. Unstable cooling water flow in condenser I resulted in the temperature variation of condensate in receiver I.

From this water model test, practical thermal effect data were obtained to compare with the estimated figures mentioned in the previous "construction section". The actual operation data were close to the estimated figures.

Table 13. Estimated and Actual Operating Data

	Estimated Data	Actual Operation Data
Feed-in Rate	6,000 ml/hr	5,600 ml/hr
Preheater Steam Pressure	1.0 psig	1.0 psig
Preheater Length	9.2 ft	9.0 ft
Evaporator Steam Pressure	10.0 psig	7.5 psig
Evaporator Length	5.2 ft	5.0 ft
Partial Vaporization Rate	30%	30%

Theoretical calculation of preheater size was very close to the operating conditions. Notable deviation existed in the calculated size of the evaporator and the practical operating figures of the evaporator. The critical factors of heat-transfer calculation were h_o(surface-transfer co-

efficient of condensing steam) and h_i(surface-transfer coefficient of water in pipe). The figures used for calculation in this test were chosen from reference tables which gave similar operating conditions. The difference between calculation and actual data indicated that the value chosen for h_o of 1,000 Btu/hr-ft^{o}F needed to be increased for our use in this type of operation. There might also exist, some other unknown factors which would affect the results, such as viscosity of juice v.s. water, and purity of steam.

Calibration with Apple Juice

Apple essence recovery from apple juice is well developed and has been widely applied in apple juice manufacturing industry for many years. Therefore, this test was conducted using apple juice as the test material to calibrate the unit. Under set operating conditions, the reboiler heater was adjusted to give 192 watts of heat during the first hour of running, then, it was reduced to 134 watts for another hour of running. No apple aroma was detected from the collected samples of reboiler discharge liquid, or from the drained juice through separator bottom outlet. the drained juice through separator bottom outlet. Thus, for complete stripping of the aroma from the juice. It also showed that 134 watts of reboiler heat was adequate for driving the aroma components upward in the fractionating columns. The collected samples from reflux feed-back line

were examined organoleptically. They all possessed good apple aroma, and no noticeable difference existed among those samples. After half an hour of running the juice, product was collected for the rest of operating period. The product was judged to be high quality apple aroma. The success of apple essence recovery established the effectiveness of this essence recovery unit.

Table 14 showed the recorded temperature of each thermocouple. High temperature obtained from thermocouples No. 1 and No. 2 were due to the high pressure in the system.

Table 14. Detected Temperature in Apple Juice Test

Thermocouple No.		1	2	3	4	5	6	7	8
Reboiler Heat	192 watts	214	216.5	215	217	130-150	215	214	214
	134 watts	213	215.5	214	213	130-150	213.5	212.5	212.5

Thermocouple no.		9	10	11	12	13	14	15	16
Reboiler Heat	192 watts	214	214	214	214	214	214	214	214
	134 watts	212.5	212.5	212.5	212.5	212.5	212.5	212.5	212.5

Heat provided by reboiler could influence the internal pressure. When the reboiler heater was reduced from 192 to 134 watts, the temperature from thermocouples No. 1 and No. 2 decreased $1^{\circ}F$. The same temperature drop was noted on the reboiler water temperature. When 192 watts of heat was applied to the reboiler during the first hour, there

was no appreciable difference among the temperatures recorded by thermocouples which were located inside the rectifying section. The same temperatures were obtained from the second hour of operation.

PART II ONE-STAGE PEAR ESSENCE RECOVERY TESTS

Pretest

This was the first test of running pear juice through the unit to obtain the primary test results and so necessary modifications could be made.

Partial vaporization rate was 30% under the controlled operating conditions. From the previous work (Jennings, 1969), indicated that a 30% vaporization rate for Bartlett pear juice was enough to strip all the pear aromas from the juice. Examining the discharged juice from separator, no pear fragrance but a slightly cooked odor was detected. This verified that 30% vaporization removed all the pear aroma from juice. The purpose of collecting reflux samples every 15 minutes was to determine the time when the typical ripe Bartlett pear aroma reached the top of fractionating column, where, it would be condensed and accumulated in the receiver I. The product pump was not started until the typical pear aroma was detected in the receiver I. By simple organoleptical examination of 23 collected reflux samples, it was shown that no detectable difference existed among first six samples. The following samples possessed

strong odor, but not Bartlett pear aroma.

Using the same procedure as in the apple essence test, product collecting was started after the juice had been running one half hour. The final product had strong fruity flavor but was totally lacking in typical Bartlett pear aroma. Tap water was pumped into the unit after the juice run to wash the whole system. It was found that the typical ripe Bartlett pear aroma was carried out by the washing water. The characters of components responsible for the distinct fragrance and aroma of Bartlett pear made Milleville believe that those components were trapped in the rectifying section of fractionating columns (Milleville, 1977). Obviously, those compounds with high boiling points had lower relative volatility in the upper part of fractionating column than they had in the feed section. As mentioned before, 5-8% of aroma composition is low-boiling alcohols which will reach the column top easily, compared to those trace amounts of high boiling ester compounds of the aroma. Thus, the change in relative volatility could be explained by high alcohol concentration that was presumed to occur in the upper part of column.

Milleville suggested a side-arm withdrawal device to recover the trapped components. First, the location where the typical Bartlett pear aroma components were trapped in the column needed to be determined. For this purpose, thermocouples were inserted in the rectifying section every four

inches apart to detect any temperature variance in the different points of column. It was assumed that the section where pear aroma stayed in the column would show a higher temperature compared to the other sections.

Low Heat Tests

Test I

The main purpose of this test was to detect temperature change at different locations in the rectifying section. To avoid the effect from unnecessarily high heat provided by reboiler, the reboiler heater was set at low heat so that it would not dominate the temperature distribution in the column.

Table 15. Detected Temperature in Low Heat Test I

Thermocouple Nos.	1	2	3	4	5	6	7	8
Temperature ^{o}F	212.5	215.5	214	212	150-170	214	212.5	212.5

Thermocouple Nos.	9	10	11	12	13	14	15	16
Temperature ^{o}F	212.5	212.5	212.5	212.5	212	212.5	212	210.5

Reboiler heater set at 118.8 watts could boil the water at 212^{o}F. No product was collected during the whole run to insure that the system reached its steady state. From the above table, no significant difference was observed among the nine thermocouples in the rectifying section.

Juice was heated to 212.5°F in the preheater, then, it was partially vaporized in the evaporator at 215.5°F. Higher than the normal boiling point temperature meant that certain back pressure was built up in the evaporator. Heat loss through the tygon tubing which connected evaporator and separator reduced the vapor-liquid mixture temperature by 1.5°F. The heat generated by reboiler kept rectifying section at around 212.5°F. Vapor leaving the rectifying section was at 210.5°F which was 1.5°F lower than the temperature detected from the lower sections. This might have been caused by the change in composition of components in that section. Another possible reason might be that the lower temperature of the returning reflux condensate decreased the temperature of vapor at the column top section. After 1½ hours of running the juice, strong pear aroma was found in reboiler discharge water. The collected reboiler discharge water sample was evaluated and judged to have typical and good Bartlett pear aroma. All the samples collected from the reflux feed-back line showed strong perfume-like odor but not Bartlett pear aroma. It could be explained that the "decadienoate" compounds (typical Bartlett pear aroma), never arrived at the top of the rectifying column in this test. The heat provided from reboiler might not have been high enough to drive those high-boiling aroma compounds to the top of the column. Instead, after 1½ hours of running, the accumulated aroma compounds dripped

downward into the reboiler. It was deemed necessary to conduct a long term operation to confirm the steady state conditions, and to recheck the temperature variance in the fractionating column.

Test II

Table 16. Detected Temperature in Low Heat Test II

Thermocouple Nos.	1	2	3	4	5	6	7	8
Temperature ^{o}F	209	215.5	214	213.5	160-180	214	212.5	212.5

Thermocouple Nos.	9	10	11	12	13	14	15	16
Temperature ^{o}F	212.5	212.5	212.5	212.5	212.5	212.5	212	210

In this four hours operation, reboiler heater was adjusted to give 138 watts which was 20 watts higher than it was in Test I. From the above table, reboiler temperature was 213.5^{o}F which was 1.5^{o}F higher than it was in Test I. No temperature differential existed among nine thermocouples in the column. Vapor leaving the column was at 210^{o}F which was 2^{o}F lower than the No. 15 thermocouple, which was the same as was observed in Test I. Light pear aroma appeared in the discharge water from reboiler after 1½ hours of running the juice. One hour later, by examining the collected samples from reflux feed-back line, some typical pear aroma was found. It indicated that some typical aroma components were driven out from the column top

after a long running time. Cloudy product was collected after three hours of running the juice. The cloudy state of the product could be caused by a solubility change among all components. One drop of product diluted to 20 mls showed satisfactory typical pear aroma. Since the full flavor aroma of Bartlett pear is composed of all low-boiling alcohols, high-boiling esters and other components, a much better effect was obtained by also adding one drop of air-scrubbing washings.

High Heat Test

In the low heat tests, it was found that the high-boiling compounds were driven out by the heat supplied from reboiler when the system reached steady state. In this test, high heat (522.5 watts) was provided by the reboiler heater to improve the fractional distillation efficiency and to prevent the aroma from leaking in the reboiler discharge water. From the table below, the detected temperatures in fractionating column showed results similar to those in the

Table 17. Detected Temperature in High Heat Test

Thermocouple Nos.	1	2	3	4	5	6	7	8
Temperature ^{o}F	206	215.5	214	216.5	160-180	214	213	213

Thermocouple Nos.	9	10	11	12	13	14	15	16
Temperature ^{o}F	213	213	213	213	213	213	213	210.5

low heat tests. However, the high heat from reboiler increased the stripping effect so that no pear aroma was detected in the discharge water.

Product was cloudy and possessed a strong typical Bartlett pear aroma. One drop of product added with one drop of air scrubber washing diluted to 15 ml gave a fair Bartlett pear aroma.

Pear Essence Recovery

Five hours of running with water was used to wash out any juice residual in the unit and to ensure the steady state of the system. Eight hundred and fifty watts of heat from reboiler heater raised the reboiler temperature up to 217°F.

Table 18. Detected Temperature in Pear Essence Recovery

Thermocouple Nos.	1	2	3	4	5
Temperature °F	207	216.5	216	217	174-180

Although it was only an increase of 0.5°F compared to the reboiler temperature in the last test, 330 watts more heat was applied to the fractionating column to obtain better separation efficiency. Reboiler vaporization rate thus was raised to 93% of the vapor feed to enhance stripping capacity.

Calculation of reboiler boiling rate as follows:

1 KW = 3,413 Btu/hr

Latent Heat: 960 Btu/hr-lb
850 watts = 0.85 KW
0.85 x 3,413 = 29,010.5 Btu/hr
29,010.5 / 960 = 30.2 lb/hr = 1,359 ml/hr
Feed-in Vapor Rate: 1,450 ml/hr
1,359 / 1,450 = 93%

During the total five hours of juice running, no pear aroma was detected in the reboiler discharge water. For a better effect, vaporizer steam pressure was set at 5.0 psig to reduce the partial vaporization rate of juice to 25%. Although it was 5% less than the recommended stripping rate (Bomben, et al, 1969), no detectable pear aroma was found in the stripped juice at one ml/min rate. Two ml of clear product blended with a few drops of air scrubber washing was diluted to 50 mls. By organoleptic examination, a strong and excellent characteristic ripe Bartlett pear aroma was detected. The pear essence produced in this test was further analyzed to confirm the existence of 2,4-decadienoates, the characteristic pear aroma compounds.

This test was conducted as an extension for high-heat test to confirm the acceptability of the high-heat driving method. Decadienoates -- characteristic Bartlett pear aroma components, are completely miscible with alcohols in all proportions. In the upper part of rectifying column where the alcohol concentration is high, the relative volatility of decadienoates decreases and can hardly be separated by distillation.

There is no research report available on the physical-

chemical properties of decadienoates. However, the problem in Concord grape essence recovery can be considered similarily for Bartlett pear essence recovery. Roger (1961) discovered that if the ethanol concentration was below the critical point of 55-60% by weight, the methyl anthranilate -- characteristic Concord grape aroma compound with high boiling point, should be readily recovered as overhead product. The losses of methyl anthranilate was only due to the inefficient stripping effect of the stripping section. For recovering the high-boiling volatile compounds, as high as 50% of reboiler vaporization rate of feed was required (Roger and Turkot, 1965). In the low heat tests, reboiler heater only provided 170-190 watts of heat to give a 20-22% vaporization rate. When the applied heat was increased to 522 watts, the reboiler vaporization rate was increased to 50%. These calculated data could be used to explain the losses of decadienoates from reboiler discharge water in low-heat tests, and the gaining of decadienoates from the overhead product in the high-heat tests. Since the alcohol concentration at the upper part of rectifying section will never reach 55-60% by weight in the 100-150 fold essence recovery process, the side-arm withdrawal device would not be considered for recovering 100 fold essence product.

Two-Step Split Essence Recovery Test

From the previous tests, it was found that low heat generated from reboiler could allow the high-boiling aroma components to condense and drain with the discharge water into the reboiler. The removal of low-boiling, high-volatile compounds were not affected by low reboiler heat but they were concentrated and reach the top outlet of column, where they were condensed and collected. Therefore, this test was conducted to split the essence recovery process into two steps. In the first step, 30% of juice was vaporized, and the vapor entered the fractionating system. Under the low reboiler heat operation, 4.5 gallons of reboiler discharge water having strong, typical ripe Bartlett pear aroma was collected. The overhead product collected from the column top which contained low-boiling compounds was product #1. In the second step, 4.5 gallons of feed material was pumped into the unit at 5,800 ml/hr rate. Some pear aroma was detected in the drained water from separator when the evaporator steam pressure was first set at 7.5 psig. It was immediately raised to 10 psig to avoid uncomplete stripping of aroma from feed material. One hour later, product #2 was collected at 3 ml/min rate to match the 100:1 ratio between product #2 and original feed-in juice. Considering the thorough removal of aroma from feed material, steam pressure was increased to 2.0 psig for

preheater and 12 psig for evaporator to get 40% of vaporization rate. Eight hundred and fifty watts of heat provided by reboiler was high enough to drive the high-boiling compounds out from the column top, as no pear odor was detected in the reboiler discharge water. Fifty eight percent of vaporization rate by the reboiler was satisfactory for stripping.

One ml of each #1 and #2 product blending with a few drops of each #1 and #2 air scrubber washing was diluted to 100 mls. The existence of good, strong and characteristic ripe Bartlett pear aroma in the diluted sample was determined by organoleptic evaluation.

This split two-step test was the primary trial for the development of a two-stage essence recovery unit. After evaluating the results obtained, it was decided that a two-stage unit would combine two fractionating systems together to conduct a two-stage, one-process essence recovery operation.

PART III TWO-STAGE BARTLETT PEAR ESSENCE RECOVERY TEST

Following the success of the split two-step test, a two-stage essence recovery unit was designed and constructed. As mentioned earlier, this two-stage unit combined two fractional distillation systems together to give a two-stage, one-process system. The main purpose of this unit was to split the high-volatile components of pear aroma from the

low-volatile components in the first stage. Then, each group of aroma components would be concentrated in the individual fractionating system separately. By applying 97 watts of low heat to reboiler I, the low-boiling, high-volatile compounds would be distilled and driven upward in the first fractionating system. The high-boiling and low-volatile compounds thus were separated and migrated downward to the bottom of the column, then, into the reboiler. From the results obtained earlier (Part II, Low-Heat Tests), 97 watts of reboiler heat should be suitable for the components separation purpose. By examining the collected reboiler I discharge liquid samples, typical ripe Bartlett pear aroma was detected after 30 minutes of running the juice. One and one half hours later, a very strong and good characteristic ripe Bartlett pear aroma appeared, thus, the separation effect was confirmed.

Samples collected from reflux II feed-back line were examined to determine the presence of high-boiling pear aroma components in the column top. Significant characteristic ripe Bartlett pear aroma was detected in the sixth sample, and the odor became increasingly stronger in the following samples. Very strong and good quality of ripe Bartlett pear aroma was shown in the tenth sample, which was after $2\frac{1}{2}$ hours of running the juice. No pear aroma was detected in the reboiler II discharge liquid. This confirmed that 756 watts of heat provided by reboiler II was high enough to drive the

high-boiling components of pear aroma to the column top.

Each of over-head product pumps was started at different rate after $2\frac{1}{2}$ hours of running the juice. Product pump I was set at 0.7 ml/min and product pump II was set at 0.3 ml/min so that the final product collecting rate would be 1 ml/min to obtain 100 fold essence. In this operation, 30% of original feed was vaporized thru the evaporator I, then, the vapors entered fractionating column I. Because of the low heat applied from reboiler I, only low-boiling components of pear aroma would reach the column top in the process. The amount of low- boiling components was very small, compared with the feed-in volume, so the loss of volume could be neglected when calculating the material discharged from the reboiler I. Therefore, 30% of original feed was estimated as the feed-in capacity for evaporator II, and 0.3 ml/min was set as the product pump II rate. When the overhead product from each fractionating distillation system was combined, a 100 fold full aroma ripe Bartlett pear essence was obtained.

Through organoleptic evaluation of final product, the product was judged to possess a good characteristic and strong ripe Bartlett pear aroma. This product was further analyzed by ultraviolet spectrometry to confirm the existence of "decadienoates" -- the dominant typical Bartlett pear aroma components.

PART IV IDENTIFICATION OF BARTLETT PEAR ESSENCE

GC-MS Method

The product obtained in "Essence Recovery Test" was organoloptically evaluated by several persons, and it was judged to have typical and strong ripe Bartlett pear aroma of good quality. So, a GC-MS experiment was conducted to analyze the essence composition for further verification.

As mentioned previously, GC method was applied mainly for separation of a complex mixture into fractions. Forty-two significantly separated peaks were shown on the GC chromatogram (Figure 11) after 73 minutes. Six of 42 fractions were picked out and identified by matching MS spectra. The first four were determined to be ethyl acetate, 1-butanol, hexyl acetate and hexanal. The first three compounds were indicated as the components of Bartlett pear aroma by Lim (1963) and Jennings (1966). The presence of hexanal in the Bartlett pear essence was not observed by Jennings. Hexanal might be the product of fatty acid auto-oxidation. Unsaturated fatty acid could be oxidized to become hydroperoxide. Then, the first six carbon portion would be broken down to hexanal. This could have happened as the sample used for analysis was stored at 34°F for six weeks after extraction by ethyl ether, and could have become oxidized.

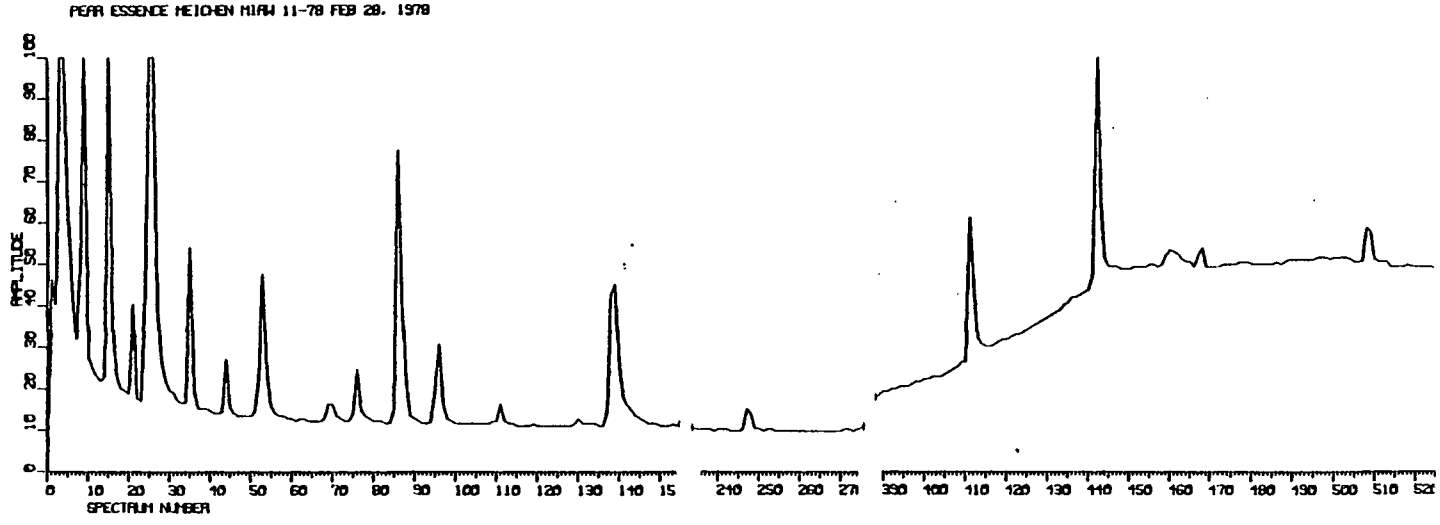


Figure 11. Chromatogram of Pear Essence

The other two fractions were picked out from GC chromatogram by molecular weight searching for 182 and 196 individually. The spectrum (figure 12) of the component with molecular weight of 182 could be interpreted to be methyl decadienoate. The purpose of this analysis was to confirm the existence of methyl decadienoate and ethyl decadienoate which were determined to be the characteristic ripe Bartlett pear aroma compounds, but, no standard MS spectra were available for confirmation of these two compounds.

Larson (1974) conducted analytical work on Bartlett pear aroma by GC-MS. He reported the identification of methyl decadienoate and ethyl decadienoate. Comparing the MS spectrum of the component having molecular weight 182 with that of methyl decadienoate Larson obtained, only three minor lines at m/e 93, m/e 97, and m/e 100 were unmatched. That could be caused by the migration of double bond, or shift of hydrid ions and hydrogen radicals.

Another spectrum (Figure 13) possessing molecular weight 196 was compared with the spectrum of ethyl decadienoate obtained by Larson. A very satisfactory matching of the two spectra was observed. Thus, the presence of ethyl decadienoate in the essence sample analyzed was positively verified.

However, there was a quite a difference of intensities among the six identified compounds and those same compounds identified by Jennings (1966). Hexyl acetate was indicated

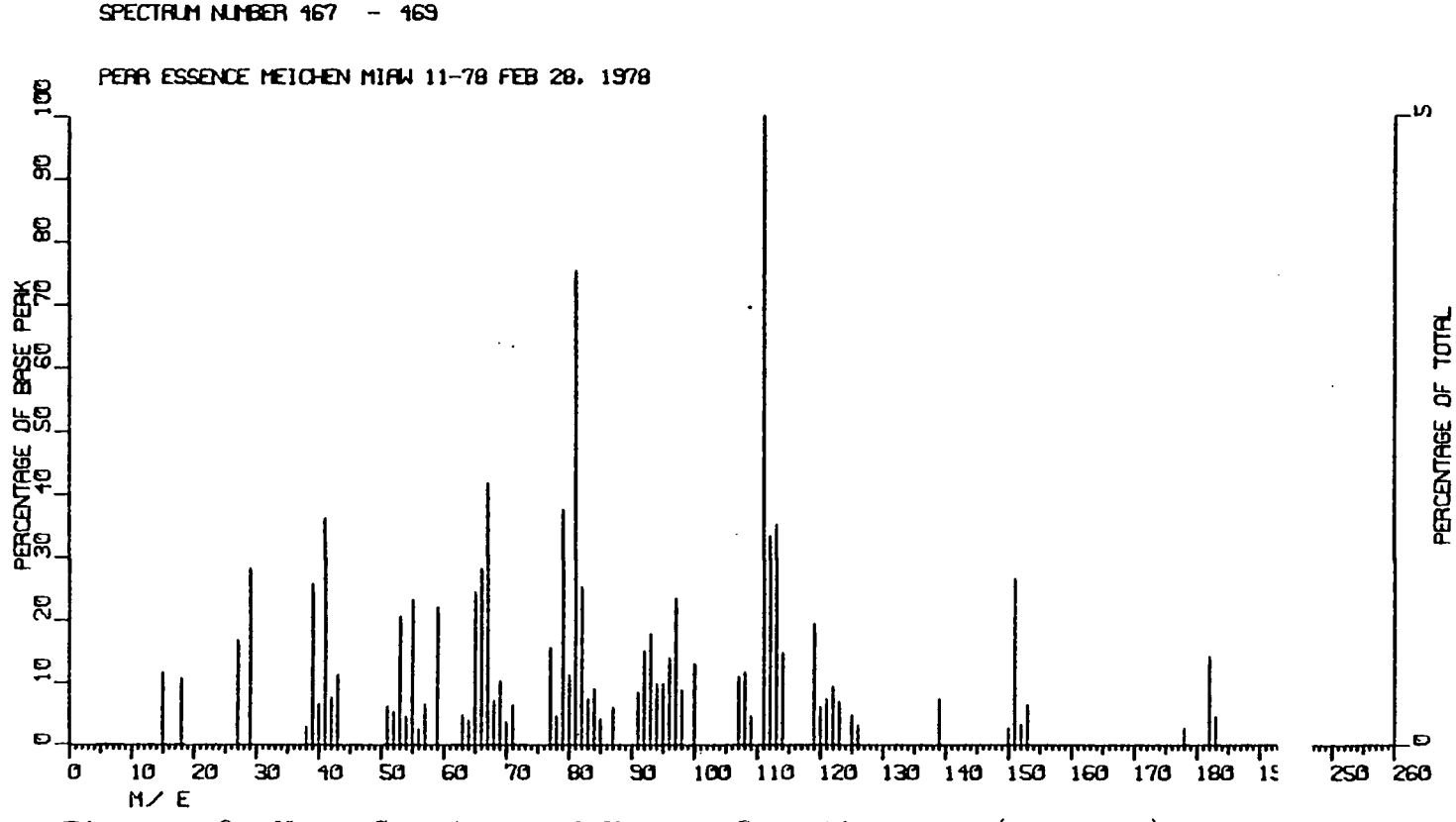


Figure 12. Mass Spectrum of Methyl Decadienoate (assumed)

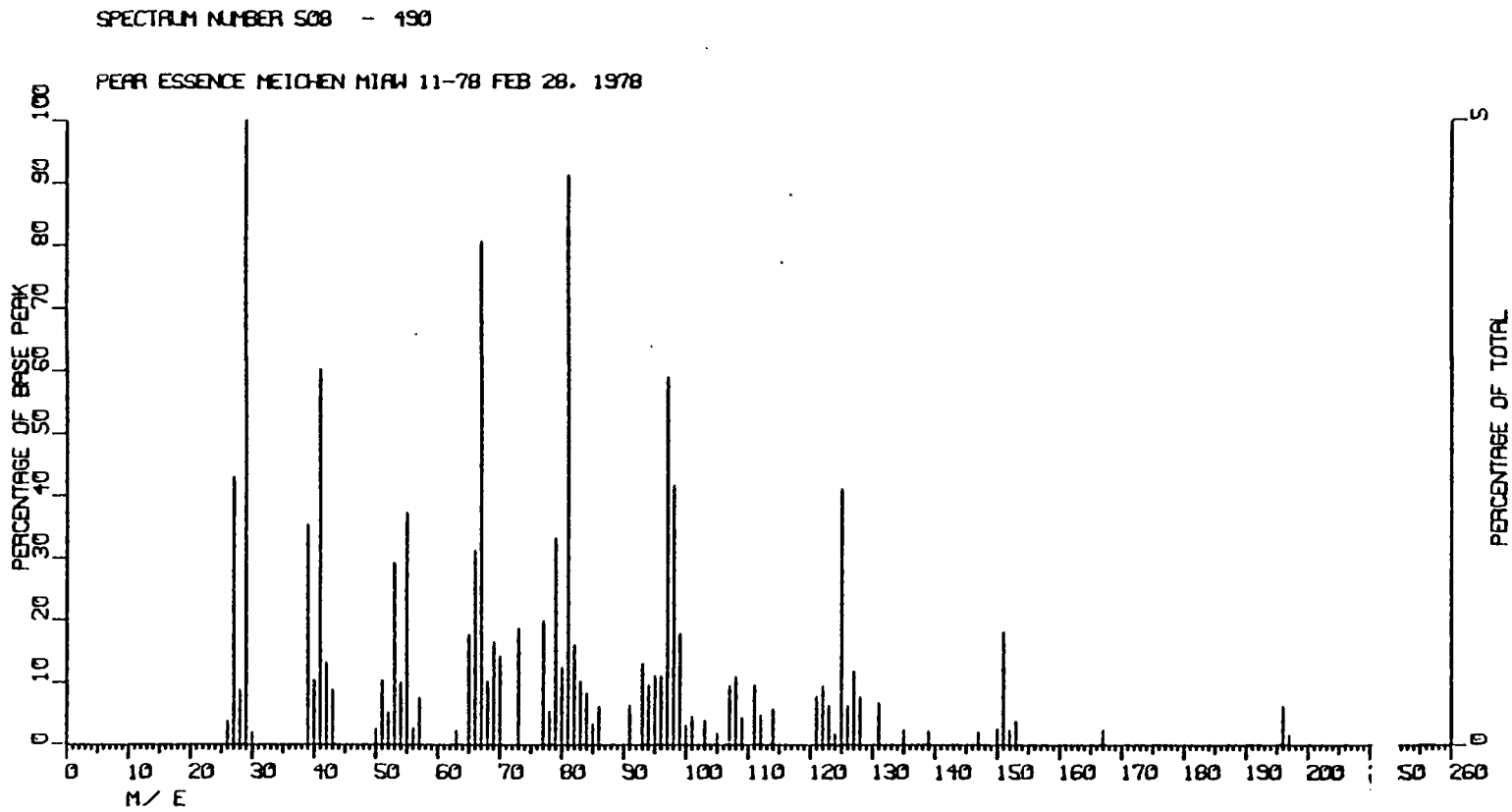


Figure 13. Mass Spectrum of Ethyl Decadienoate

as "contributory flavor component" by Jennings (1966), which should have been a larger quantity. In this experiment, only small amount of hexyl acetate was observed, and 1-butanol was shown to be the highest intensity. This difference might be due to the nature of pear juice, the conditions of essence extraction, or the sample storage time and temperature.

UV method

GC-MS is a delicate, qualitative and quantitive analytical method for the dectection of individual components, in a mixture, but, the identification of each GC fraction by mass spectrometry is complicated, considering the double bonds migration and shifts of hydrid ions and hydrogen radicals. The triconjugated system of trans:2-cis:4-decadienoate isomers exhibit maximum absorbance at 263-267 mμ (Heinz et al, 1964). It is a simple direct way to prove the presence of characteristic ripe Bartlett pear aroma-methyl decadienoate and ethyl decadienoate by ultraviolet spectrometry.

The essence sample investigated in this experiment was Bartlett pear essence produced in the "Two-Stage Essence Recovery Test" which was evaluated organoleptically and was considered to be typical and strong ripe Bartlett pear essence of excellent quality. The reboiler II discharge water sample was used here as a comparison blank.

Essences containing high concentrations of dissolved solid and/or suspended matter may entirely mask the absorption at 263 mu. In this case, each of the aqueous test samples was extracted with purified pentane to avoid any effect caused by the above factors.

The absorption spectra (Figure 14) indicated that the pear essence sample had the maximum absorbance at 265 mμ, which meant that this pear essence product contained decadienoates. The spectrum of reboiler discharge water showed no absorbance occuring at 220-320 mμ, which confirmed the completeness of aroma stripping effect. Thus, it was determined by UV measurement that the essence possessed "decadienoates". From the above results, the realiability and effectiveness of two-stage essence recovery system was established.

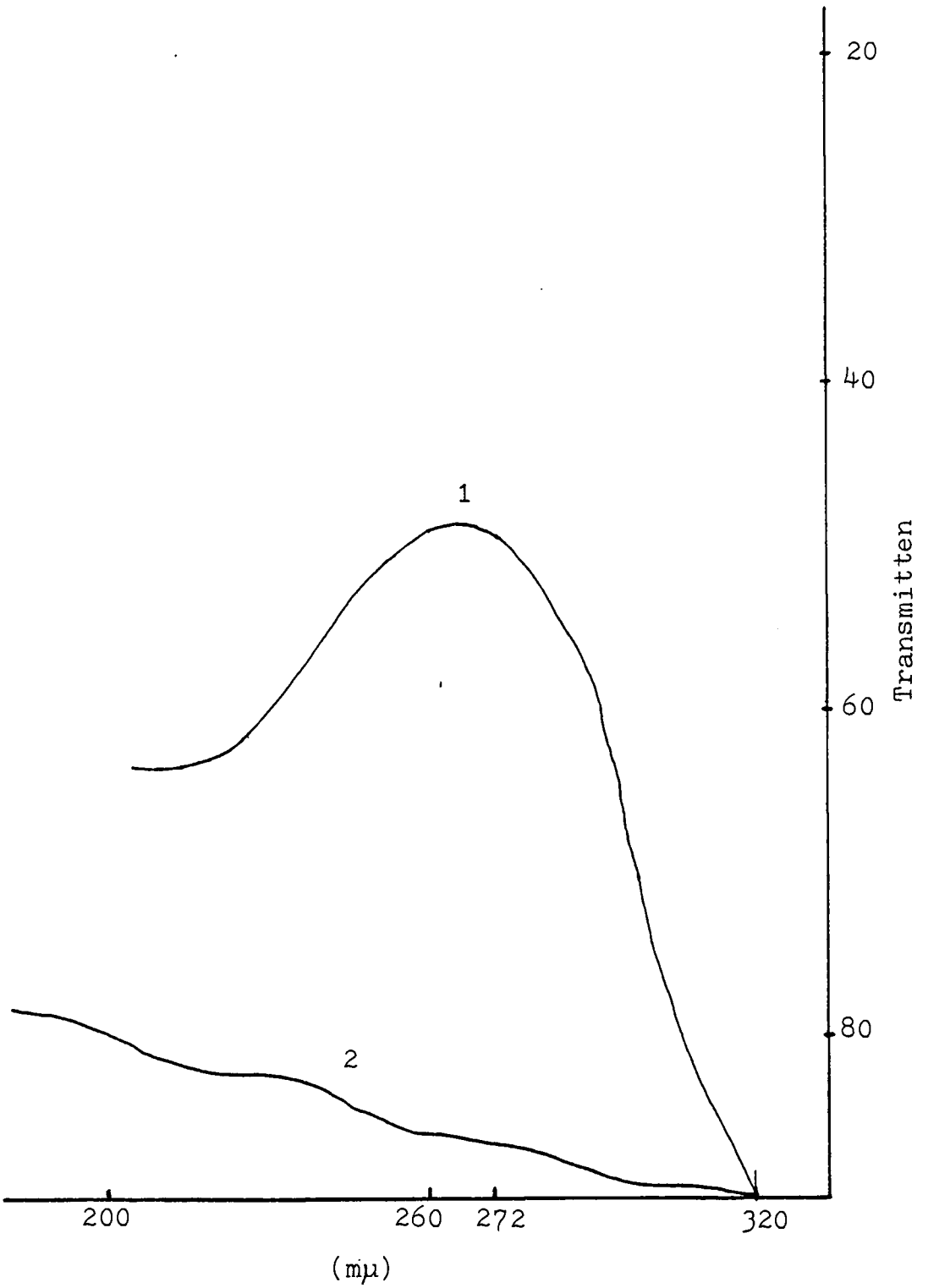


Figure 14. Ultraviolet Spectra of Pear Essence (1) and Reboiler Discharge Water (2)

CONCLUSION

This essence recovery unit was primarily designed according to the estimated operational requirements. Water was first used as a testing model to calibrate the heat transfer part of unit. Table 19 shows the actual size and operating conditions:

Table 19. Heat Transfer Section Size and Operating Conditions

Preheater	1/8 inch x 9 ft
Evaporator	1/4 inch x 5 ft
Preheater Steam Pressure	1.0 psig
Evaporator Steam Pressure	5.0 - 10.0 psig
Partial Vaporization Rate	25 - 30%
Juice Temperature, (leaving preheater)	210°F
Juice Temperature, (leaving evaporator)	216°F

Apple juice was used in the testing trial for the basic essence recovery function of this unit. The success of apple essence recovery established that the unit functioned properly and confirmed that the design was functional. The pretest pear juice trial confirmed that 30% partial feed-in juice vaporization was sufficient for the aroma stripping effect.

In the whole 5-3/4 hours of running, no typical pear aroma was collected in the receiver, but, was found in the washing water. This agreed with the result described in

pear essence recovery experiment by Beavers and Milleville.

Accidentally, the typical pear aroma was found in the reboiler discharge water, which was due to the low heat applied by reboiler heater in low-heat tests. It was also found in the long-term, low-heat test with pear juice that some typical pear aroma would arrive at the column top outlet after operating the unit for four hours.

A further high-heat test was conducted to confirm above observations. In the high-heat test, the unit was operated four hours with 532 watts of heat provided by reboiler heater. This high-heat test confirmed that the high-boiling, low-volatile components of pear aroma could be driven to the column top outlet by high heat provided from reboiler heater after a certain operating period, and no pear aroma was detected in the reboiler discharge water. Following the success of high-heat test, a formal pear essence recovery test was conducted under carefully controlled conditions so as to obtain a 100 fold pear essence. Eight hundred and fifty watts of heat was applied to the reboiler to enhance the rectifying efficiency and ensure the complete stripping effect. The product was a clear liquid with strong and typical ripe Bartlett pear aroma. It was, then, analyzed by GC-MS method. The existence of ethyl decadienoate was positively confirmed through the MS spectrum. Another spectrum of compound with molecular weight of 182 could be possibly interpreted as methyl decadienoate. Since both

methyl and ethyl decadienoates are the characteristic ripe Bartlett pear aroma components, the essence from this test was evaluated as a typical and desirable ripe Bartlett pear essence.

The high-heat concept applied in this essence recovery process agreed with the report from Roger and Turkot (1965) in which the Concord grape aroma components were studied. Decadienoates -- characteristic Bartlett pear aroma compounds, and its relative volatility decreases when alcohol concentration increases. For this reason, a two-step split method of essence recovery was conducted. The high-boiling, low-volatile compounds were separated from those low-boiling, high-volatile compounds in the first step. By applying low heat to the reboiler, the high-boiling compounds of pear aroma were collected in the reboiler discharge water. The low-boiling components of pear aroma were driven up and concentrated in the rectifying section, then were collected as over-head product.

In the second step, all the reboiler discharge liquid was pumped into the unit as feed material, and then the same vaporization, distillation, concentration processes were conducted. Without the interference from low-boiling compounds, such as alcohols, better distillation and concentration effects were achieved for those high-boiling compounds, and finally, they were collected as overhead product. The overhead product from each operation combined together to

give the full-flavor ripe Bartlett pear essence. The final combined essence product from two-step split process was organoleptically evaluated to be good essence possessing strong and typical ripe Bartlett pear aroma.

Following this success, a two-stage essence recovery unit was designed and built. Another set of fractional distillation system and evaporator was connected with the original equipment to become a new, two-stage, one-step operation unit. The discharge liquid from reboiler I was directly pumped into evaporator II as feed. The low-boiling material was distilled and concentrated in the first fractional distillation system, as was the high-boiling material in the fractional distillation system II. Overhead product from each system was combined together with material from the air scrubber to become the final full-flavored 100 fold essence. Organoleptic evaluation of the final product indicated that this clear, aqueous product was an excellent ripe Bartlett pear essence, full of strong and delightful Bartlett pear aroma. Further proof was made by UV measurement. The maximum absorbance occuring at 263-267 mμ identified the existence of decadienoates. This UV method is a quick, simple and accurate way to detect the presence of typical ripe Bartlett pear aroma components -- decadienoates. Thus, the final product from two-stage essence recovery test was analyzed by UV to positively confirm the existence of decadienoates in the product. Up to this point, it showed

that the constructed equipment is effective for the essence recovery. Under the conducted operating conditions, good and typical ripe Bartlett pear essence of 100 fold can be recovered.

This is the first time that a good characteristic typical 100 fold ripe Bartlett pear essence has ever been produced. This production of a high quality Bartlett pear essence substantiates our concept of separating the three phases of Bartlett pear essence into two two-phase systems, then, recovering the full-aroma essence without loss of components. Industrial size units can now be built to obtain aroma concentrate (100 fold essence) from ripe Bartlett pears.

Suggested Future Research

1. Now that a Bartlett pear essence has been obtained, studies should be conducted to determine stability and necessary storage conditions for industrial handling and uses.
2. In the grape essence manufacturing process, a considerable amount of grape aroma is lost in the reboiler discharge water (Roger and Turkot, 1965), and in the juice partial vaporization and juice stripping section.

   The aroma loss in the reboiler section could be reclaimed by use of our two-stage Bartlett pear

unit. The loss in the juice vaporization and stripping section could possibly be prevented by a parallel stage concept whereby another identical unit with same preheater, evaporator, and fractional distillation system could be connected with the first unit. The discharge juice which was not completely aroma stripped from the first separator would enter the second preheater and evaporator to be partially vaporized again for better aroma stripping effect. Also, it is possible that the double fractionating effect of two columns and two reboilers might prevent the aroma loss in the reboiler discharge water.

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