

THE UNIVERSITY OF MANITOBA

CLOSED-LOOP BLANCHING OF APPLE SLICES

BY

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ANA VIRGEN DEYANIRA MULLER

A thesis submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
of the degree of

MASTER OF SCIENCE

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ABSTRACT

Closed-loop blanching of apples slices, with minimal purification between recycles, was carried out, with continuous monitoring of the following factors: pH, Soluble Solids (SS), Phenolic Compounds (PC), Absorbance at 280 and 450 nm, Turbidity, and Standard Plate counts. However, deterioration of the blanch water and blanched product occurred. Thus, in order to implement closed-loop blanching, proper purification of the recycled water is required.

Simulated Recycled Blanch Water (after six recycles) (SRBW), was successfully purified by Powdered Activated Carbon (PAC) at the normal pH of the blanch solution (4.2 - 4.4). The ultimate capacity of PAC for this SRBW solution was 0.27mg of Phenolic Compounds (PC)/mg of PAC. Blanching of apple slices in Simulated Recycled Blanch Solutions (SRBS) with levels of SS that range from zero to 20%, changed the total solids of the blanched product (from -34 to +38% when compared to the total solids in the unblanched product) as well as the hedonic responses (from dislike slightly to like moderately). Changes in turbidity and total residue of the blanch solutions decreased, as percentage of SS in the SRBS increased.

Microscopical observations of PAC in various solutions showed that de-aggregation of PAC particles occurred in the presence of pectin, requiring finer filters, for efficient PAC removal.

Major recycling of blanch waters is possible, and with proper purification, it should yield great benefits to the processing of apples and other fruits, at improved quality and consumer appeal, and with major savings in energy, water effluent volumes/loads and blancher effluent waste treatment costs.

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INTRODUCTION

Blanching is a heat process frequently applied to fruits and vegetables prior to freezing, canning or drying. However, conventional blanchers discharge the hot water continuously, generating significant product losses and highly polluted effluents. Fortunately, various studies have shown that properly monitored and controlled water recycling could be the answer to those problems.

The research objectives were:

- 1) To study the interactions between apple slices and blanch water, with the water being reused many times on sequential lots of tissue, under controlled conditions and with minimal purification.

- 2) To study the rates at which thermodegradation products and other undesirable constituents develop and/or accumulate in the recycled blanch water, by using simulated systems.

- 3) To develop scientific means to readily control such problems within very low, acceptable limits, during extended reuse of the blanch water, by focusing on their selective purification by means of Powdered Activated Carbon (PAC).

- 4) To microscopically observe PAC aggregation

patterns in various solutions, in order to explain variations in PAC filterability.

5) To demonstrate the advantages of a "Closed-Loop" system versus an "Open" one, by studying the changes occurring, in the blanch solution and in the blanched apple slices, when blanch water solutions of various concentrations were used.

1 LITERATURE REVIEW

1.1 BLANCHING

1.1.1 Blanching and its importance during fruit and vegetable processing

One of the most important methods developed by man for extending the storage life of foodstuffs is heat processing. Blanching or scalding is a heat process frequently applied to fruits and vegetables prior to freezing, canning or drying, and involves the treatment by means of some form of heat, usually either steam or hot water. The time and temperature used depend upon the final processing to be employed, as well as on the nature and size of the material being processed. The "holding time" is usually a few minutes only and the temperature ranges from 85 to 100°C.

The most important effects of blanching as a pretreatment in fruit and vegetable canning, are that of shrinkage of the material as a result of expulsion of gases and the collapse of the tissues. In some cases, the swelling of starches, by water uptake, may increase tissue weight/volume. Prior to freezing or dehydration, it is the inactivation of naturally occurring enzymes in the fruits and vegetables that is important. And in general, blanching reduces bacterial content and removes some of

the off-flavors/odors present in the raw material.

1.1.2 Current techniques being used

The blanchers currently used in the food industry vary widely in specific design. However they can be classified into two basic categories:

- a) Steam
- b) Water blanchers

a) Steam blanchers use steam as a heat transfer medium. Some common examples of steam blanchers are: i) Conventional Steam Blancher (CSB), where a multilayered bed of prepared vegetables is passed through the steam chamber. ii) Hydrostatic Steam Blancher (HSB), which is an improved version of the CSB. It uses water to seal the feed and discharge of a CSB. iii) Individual Quick Blanch (IQB) models, in which pieces of vegetables are spread in a single layer on a mesh belt moving rapidly through a steam chamber, followed by discharge into a deep bed, for sufficient time, to equilibrate the mass average-temperature high enough to achieve enzyme inactivation. iv) Vibratory Spiral Blancher-Cooler (VSBC), which use a vibratory spiral conveyor to move the vegetables, and separate the blanching step into two operations, heating and holding. Such blanchers are usually combined with an air cooler.

b) Water blanchers using water as a heat transfer medium.

Some common examples of water blanchers are: i) Conventional Water Blancher (CWB) in which the produce entering the blancher is conveyed by a spiral through a bath of clean hot water usually heated by direct injection of steam. ii) Rotatory Water Blancher (RWB) comprise a rotating drum of perforated material fitted with a continuous spiral, and a contra-flow system of operation. The drum rotates in a sheet-metal casing. iii) Pipe Water Blancher (PWB) in which the water/produce suspension is fed into an insulated heated tube (approximately 7.3m long with 10.2cm internal diameter) at a controlled rate to give an adequate blanching time.

Additional blanching methods using heating media other than hot water or steam have also been reported. Ralls and Mercer (1973) developed a Hot-Gas blancher that uses the products of combustion along with steam as a heat transfer medium.

Moyer and Stotz (1945) suggested the use of high frequency energy as a blanching method, and since then several studies have been carried out. Decareau (1972) presented an extensive review of several infrared, microwave and combination microwave-steam blanching methods reported in the literature. Mizrahi and co-workers (1975) developed a method for electro-conductive heating of large size products immersed in a liquid whose electric conductivity is close to that of the product.

1.1.3 Problems associated with conventional blanching methods

There are four major problems that are commonly associated with blanching, during fruit or vegetable processing:

- a) Loss of nutrients : Thermal, leaching and oxidative
- b) Energy consumption and cost
- c) Product yield and solid losses
- d) Generation of highly polluted effluents

a) It is well known in the food industry that fruit and vegetables lose nutrients during processing, particularly in the blanching step. The degree of nutrient losses depend on the blanching method being used, and the effect of those methods on nutrients can be assessed by considering thermal, leaching and oxidative losses.

Although several review articles have been published on the effects of heat processing on nutrients, few authors have attempted to summarize the kinetic data which can be used to describe the time/temperature effects on nutrients during blanching. According to Harris and Karmas (1975) there would not appear to be an advantage between a high temperature-short time (HTST) or a low temperature-long time (LTLT) processes when only thermal losses are evaluated.

Hough and Alzamora (1984) developed a mathematical

model to predict the thermal losses of vitamins and other quality characteristics during blanching of peas. They reported that loss of vitamins due to thermal destruction was negligible for different blanching temperatures and external heat transfer characteristics (condensing steam, water in natural or in forced convection).

Since all blanching methods require heat to achieve a "blanching" condition, some thermal losses seem unavoidable; therefore, the leaching and oxidative losses are the remaining factors that can be used to compare the various blanching methods currently used.

The relative merits of water blanching versus steam blanching have been studied intensively. Lee (1958) and Harris and Karmas(1975) have presented two excellent reviews of data published prior to 1958 and from 1958 to 1975 respectively; Appendix I is a supplement to those reviews. It seems that steam blanching is the more effective of the two for the conservation of water-soluble nutrients. The factors expected to affect losses during water blanching would be those related to mass transfer: i) surface area, ii) concentration of solutes in the hot water, iii) agitation of the water and iv) contact time.

Ralls and Mercer (1973) reported the content of selected nutrients in spinach after blanching in water and hot gas. The authors concluded that there was no significant difference between the two blanching methods. This indicates that oxidative losses during hot gas

blanching may be equivalent to those caused by leaching during water blanching.

In general, it appears that the blanching operation can significantly reduce the nutrient content of foods, the extent being dependent on the blanching method and the product.

b) Energy consumption and cost

Blanching of fruit and vegetables consumes large amounts of energy and is a costly operation. Chhinnan et al. (1980) reported that blanching of spinach consumed 34% of the total energy required to process the product. Of this, 10.5% was required to blanch the product whereas 23.5% was lost.

Bomben (1977;1979) compared the energy use and blanching cost for four different blanchers. Two were modified steam blanchers, one was a water blancher and other was a hot-gas blancher. These results showed that the low investment cost of the water blancher is the main reason for its low cost of operation, even though one of the steam blanchers had a lower energy consumption. Rose et al. (1981) measured the energy used in blanching and they concluded that water blanchers are more energy efficient than steam blanchers. Steinbuch (1983) described several industrial blanching methods, including data from the literature on energy consumption, yields, pollution losses, and costs.

Several of the new and modified blanching methods base their success or failure on these two parameters: cost and energy consumption. One example is microwave blanching. Dietrich et al. (1970) compared microwave, steam, and water blanching and found that microwave resulted in better nutrient retention. However, further studies showed that on the basis of what is now known about microwave blanching, it is questionable if microwave or combination blanching with microwave energy and steam would be significantly better than steam blanching of diced vegetables. Furthermore, process time is not reduced much and the cost is substantially higher. Thus, microwave blanching is not a good alternative at this time (Decareau 1972, Drake et al. 1981, and Gullet et al. 1984).

c) Product yield and solid losses

Loss of total solids from blanching and cooling systems used in the production of processed fruits or vegetables is important in considering overall processing losses and product quality and yields.

In two carefully controlled studies of steam blanched vegetables, Bomben et al. (1975) and Bomben and Hudson (1977) quantified yields and solids losses for six vegetables. Results showed that most of the vegetables lost weight in blanching. Losses were high when the total and soluble solids contents are high; they decreased when the insoluble solids content increased. The COD of the

effluent follows a similar pattern, and maximum COD was observed for vegetables with high total and soluble solids contents, like peas.

Carroad et al. (1980) compared the overall product yield and solids content using broccoli spears for several blanching and cooling processes. Blanching was in steam or water, the latter including fresh water and recycling water in a screw blancher system. Their results quantify the lower solids loss of steam blanching compared to fresh water blanching, but indicate that recycling blanching water may result in even lower losses than steam blanching.

d) Generation of highly polluted effluents.

The waste water produced by blanching of vegetables for freezing or canning contains a large fraction of the total wasteload of the vegetable processing industry. The National Canners Assoc. (1971) and Ralls and Mercer (1973) reported that, on average, 40% of the plant BOD was due to blanching.

Bomben (1977) described the characteristics of waste water from conventional steam and water blanchers. His results showed that water blanchers produce a higher hydraulic load, but their organic load is about the same as that for steam blanchers. He pointed out that comparison between various blanchers is extremely difficult; they are operated at varying conditions, and

as a result, the characteristics of the waste water can be quite different at different times in the same plant and from plant to plant. Furthermore, the amount of make-up water added to a water blancher is not a well controlled variable; Lund (1974) and Ralls and Mercer (1973) reported large variations in the measurement of the effluent from water blanchers in vegetable canning plants.

Cumming and Stark (1980) reported an effluent volume of 9Kg of waste water/45Kg of product for a steam blancher and 18-82Kg of waste water/45Kg of product for a water blancher.

1.1.4 Current answers to the problems caused by blanching

One of the newest developments in the thermal processing of foods has been an attempt to optimize the thermal process for nutrient retention; even though most of the research into new blanching techniques has been directed mainly at the more efficient use of energy and at the generation of less effluents.

Optimization of the blanching process with respect to nutrient retention involves consideration of losses of nutrients through leaching or oxidation, in addition to losses by thermal degradation.

Adams (1981;1983) pointed out that reduction of the heat treatments, particularly in the frozen vegetable sector, is feasible. This reduction can be achieved by using a more relevant enzyme test than the peroxidase test

in the determination of blanching requirements. Besides, it is now accepted that a significant though not well defined, proportion of active peroxidase can be left in many vegetables after blanching, and long shelf-life in frozen storage can still be achieved (Steinbuch, 1984).

Steinbuch (1984) proposed a "heat-shock" treatment for vegetables to be frozen, as an alternative for blanching. He reported that exposure of beans to boiling water or condensing steam during 5-15 seconds gave satisfactory results, in spite of the residual activity of peroxidase, and even catalase and lipoxygenase.

Alternatives replacing conventional blanching have been studied. Steinbuch (1979) evaluated vacuum-packaging as an alternative to blanching for frozen vegetables. He found that vacuum packaging was not as effective as blanching for long-term frozen storage periods, and that removal of oxygen by this procedure does not contribute to stabilization of chlorophyll.

Agulhon (1983), patented a process to improve the quality of preserved fruit, vegetables and mushrooms, by avoiding blanching. The process is based on simultaneous action of vacuum and monitoring the osmotic balances before bottling. This process reduces effluent, saves energy and improves product quality, by eliminating the losses through blanching fluids.

However, as was pointed out by Katsaboxakis (1984), blanching remains necessary as part of the preparation

for freezing preservation of vegetables, and its optimization should be studied in each case. Variations of nutrient losses between blanching methods can be understood on the basis of losses by leaching and oxidative degradation.

The development of more efficient blanching units has led to a series of studies that attempted to minimize the disadvantages of the conventional blanchers. The development of modified steam and water blanchers has resulted in the creation of more energy-efficient blanchers, with lower effluents and higher nutrient retention.

Work on improving the quality of the preserved vegetables using new blanching techniques is rather limited, but as long ago as 1960, various studies have been reported (Steinbuch 1979).

Rumsey et al. (1982) carried out a pilot scale experiment with a water blancher heated with heat exchange and by steam injection. He confirmed the energy savings potential of heating with an exchanger to minimize escape of steam, rather than by steam injection.

However one of the most recent approaches is the introduction of "closed-loop" systems. Some of the first attempts were carried out in steam blanchers. Bomben et al. (1976;1979) introduced the vibratory spiral blancher-cooler. This design is smaller than a conventional water blancher, and its heat losses are lower than those of a

steam blancher. The condensate from the blancher is sprayed on the vegetables as they are air-cooled. Thus the only effluent for both blanching and cooling is the unevaporated unabsorbed liquid leaving the cooler.

Using the IQB technique, the Canada Department of Agriculture and ABCO have developed the K2 System (1982) based on the study carried out by Cumming and Stark (1980). This modified steam blancher uses only one tenth of the steam required by a water blancher, and it will produce one tenth of the volume of effluent at one fifth to one fourth the total BOD load, as compared to the water blancher. It showed a 52% increase in retention of ascorbic acid in broccoli as compared to conventional water blancher/cool procedures. Further improvement in steam efficiency was achieved by using a venturi for recirculation of uncondensed steam.

Recycling of the blanch water to reduce water consumption and pollution, has been investigated by Swartz and Carroad (1979). In this system, the vegetables and the hot water pass through the blancher and are separated at the exit. The water is recycled through a heat exchanger for temperature control. Later it was found that recycling may result in even lower losses of solids than caused by steam blanching (Carroad et al. 1980).

Cabinplant a/s (1983) introduced an integrated blancher-cooler. It combines the advantages of water-blanching and steam-blanching and claims to have

eliminated their major drawbacks. It uses minimum resources, reduces pollution and at the same time cuts production costs. The system has three major zones: a) preheating b) blanching and c) cooling. The blancher uses the IQB principle, and the product is instantly blanched by using recirculated hot water and steam. The product is counterflow water cooled. Up to 70% of the heat is recovered by the heat exchanger and used to heat the incoming raw product before the water is recycled back into the counterflow cooling system.

1.2 BLANCHING OF FRUITS

1.2.1 Main constituents present in the fresh fruits

The chemical interaction between the fruit tissue and blanch water, as well as the changes expected and observed in blanch water during recycling, will largely depend upon the nature of the fruit constituents. Thus, if the major fruit constituents and their characteristics are known, it will be possible to predict, to a certain extent, the changes occurring during blanching.

a) Sugars

Sucrose, a non-reducing sugar, is almost invariably the major disaccharide in fruits. Hence, the values for reducing sugars are fairly accurate measure of total monosaccharides. In apples, the levels of sucrose and

reducing sugars as percent weight of fresh edible portion are 3.06 (1.28-6.64), and 8.37 (6.33-10.67) respectively. Glucose and fructose are the main monosaccharides in apple tissue and are found in concentrations of 1.72 and 6.08 percent respectively (Hulme, 1970).

Various sugar derivatives are present in fruits. However they are normally found in trace amounts only. Sugar acids such as D-galacturonic, D-gluconic and galactaric acid and L-ascorbic acid; polyols such as D-glucitol; sugar phosphates; sugar nucleotides and glycosides are the major groups of sugar derivatives found in apples.

b) Organic acids

The most common and abundant acids of fruits are citric and malic. Malic acid, in a concentration of 0.20-1.27g/100g of fresh weight, is the predominant acid in apples.

Free weak acids associated in the cell with their potassium salts constitute buffer systems, which play an important role in the cell, particularly in relation to the proteins of the cell, especially the enzymes.

c) Amino acids and proteins

In general, not much work has been done on the amino acids and proteins of fruit, probably because fruit is essentially a low-nitrogen product and of little nutritional significance as a protein source.

The free amino acids of fruits being essentially water soluble, exist as such in the juice, and considerable interest arises when their presence influences the processing of the fruits. The soluble nitrogen content of twenty varieties of cider apple varied from four to 33mg N/100ml (Hulme, 1970). Asparagine was the predominant amino acid of all juices except those of very low N content; and in high N juices up to half the soluble N content was attributed to asparagine.

The protein content of apple expressed as total nitrogen x 6.25 is 0.2% and the moisture is 84.8% (Watt and Merrill, 1963).

d) Lipids

The following lipid classes have been distinguished in apples: cuticular waxes, neutral lipids (mainly triglycerides and diglycerides), galactolipides and phospholipides. Apple peel contains all these classes, and the cells of the internal parenchyma contain mostly phospholipids (75% of the total lipid weight). The lipid content in apples is 0.06-0.1% dry matter weight (Hulme, 1970).

e) Enzymes

Considerable progress has been made in recent years towards understanding the intracellular distribution and function of multiple enzyme systems and their independence in the highly co-ordinated cellular metabolism of fruits.

Cellulase, pectinesterase, polygalacturonase, polyphenolase, lipase, malic enzyme and chlorophyllase commonly occur in apples and have been linked to the tissue softening during fruit ripening.

f) Volatile compounds; the aroma of fruits

Ethyl 2-methylbutyrate, although present in Delicious apples only in very small amounts, has a quite disproportionate effect on the aroma, since it has an olfactory threshold of 0.0001mg/kg. It provides the ripe note to the aroma, whereas hexanal and 2-hexanal, with thresholds of 0.005 and 0.017mg/kg, respectively, are important as regards the odours of green unripe apple fruits (Hulme, 1970).

g) Fruit Phenolics

According to Walker (1962) the total phenolics in apples of various varieties range from 0.11 - 0.34g/100g fresh weight.

The common phenolic compounds in fruits, particularly apples, can be classified as follows: a) cinnamic acid derivatives, b) flavanes, c) anthocyanidins and anthocyanins, d) flavonols and flavonol glycosides and e) condensed polyphenols.

h) Polysaccharides of cell wall of fruit

The polysaccharides present in apple pulp (excluding pectic substances) are hemicellulose A and B and α -

cellulose.

Pectic substances are part of all higher plant tissues. Pectins are mainly deposited in the primary cell wall and the middle lamella. In apples, the total pectin level ranges from 0.6 to 0.8% (Hulme, 1970).

i) Vitamins and minerals

Fruits and vegetables are important nutritional sources of vitamins and minerals.

The concentration of L-ascorbic acid in apples range from two to 10mg ascorbic acid per 100g of edible portion. The concentration of the vitamin is two to three times as great in the peel as in the pulp (Hulme, 1970).

Samuelson and Holland (1983) determined the concentration of various minerals in apple tissue. Their results were (expressed in mg of mineral per 100g of fresh whole apple) : Phosphorus 10.9, Potassium 132.0, Calcium 5.53 and Magnesium 5.11.

1.2.2 Observed and expected effects of blanching on the main constituents of vegetables and fruits

Vegetable and fruit tissues are living materials, and heat applied by blanching kills the cells, causes irreversible changes in the cell structure, and the solubilization and/or destruction of some nutrients and other cell constituents. Katsaboxakis (1984), presented a diagram showing the main effects of blanching in a generalized plant cell (Figure 1).

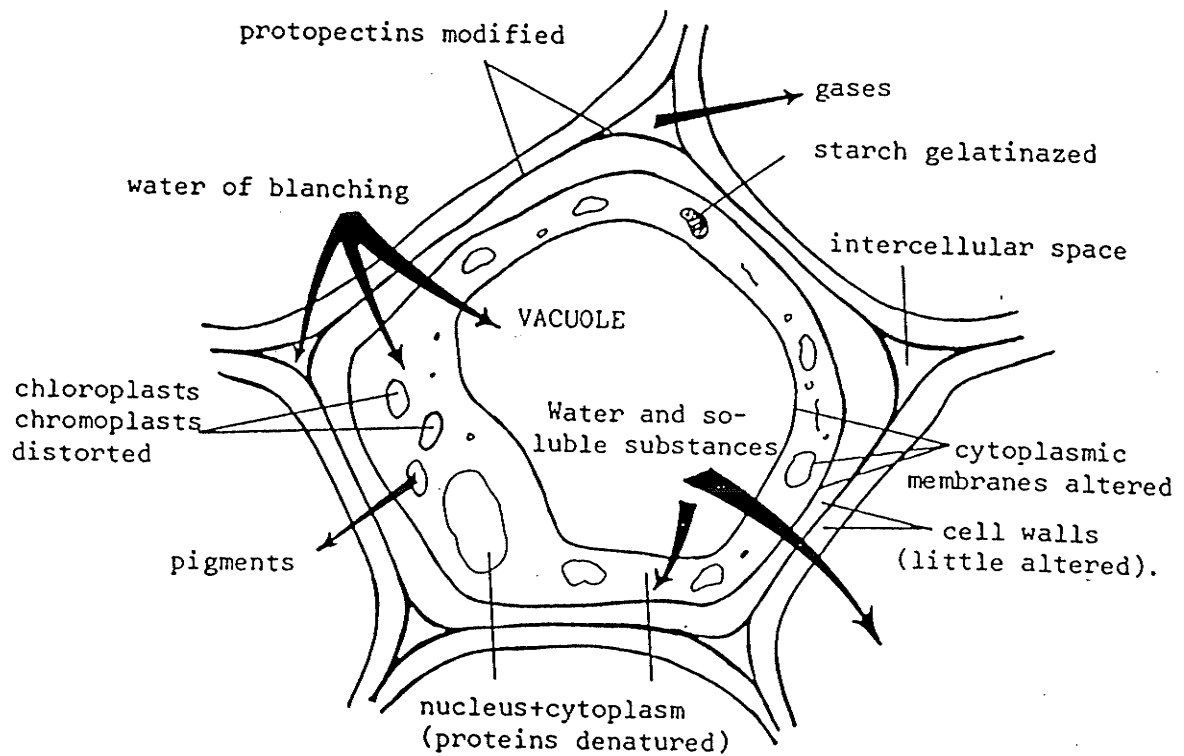


Figure 1 Diagram showing the main effects of blanching on a generalised plant cell (Katsaboxakis, 1984)

1.2.2.1 The effects of leaching on cell-wall degradation

Freshness and turgidity depend largely upon structural conditions and arrangements and chemical composition of the cell wall and of the intercellular spaces where pectic substances are the primary constituents. The most important initial change during blanching is the alteration of texture due to the destruction of the selective permeability of the cell membranes. The disruption of the cytoplasmic membranes increases their permeability. Some cell-wall rupture usually occurs. Blanch water enters the cells and the intercellular spaces, expelling gases and other volatile products. Proteins become denatured and the loss of soluble nutrients (vitamins, sugars and minerals in particular) occurs at the same time. In addition, significant losses occur when exposed contents of mechanically damaged cells (by slicing or peeling procedures), are washed out.

Under conventional blanching conditions, particularly for water blanching, the loss of soluble solids into the blanch water through damaged cells is almost unavoidable.

As pointed out in section 1.1.3, this mass transfer will be affected by variations in surface area of the product, concentrations of solute in blanch water, agitation in the blancher and temperature. However, temperature, surface area and agitation, are usually fixed parameters during blanching; thus the concentration of

solute in the blanch water plays the major role during mass transfer.

When conventional water blanchers are used the concentration of solute in the blanch water is minimal; since one of the main mechanisms of the mass transfer is through molecular diffusion as a result of concentration gradients (Schwartzberg and Chao, 1982). Under conventional blanching conditions, mass transfer from tissue to the water is maximized; with uptake of water into the tissues for gelling starches, etc.

1.2.2.2 Degradation mechanisms expected in the recycled blanch water

The accumulation of soluble solids in the recycled blanch water, due to leaching mechanisms, will promote degradation reactions. During blanching of apple slices, the major constituents expected in the blanch solution are sugars, along with lower amounts of other soluble constituents, such as organic acids, amino acids, phenolic compounds, minerals and others.

Since blanching is carried out at 98°C, the major expected degradation reactions are caramelization and Maillard reactions. Degradation effects from enzymes are not expected, since at that high temperature most enzymes will undergo denaturation, and usually consequent major loss of activity.

Many foods are subject to the so-called "non-enzymic" browning reactions, either during processing or upon

storage of the finished product. While it is not necessarily true in all cases, reducing sugars are usually the principal non-enzymic browning reactants. The reactions are accompanied by flavor/odor development, texture alteration, and the initiation of yellow, red, brown and black coloration. Food nutritive value is invariably lowered.

1.2.2.2.1 Caramelization

The levels of reducing sugars in the blanch water are expected to be relatively low (under 10%). Studies found in the literature have shown that in diluted solutions of reducing sugars, the initial stages of the caramelization reactions parallel the events described for the enolization, isomerization, dehydration and fragmentation reactions. Subsequently, polymerization reactions occur, which lead to the formation of pigments similar to those formed in caramelization reactions at either higher temperatures or in more concentrated solution (Shallenberger and Birch, 1975).

1.2.2.2.2 The Maillard reaction

Classically, a Maillard reaction occurs between an aldose or a ketose group of a sugar and an amino group of an amino acid. However, it can be extended to many aldehydes and ketones reacting with various amines, present in a solution. Simultaneously, however, the sugar undergoes a heat degradation (caramelization or similar

phenomenon) without the interference of the amino acid. This explains why products of the Maillard reaction and caramelization are mixed in the reaction medium. Both of those reactions produce many molecules that are identical, or nearly so, e.g. furfural and reductones. The interactions possible between caramelization and the Maillard reaction are shown in Appendix II.

The terms "premelanoidins" and "melanoidins" designate the intermediate and the final products during Maillard reactions. Premelanoidins is reserved for the entire amount of soluble compounds and colorless and coloured products, formed during the reaction. The term melanoidins, precisely define the insoluble residue, dark or black, that correspond to the ultimate stage of a Maillard reaction. Adrian (1982) reviewed hundreds of published works that dealt with the Maillard reaction, and Baltes (1982) focused his attention on the published literature dealing with chemical changes in food induced by this reaction. In 1986, Danehy reviewed the Maillard reaction with special reference to the development of flavor.

1.2.2.3 Factors affecting non-enzymic browning reactions

It is not possible to discuss the effect of any one factor in the browning reactions without mentioning, in a qualifying manner, the effects of others. This is because temperature, pH, nature and concentration of the

reactants, time and moisture content, interact to such an extent that the reaction shows qualitative changes as it progresses.

1.2.2.3.1 Temperature

The effect of increasing temperature on any one browning system is manifested in several ways: a) as temperature is increased, compounds are generated that may either enter into or inhibit the reaction; b) the rate of browning in model systems increases two to three times for each 10 °C rise in temperature, whereas in natural systems containing fructose, the rate will increase five to ten times faster; c) the browning reactions appear to increase uniformly, with rise in temperature between zero and 90° C; d) other effects are increasing carbon content in the pigment and more pigment formed per mole of CO₂ released at higher temperatures.

1.2.2.3.2 Effect of pH

Changing the pH of a browning reaction system over a wide range leads to qualitatively different reactions. Shallenberger and Mattick (1983) studied the formation of 5-(hydroxymethyl)-2-furancarboxaldehyde (hydroxymethyl furfural, HMF) from fructose and glucose at different pH at 100 ° C. They found that fructose is most stable between pH 4 and 6 and glucose between pH 2 and 4, as measured by the formation of HMF.

Studies of the effect of pH on the nature of the

nonenzymic browning reactions are complicated by the fact that buffer components themselves may be either browning reactants or catalysts (phosphates, aminoacids, etc.).

In an attempt to distinguish between caramelization reactions and carbonyl-amine reactions, Smirnov and Geispits (1956), followed glucose caramelization and glucose-glycine browning at various pH values at 100 ° C. They reported that carbonyl-amine browning does not take on much significance until the pH is greater than 6. Similar results have led others (Schroeder et al., 1955) to take the position that in aqueous solutions, browning is primarily due to caramelization reactions; but in the nearly dry state, or at an alkaline pH, the Maillard reaction prevails.

1.2.2.3.3 Water and reactant concentration

Water catalyzes the enolization of the reducing sugars, and the enolic forms are readily fragmented and dehydrated. Therefore, moisture content would have a marked effect on the rate of browning. Changing the concentration of the reactants alters the course of the reaction, and the yield of melanoidin may be increased three to five times when the concentration of reactants is only doubled.

Wolf from and Rooney (1953) found that the reaction between xylose and glycine is maximal at 30% moisture content, and minimal, at moisture contents of zero and

90%. The decrease in reaction at moisture contents above 30%, is undoubtedly due to dilution of the reactants. According to Schroeder et al. (1955), the presence of water retards the Maillard reaction, under conditions of high temperature and relatively short times.

1.2.2.3.4 Nature of reactants

Sugars.- The reactivity of the sugars in nonenzymic browning reactions generally parallels their reactivity in other respects. Pentoses are more reactive than hexoses, and hexoses in turn are more reactive than reducing disaccharides. Non-reducing disaccharides participate in browning reactions after they are first hydrolyzed to their component monosaccharides.

Amino Acids.- The browning reactivity of an amino acid depends upon the method used to follow the reaction, on its concentration, and on the reactivity of the aldehyde generated when the Strecker degradation occurs. Some amino acids have more than one reactive nitrogen atom that participates in carbonyl-amine browning, but not all the constituent nitrogen of each amino acid is necessarily reactive.

1.3 RECYCLING OF BLANCHING WATERS

1.3.1 Water Recycling in the Food Industry

There are few examples of extensive water reuse or

recycling in the food industry. Various studies indicate that most food processes discharge once-used effluents, either to municipal treatment or land (Train et al. 1975 and Schmidt et al. 1977). However, due to rising costs of supply and discharge and to difficulties in obtaining large, fluctuating supplies of potable water, with the resultant problems of wastewater disposal, individual food processors may now need to recycle water to survive in the market place.

Water reuse in canneries was first reported by Mercer and Townsend in 1954. Since then, the food industry has been reusing and recycling waters to various degrees, in an effort to reduce waterborne discharges and to conserve water. Cooling waters are the most commonly reused or recycled, followed by initial washing waters used in fruit and vegetable processing. The recycling of food processing brines can be carried out without deleterious effects on the final product (Mercer et al. 1970).

Rissmann et al. (1981), carried out a literature search which examined the use of water, reuse and recycle technology in 39 industry segments, including the food industry. They found six case histories and six articles, in which the reuse or recycling of water during food processing was carried out to a significant extent, after filtration, and biological and/or chemical treatments. They also found that in many areas, recently developed

water reuse and recycle technology is already economically competitive with conventional treatment methods.

Water recycling is a common practice in various stages of the food processing industry. A number of process water flow patterns ranging from once-through to complete reuse have been developed by food processors, and can briefly be described as follows:

a) Once-through (no reuse or recycle) is the conventional method of introducing fresh water for cleaning or process use and discharging it as wastewater after a single use.

b) Reuse, involves the use of treated process wastewater (end-of-pipe discharge), after bleed-off and the resultant addition of make-up water for salt balance and water quality control.

c) Counter current water recycle, where the water flows sequentially through each unit process, countercurrent to the product flow.

d) Modular closed-loop pattern, recycles water in a single unit process continuously, until contaminant concentrations reach an undesirable level with respect to sanitation or product quality. Then they are either adequately removed, or the bleed-offs are discharged as effluents for proper treatment.

e) Combination recycle, involves the combination of two or more of the water recycle patterns.

Major emphases have been placed on incorporating both in-plant modifications and end-of-pipe upgrading by biological treatment (Esvelt and Hart, 1982). However, the end-of-pipe "omelette" created has little chance of being accepted by regulatory bodies for reuse and recycle in the plant, even though it is technically-economically feasible to purify them back to potable-grade composition. It is much wiser not to waste and degrade potable water initially, than it is to try to reclaim it subsequently, especially from floor drains. Problems are best controlled, at the beginning, not the end, of a series of stages. An alternative strategy is the approach taken by Gallop (1968) and others (Yau, 1976; Perkins, 1977; Gallop and Hydamaka 1979, 1982; Gallop et al. 1982; and Russell et al. 1981), who have demonstrated that the ideal water for a specific function is water which is recycled continuously with intermittent partial modular physicochemical treatment, only when necessary at a unit process stage. Furthermore, water recovered at each stage for recycle or reuse in a nearby stage or cascading will be more acceptable and less costly than the water recovered by purification of the end-of-pipe effluent to drinking water composition.

1.3.2 Present situation of blanch water recycling

The concept of recycling blanching water has not been widely implemented. But has been used successfully in

several food processing operations (Russell et al. 1981). In a water blanching system with recycle, unblanched vegetables and hot water pass through the blancher and are separated at the exit; the water may be recycled through a heat exchanger for temperature control, and/or treatment. Water in the form of steam or as make-up water is added to the system to compensate for the evaporative losses and for water carried away with the product.

Farkas and Lazar (1969) studied the osmotic dehydration of apple slices. They recycled the syrup used in the blancher, where the dehydrated product was blanched, for over one-month periods. However, no studies were made on syrup recycling.

Swartz and Carroad (1979), studied the effects of recycling blanching water on the quality of various vegetables. They found that product quality was not reduced by recycling the water in the blancher, as long as a near neutral pH was maintained.

In recent years, several industrial blanchers with water recycling have been introduced in the market. Anonymous (1983) and Cabinplant a/s (1983) claim to successfully recycle vegetable blanch water with only minimal treatment and continuous addition of make-up water.

The implementation of recycling during blanching in the industry, follows the same pattern that water recycling in food industries does. Roussell et al. (1981)

and Gallop et al. (1982), pointed out that the technology for cost-effective recycle exists; however, the industry is delaying implementation primarily because of a) the uncertainty of potential health effects; b) relatively low-cost impact in most cases, due to complicated federal standards; c) the clouded division of regulatory authority and obsolete regulatory concepts and practices and d) the inconsistency of standards for both discharge and in-plant water quality.

1.3.3 Observed and expected advantages of water recycle in the food industry

The advantages of water recycle, include water and energy conservation, higher product recovery, generation of less pollution, and only periodic discharge of any high strength wastewater. These can result in the improved competitive position of processors, especially in water-short areas.

Recycle reduces discharge volume and increases the levels of inorganic and organic compounds in solution. The low volume of highly concentrated wastewater produced, frequently can be treated more cheaply than larger volumes of diluted wastewaters due to reduced capital costs and improved treatment efficiency, especially by physicochemical means.

Furthermore, specific contaminants or degradation products at each unit operation during closed-loop

recycling, can be detected and controlled more efficiently than during end-of-pipe reuse, where a more complex and unpredictable mixture must be expected.

The major roles of water in the food industry are transfer of precise processing requirements, solids and heat, and they can be optimized by recycling. For example, the energy requirements during recycling of blanch water, are expected to be minimal, since only small volumes of make-up water are required, compared to the appreciable volume of make-up water continuously added to the conventional blancher.

Swartz and Carroad, (1979) reported that during closed-loop blanching, the concentration of solids in the blanch water as well as in the blanched product, builds up until it equilibrates with that in the raw product. The total solid content of blanched vegetables is higher when blanched in recycled blanch water, than when blanched in a conventional blancher (Swartz and Carroad, 1979 and Carroad et al., 1980).

After an initial period of product leaching, no further major solids loss will be expected because the concentration gradient promoting such mass transfer would have been eliminated. This will produce high solids levels in the final product of increased economic and nutritional value.

1.3.4 Merits and demerits of the existing systems

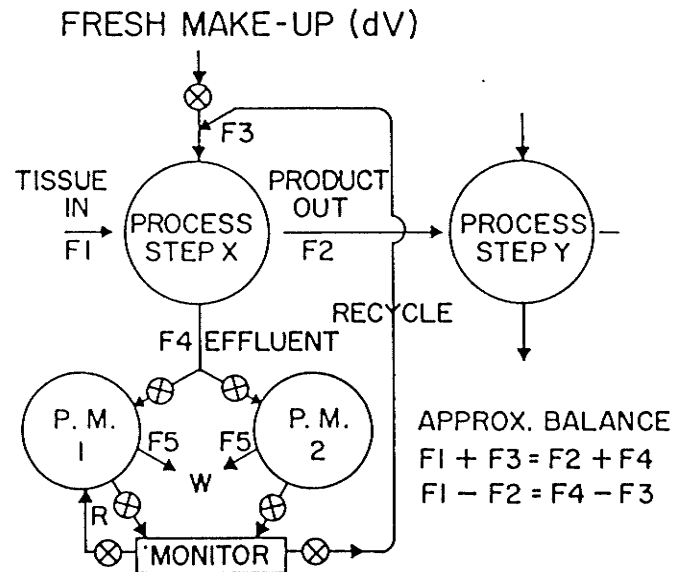
The majority of food industries, have introduced recycling to a certain extent. In plant modifications (e.g. counter current flow and reuse), along with the limited recycle of process water in some stages such as cooling, have been carried out. The conventional "once-through" and the various recycling patterns introduce several advantages and disadvantages into the process. The once-through, is a linear system that has been widely accepted by the food industry. However, it has some serious disadvantages, since it incurs the highest water supply costs and wastewater treatment, in addition to the production of heavily leached products.

Reuse will significantly reduce the water cost, but the unknown variable complex end-of-pipe mixture generated, the special sanitary requirements, and high consumptive use of water in the food industry, make reuse difficult to implement. Furthermore, the conventional emphasis on the use of biological treatment before reuse, is unsanitary and may give the reused water less chance of being effectively purified especially of non-biodegradable, potentially toxic constituents.

Countercurrent water recycle, can significantly reduce the water usage from that of a once-through system, produce more concentrated wastewater and increase the solids in the final product.

A modular closed-loop system not only reduces water use, but also allows precise process control with

reclamation of heat and potential recovery of products and by-products (see following diagram).



Symbols: P.M.- Purifier modules, one on load, one on standby

W - Waste solids, to use or destruction

R — Reject for re-purification or discharge

G — Accept for re-use

V - Cyclic base volume

dV — Make-up volume/cycle

F - Mass

(Gallop et al., 1976)

An added advantage is that treatment methods may be tailored to remove known groups of undesirable factors specific to the unit process flow, better than to the

unknown mixture in combined wastewater (end-of-pipe effluent) from all unit processes.

Cyclic processes permit each factor in the process design to be programmed, monitored and closely controlled by "feed-back" procedures. When such unit process loops are closed, except for "bleed-offs" and "make-up", they come to dynamic equilibrium with in a few minutes in both phases under batch or continuous product flows. They can then be operated in a predictable "steady-state", whereas present "open" linear process cannot.

Combination recycling, allows every plant to adopt a combination of recycle patterns to suit their economical and processing needs, with the added advantages of the recycle patterns involved in the design.

1.4 POWDERED ACTIVATED CARBON (PAC) ADSORPTION DURING THE TREATMENT OF RECYCLED WATERS

1.4.1 Description of PAC adsorption and its current applications in the food industry

The generic term "activated carbon" encompasses a broad range of amorphous carbon-based materials having high degrees of porosity and extensive surface areas. The large surface areas are associated with near-molecular size pores and larger capillaries formed within the carbon granules by selective charring and oxidation of raw material during activation. Commercial carbons typically

have total surface areas in the range from 450 to 1500m²/g, and this enormous area makes them effective makes them adsorbents.

Activated carbons can be prepared from many materials, but those commonly used commercially are: peat, coal, lignite, wood, animal bones (for bone-char) and coconut shell. They are produced in several forms: granular, powder, extruded, balls and recently as cloth. The powdered activated carbons are produced in the largest quantities and are widely used in liquid phase applications.

The phenomenon of adsorption is of major significance in most physical, chemical and biological water and waste water operations. It fundamentally involves the concentration of soluble and quasi-soluble impurities from solution at an interface or surface. The material concentrated is the adsorbate; the material at whose surface the concentration occurs is the adsorbent.

Adsorption of organic compounds from water by activated carbon results from several types of binding forces, between the organic molecules and the carbon surface, all having their origin in electromagnetic interactions. Generally, it is a combination of physical adsorption resulting from weak "van der Waals" forces and chemisorption, based upon the formation of stronger chemical bonds. The affinity of a chemical for the internal surface area of activated carbon will depend

greatly upon its chemical nature, and the adsorption process is governed by the equilibrium between adsorption and desorption reactions.

The concept of adsorption of organic materials onto carbon is not new. Historical evidence predating the Christian era, has shown that activated carbon (in the form of charred wood) has been used for centuries in medicine and to improve the potability of drinking water. Prior to World War I, however, activated carbon was used more widely in the sugar industry as a decolorizing agent than in the water industry.

Activated carbon systems are currently in use throughout the world in various water and wastewater reclamation applications. While activated carbon systems are in widespread use, very little consideration to date has been given to the physical and chemical factors involved in adsorption phenomena.

Adsorption on activated carbon is one of the best commercially proven methods for removing toxic organic chemicals from industrial wastewaters. The preferential adsorption of one organic over another organic contaminant, has been studied extensively. Among many factors, the following summarizes the more important characteristics of the contaminant:

a) Molecular weight. Higher molecular weight usually favors adsorption up to weights of 10,000.

b) Ionic character. Hydrophobic contaminants are

preferentially adsorbed over hydrophylic materials.

c) Aromatic/aliphatic. Ringed and multi-ringed compounds are usually preferentially adsorbed over analogous aliphatic contaminants. Substitution of active radicals on the ring can, however, produce dramatic changes in adsorbability.

The use of activated carbon is well established in the food industries, since it constitutes an integral part of the processing of many food products. Activated carbon has been used in the sugar industry for over one hundred years for removal of color, and organic contaminants. The wine and beer industries use it to remove undesirable odours, flavours and coloured compounds. Activated carbon has also been used in the purification of various products, such as oils, fats, fruit juices, gelatin, pectin, alginates, maple syrup, honey, candy, and soy protein extracts (Perrich, 1981).

In only a few cases, activated carbon has been used in the purification of food processing brines for reuse, and in the treatment of various cannery wastes (Mercer et al. 1970 and Panasiuk et al. 1977).

The widespread use of activated carbon in the food industry, has been limited because carbon technology has too often only been considered as a tertiary treatment stage following secondary (biological treatment); or has

been evaluated as a means of removing gross amounts of organics. The use of carbon in the above manners has been shown to be economically non-feasible for the food processing industry (Perrich, 1981).

1.4.2. Advantages observed and expected during PAC-treatment of recycled water

During the modular recycling of water in the food industry, quality control factors, such as the physical, physico-chemical, biochemical and biological ones, must be controlled. The use of activated carbon, may be the essential key to controlling all those factors. The present practice of recycling with inadequate or no purification does not satisfactorily fulfill all the quality control requirements.

Gallop et al. (1976) pointed out that activated carbon has obvious, major roles to play, in the quality control of recycled water, particularly in the food industry, where organic and biological materials are involved. These include the following:

- a) As an efficient, rapid, controllable adsorbent for large molecules which are the product of degradation reactions and/or accumulation during recycling; including enzymes and their substrates and products.

- b) As a collector and "weighting substance", for microbial cells, and for suspended solids, in

sedimentation, filtration or centrifugal processes, thus reducing these problems as a secondary benefit.

c) As a filter-aid, to enable the treated solution to be "polished" easily and rapidly, prior to reuse.

d) As a regenerable agent for all those functions, on which to destroy the wastes, with minor losses carbon/cycle, at low costs.

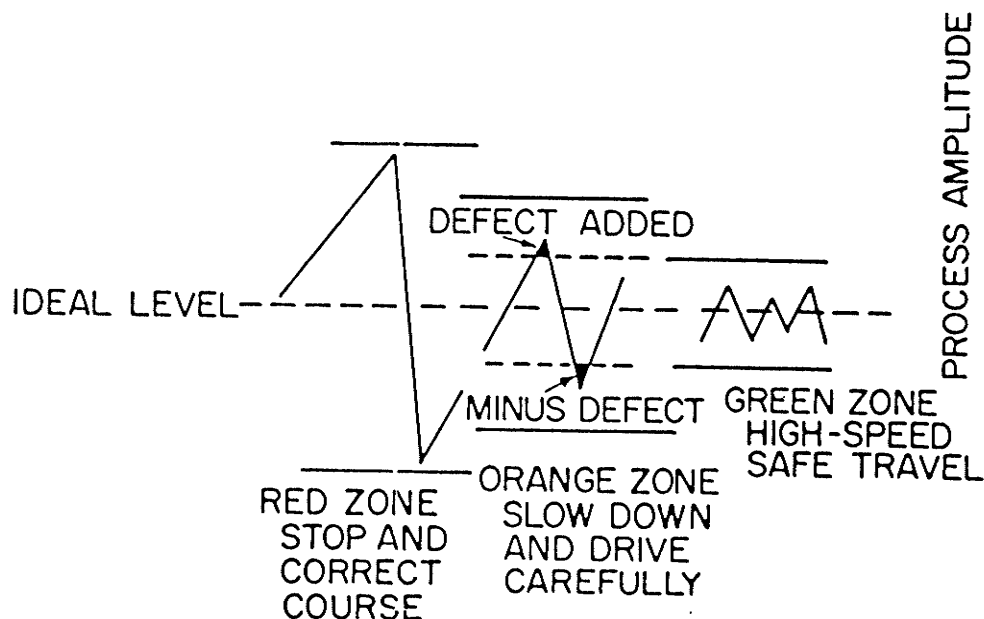
e) Finally as a source of some energy, when too high in ash to warrant regeneration.

1.4.3 Feasibility of adequate purification of closed-loop blanch water by PAC adsorption during blanching of apple slices

During closed-loop blanching of apple slices, major changes are expected in the composition of the blanch solution, which have to be monitored and dealt with accordingly, to insure high quality in the blanched product.

Based on the results presented by Swartz and Carroad (1979), the first major change expected in the blanch solution will be the increase in the level of soluble solids, until equilibrium is reached. This increase in the level of soluble solids, however, will promote the formation of degradation products, and the accumulation of contaminants and natural constituents being leached from the product (e.a. furfural, pesticides and polyphenolic compounds), which are associated with off-flavours, off-

colours and off-odours, and some are a potential health risk. Hence the need for a high efficiency quality control system, like the one suggested by Gallop and Hydamaka 1979, in which the required quality assurance and quality control of the process can be achieved by keeping the process in the green zone (see following diagram)



Cyclic processes can greatly benefit by periodic PAC treatments to insure the background levels of the undesirable compounds is kept down (green zone) during recycling.

Periodic PAC treatment will insure that background levels of those undesirable compounds is kept down during recycling. It is expected that PAC will suffice as a purification agent, since most of the undesirable

compounds found in the blanch solution are fairly large molecules, of similar chemical configuration of those tested previously, and which are expected to be readily adsorbed by the PAC.

The increase in insoluble suspended particles in solution during recycling is expected and can be easily reduced by filtration or other physical method, prior to or during adsorption.

The pH of the blanch water can greatly affect adsorption. Treating the same solution at different pH values with the same carbon, generally shows better adsorption at the lower pH region. Since the pH of the recycled blanch water during apple blanching is expected to be similar to that found on the apple, low pH values are expected and in it; and minor or no pH modification should suffice for optimum adsorption.

Microorganisms are assumed to be limited to the surface of whole, sound fruits, and it is presumed that the internal tissue of the fruit is normally sterile. The predominant native flora of sound apples are typified by the weakly fermentative nonsporing yeasts rather than bacteria or molds. Due to the composition and pH of apples, the native bacterial flora is limited to acidophilic species. Total yeast count ranges from 10^2 to 10^6 organisms per apple, whereas the mold count goes from 10^3 to 10^5 organisms per apple, fruits having mold count greater than 10^5 can be considered damaged fruit. Doores

in 1984, pointed out that washing fruit can decrease the microbial load by one to four cycles.

The fruit reaching the blancher usually has been washed, and unless whole fruit is to be blanched, peeling and slicing takes place prior to blanching. Therefore, the expected microbial loads on the fruit at that stage should be low. In peeled tissue it is mostly caused by airborne and handling contamination. If the microbial load of the incoming fruit is low, no microbial problems are expected during blanching, and more likely the blanch water will be free of microorganisms, but for some heat-resistant molds, which produce ascospores sufficiently resistant to survive the usual heat treatment.

Carbon treatment of the blanch water is expected to be carried out at the process temperature, since it is seldom economical to change it. That implies high temperatures, which will affect both the rate of diffusion and the final adsorption equilibrium. The rate of diffusion, which is related to changes in viscosity and other factors, will increase with temperature and hence the equilibrium value will be reached more quickly; but the final quantity adsorbed will be lower.

As was pointed out by Gallop et al. (1982), recycling in the food industry is feasible. Results from other studies prove that recycling with the use of advanced PAC purification technology, have been successfully carried out for other food groups. The technology exists and this

could be extended to other fruits, with only minimal modifications. Furthermore, the implementation of closed-loops in the food industry, particularly during blanching, can make effective use of the existing equipment with minimal in-plant modifications.

The expected results are a considerable reduction of energy and water consumption, as well as, wastewater loads and finally a product of higher quality, yield and value.

2 MATERIALS AND METHODS

2.1 MATERIALS

The Powdered Activated Carbon (PAC) selected for this study was Norit-4N obtained from Norit Activated Carbon, Amersfoort, The Netherlands. The other two PAC samples tested were Darco KB and Hydrodarco H, obtained from Atlas Chemical Industries Canada, Brantford, Ontario, Canada. Some general characteristics and typical properties of these carbons are compiled in Appendix III.

All Chemicals used in this study were of reagent grade or better. Distilled water was used in all experiments and analyses, unless stated otherwise. Red Delicious apples were the basic material used in all experiments and were obtained in carton lots from a local store, and stored at 4°C before use. Their tendency to deteriorate rapidly during processing made them more suitable as a test-product, than other apple cultivars.

Apple juice concentrate with 68% SS was obtained from McCain Foods Ltd., New Brunswick and kept at -36°C before use.

Pectinase, for apple juice depectination, was provided by Miles Laboratories, Inc. Elkhart IN., U.S.A., under the trade name of "Clarex-L".

2.2 METHODS OF ANALYSIS AND STATISTICAL PROCEDURES

2.2.1 Physical

Turbidity (T) was determined by using a Fisher Model DRT100 Turbidity meter. Turbidity was measured in Jackson Turbidity Units (JTU) and the Turbidity changes (ΔT) in the blanch solutions were calculated by using:

$$\Delta T = T \text{ after blanching} - T \text{ before blanching}$$

Soluble Solids (SS) were determined using an Abbe Refractometer. The degree Brix readings, obtained directly from the instrument, were used as an index of approximate percentage of soluble solids.

Absorbances at 280 and 450nm were measured in a Bausch & Lomb Spectronic 710 spectrophotometer. Dilutions of the samples were made, when required, to maintain the absorbance readings under 1.2. Spectroscopic scanning, from 200 to 800nm, was carried out in a Hewlett Packard 8451 A Diode Array Spectrophotometer, using distilled water as the blank.

Total Solids (TS) were determined on 20g samples of Apple Slices (AS) by the vacuum-oven method as reported in A.O.A.C. (1975). Results were expressed as percentage and changes in Total Solids (ΔTS) were calculated by using the following equation:

$$\Delta TS = [(TS \text{ blanched AS} - TS \text{ fresh AS}) / TS \text{ fresh AS}] \times 100$$

Yield was determined by weighing the apple slices before and after blanching. The net weighing after

blanching was performed on the packaged apple slices, to avoid any further moisture loss.

Total Residue (TR) was determined on 20mL samples, by the oven method, as reported by Standards Methods for the Examination of Waste Water (1975). Samples were evaporated on a water bath and dried at 103°C for 12 hours. Results were reported as percentages. The changes of the Total Residue (Δ TR) of the blanch solution were calculated by using:

$$\Delta \text{ TR} = [(\text{TR after blanching} - \text{TR before blanching}) / \text{TR before blanching}] \times 100$$

Microscopic observations were carried out by using a Photomicroscope III by Zeiss, with an integrated 35mm camera. Two magnifications were used: 108X and 256X.

2.2.2 Chemical

Phenolic Compounds (PC) were determined by the tannin and lignin test, using Folin-Ciocalteu reagent, as described in the Standard Methods for the Examination of Water and Waste Water (1975). Tannic acid was the phenolic compound used in the standard curve preparation and the absorbance values were obtained at 700nm.

Buffer Capacity was determined by titration of 25mL apple juice samples with 0.1N HCl and 0.1N NaOH to pH 2.5 and 10 respectively. The results of the titration, are expressed as gram equivalents of acid or base per liter of juice, and reported as a titration curve. The buffering capacity or buffer index (β), was obtained graphically

from the slope of the tangent to the titration curve of gram equivalents of base added per liter versus pH (Perrin and Dempsey, 1974). The results are presented in a graph where the curve obtained will show a maximum of the weak acid involved. When more than one weak acid is present, there will be either several peaks corresponding to the pK values of the individual acids or a plateau if the pK of the individual acids are too close together.

2.2.3 Bacteriological

Standard Plate Counts (SPC counts) of the blanched apples slices and the blanched water, were performed at 3, 6, 9, and 12 recycles, for the experiments on blanch water recycling without purification, by using the method outlined by the International Commission on Microbiological Specifications for Foods (1978).

2.2.4 Statistical procedures

Each experiment was run in duplicate unless otherwise stated, and since the analysis of each sample was run also in duplicate, a total of four replicates were obtained and used to calculate each determination.

The curves obtained were statistically fitted, when possible, by using the Plotrax Omicron Software PX983-110 (1983), in an IBM PC computer. The equations were inserted in the graphs, along with their correlation coefficients (r^2).

The data from the sensory studies, were used to calculate the Analysis of Variance (ANOVA) tables, following the procedure outlined by O'Mahony in 1986, for a Two-Factor design with interaction. When significant differences between treatments were present, the Tukey's test was used to establish those differences. (Larmond, 1977).

2.3 BLANCHING STUDIES

2.3.1 Apparatus

The blancher unit was a 1L Erlenmeyer flask connected to a condenser, and heated by a hot plate with a magnetic stirrer. After blanching, the apples and blanch water were separated by a set of stainless steel screens with pore size of 1.19 and 0.11mm respectively.

2.3.2 Blanching conditions and sampling procedures

Preparation of apples before blanching:

Whole apples, were rinsed with warm tap water, and held at room temperature for 1.5 to two hours. They were hand peeled, and cut into "French Fry" style slices by using a potato chipper unit. The slices had an approximate size of 0.6x0.6x5cm. Coring was performed by removing the slices containing the seeds. To give a relatively uniform size to the slices, the small trimmings were also removed.

The Apple slices were used immediately (within five minutes) after peeling and slicing, in order to minimize enzymatic browning and airborne microbial contamination.

Recycling without purification was carried out by placing 75g of apple slices in 750mL of blanch water at 98° C for four minutes (the ratio water:tissue was 1:10). Apple slices were separated from the blanch water by filtration, air cooled for two minutes, and packaged in 500mL plastic containers before freezing. The blanch water was recycled after sampling (30mL) and addition of enough make-up water to maintain the original volume (750mL). Sampling was performed every three recycles, for both, blanched apple slices and blanch water. pH, Soluble solids, Turbidity and SPC counts of the blanch water were performed immediately and the remaining samples were frozen for later analysis. SPC counts for both, blanched AS and blanch water were carried out up to the 12th recycle (3, 6, 9, and 12).

The blanching of apple slices in the various simulated solutions (Section 3.3), was carried out under similar conditions to those used for recycling without purification. Sampling of both the apple slices and the blanch solutions, was performed, before and after blanching, for each simulated solution.

2.3.3 Preparation of Simulated Systems

Simulated Recycled Blanch Water (SRBW) was prepared by

blanching 500 grams of apple slices in 500mL of distilled water for 20 minutes and filtering through a set of stainless steel screens (1.19 and 0.11mm). The filtrate had a pH of 4.3, $3.0 \pm 0.5\%$ soluble solids and 0.65 ± 0.07 mg of Phenolic compounds per ml. SRBW simulated the recycled blanch water after the sixth recycle.

Simulated Blanch Solutions (SBS) with 0, 5, 10, 15 and 20% apple Soluble Solids (SS) were used as blanch water. They were prepared by dilution of apple juice concentrate (70% SS) until the desired level of SS was obtained. An Abbe refractometer was used to determine the levels of SS as degree Brix.

The Sugar Mixture (SM) was prepared in a one liter volumetric flask and the sugar concentrations were: 1.7% glucose, 5.0% fructose, 2.5% sucrose and 0.27% malic acid. These concentrations are similar to those found in apples as reported by Joslyn (1975).

Fresh Apple Juice (FAJ) was prepared using a food processor and filtering the juice through cotton milk-filters.

Simulated Recycled Blanch Solution (SRBS) at equilibrium conditions (12.5% SS) was prepared from apple juice concentrate; and the Degraded or Heat Treated Solution (DSRBS) was prepared by refluxing the SRBS for one hour.

The PAC treated DSRBS was prepared by addition of 1% PAC to DSRBS (previously heated up to 80°C), and placing

it in a Gallenkamp water-bath-shaker at 80°C for five minutes, followed by vacuum filtration (three times) through a Whatman GF/B glass filter with a pore size of 1.25 μ m in order to remove the PAC.

2.4 HEAT DEGRADATION STUDIES

2.4.1 Apparatus, conditions and sampling procedures

The apparatus used was a 3L flask connected to a condenser. Heating was supplied by an electrical mantle. The degradation temperature was that of the boiling point (98°C) and samples were withdrawn at regular intervals (one, two and three hours for the SM and 1, 3, 6, 13, 18, 24, 30 and 36 hours for the SRBW). Samples were placed in ice, and analyzed the same day they were obtained.

2.5 POWDERED ACTIVATED CARBON (PAC) ADSORPTION STUDIES

2.5.1 Apparatus, conditions and sampling procedures

Batch experiments with Powdered Activated Carbon (PAC) were conducted using a Gallenkamp shaker-bath. Erlenmeyer flasks (125 mL) connected to condensers, and containing a known amount of PAC and 50mL of the solution under study, were shaken (100 times/minute) at various temperatures. Adsorption times ranged from five minutes to one hour depending upon the experiment. Blanks were run with each series and samples were taken after PAC removal.

PAC was separated by filtration through a glass filter with pore size of $1.2\mu\text{m}$, and the filtered solution was analyzed.

2.5.2 Conditions for the determination of the optimum pH of adsorption

The pH of SBRW (4.2) was adjusted by addition of 1N HCl or 1N NaOH. Adsorption with 0.5% added PAC was carried out at 80°C for five minutes. Samples of the blank and PAC-treated series were promptly filtered and analyzed.

2.5.3 Adsorption properties of PAC

One liter of SM was prepared and refluxed for three hours. Samples of 200mL were removed after zero, one, two, three hours, and PAC-treated. The PAC dosages used were 0.0, 0.2, 0.5 and 1.0%, and the sample size of the treated SM was 50mL for each dosage. The temperature and contact time were 80°C and five minutes. Samples were immediately filtered through the glass fiber filter. The adsorption properties of PAC, during removal of Degradation Products (DP), were calculated from the Absorbance readings at 280nm on the filtrate, using water as a blank in the spectrophotometer.

2.5.4 Rate of adsorption

The rates of PAC-adsorption of Phenolic Compounds (PC) from SRBW at several PAC levels (0.0, 0.1, 0.2 and 0.3%), and 50°C , were determined by using 50mL samples of SRBW. The PAC was added to each sample and placed in a

Gallenkamp shaker bath at 50°C. The contact times ranged from zero to 50 minutes. When the samples were removed from the bath, they were filtered immediately through a glass fiber filter. The removal of Phenolic Compounds (PC) from the SRBW was determined by measuring the PC levels in the filtrate.

2.5.5 Adsorption Isotherms

Batch experiments with PAC on the simulated solutions, SRBW and SM, were carried out at 80°C for one hour. After PAC removal, by filtration, the filtrate was tested for phenolic compounds in the case of SRBW and degradation products expressed as Absorbance at 280nm, for the SM.

The first step in interpreting the data was to plot adsorption isotherms that described the equilibrium distribution of solute between the solid and liquid phases. The Freundlich isotherm equation used to analyze adsorption data was $\log(x/m) = \log K + (1/n)\log C$ (Benefield et al., 1982). The ultimate capacity (x/m) of the PAC, for each one of the solutions under study, was calculated from the Adsorption Isotherm plot by constructing a vertical line from C_0 , the value that correspond to the influent concentration, up to the extrapolated isotherm line.

2.6 MICROSCOPIC OBSERVATIONS

2.6.1 PAC-treatment conditions, sampling and slide preparation

The solutions were placed in a 125mL Erlenmeyer flask, and 1% of PAC was added. After a few seconds of hand shaking, they were placed in the Gallenkamp shaker bath, at room temperature, for five minutes. Samples were drawn with a dropper and one drop was placed on a slide, covered and observed under the microscope.

2.6.2 Preparation of Simulated Systems

In order to understand the PAC dis-aggregation phenomenon observed, several types of key substrates were added to the ABW, under controlled conditions.

The SABW with NaCl was prepared by adding the respective amount of NaCl to each one of the SABW samples to give the desired levels of NaCl in the solutions (0.01, 0.1, 1.0 and 2%).

The Acetic Acid/Acetate (AAA) buffer solutions at several pH values (3.4, 3.8, 4.0, 4.3, 4.66, 5.0, 5.5 and 5.9) were prepared following the method described by Perryn and Dempsey in 1974. AAA with protein was prepared by adding 1% of egg white to the various AAA solutions (pH 3.4, 4, and 5.9). AAA with Starch and Pectin were prepared by dissolving 1% starch and 1% pectin respectively, in the various buffer solutions (pH 3.4, 4 and 5.9). The samples were heated and constantly stirred until clear solutions were obtained.

SRBW treated with pectinase, was prepared by adding

0.01% pectinase to the SRBW and placed it in the shaker at 40°C for four hours.

2.6.3 Definition of the descriptive terms used during microscopic observations

The PAC particles or aggregates observed under the microscope, at each magnification, were classified according to their approximate size.

At 108X : Small <10 μ m, medium from 10 to 100 μ m and large >100 μ m.

At 254X: Small <2 μ m, medium from 2 to 20 μ m and large >20 μ m.

The aggregates were described as either "3-D flower-like" or "chunky". The former term was used when the aggregate was formed by a multitude of small PAC particles attached to each other in such a way that create the illusion of a porous 3-D structure (see Figure 28). The term "chunky" described mainly what appeared to be very irregularly shaped PAC granules, with little or no aggregation (see Figure 27).

2.7 SENSORY STUDIES

2.7.1 Panel selection

Groups ranging from 11 to 18 Food Science students, with varying degrees of experience in sensory evaluation, carried out the sensory tests. Criteria for selection

included availability, willingness and interest. The panelists were asked to evaluate the flavor and/or appearance of blanched apple slices by using a nine-points hedonic scale.

2.7.2 Preparation of samples and sensory evaluation conditions

Blanched apple slices were prepared the same day they were evaluated, in batches of 400 grams per sample, using a stainless steel kettle, and a basket, to maintain the apple slices underwater. The blanching conditions and procedure were similar to those described in section 2.3.

The sensory evaluation was held in a sensory panel room with individual booths. During flavor evaluation, red lights were used to mask any color differences that might influence the panelists judgment. White lights were used for the appearance evaluation. Five samples, of 15 to 20 grams each were evaluated in duplicate at different sitting (two consecutive days). All samples were coded with three random digit numbers and they were presented at random to the panelists. Crackers and water were available in each booth. A nine-point hedonic scale was used, where 1 = dislike extremely, 5 = neither like or dislike and 9 = like extremely (see questionnaire in Appendix IV).

3 RESULTS AND DISCUSSION

3.1 ANALYSIS OF FRESH APPLE JUICE

3.1.1 Main Characteristics

Fresh apple juice was briefly studied in order to have an idea of the main characteristics of the raw material that was being used. However, most of the information used as a reference in the simulated systems was based on information from the literature.

The percent of soluble solids present in the FAJ was estimated from its degree Brix value. In this study it was observed that this value varied considerably, depending mainly upon storage time; the value found for the original apple samples was 12.5%, but after four months of storage at 4°C, this value went up to 15.5%. This change can be expected in such a long storage period, and is mainly related to desiccation and other metabolic changes.

The concentration of phenolic compounds (PC) in the FAJ determined as tannic acid, was 0.18 percent. The total phenolic compounds in apple juice, as reviewed by Hulme in 1970, ranged from 0.11 to 0.34g/100mL.

The spectroscopic scan of FAJ is shown in Figure 2. A major peak is observed around 280nm, which is mainly associated with $\pi - \pi^*$ transitions. This type of transitions occur in unsaturated compounds, particularly those containing conjugated double bonds (e.a. phenolic

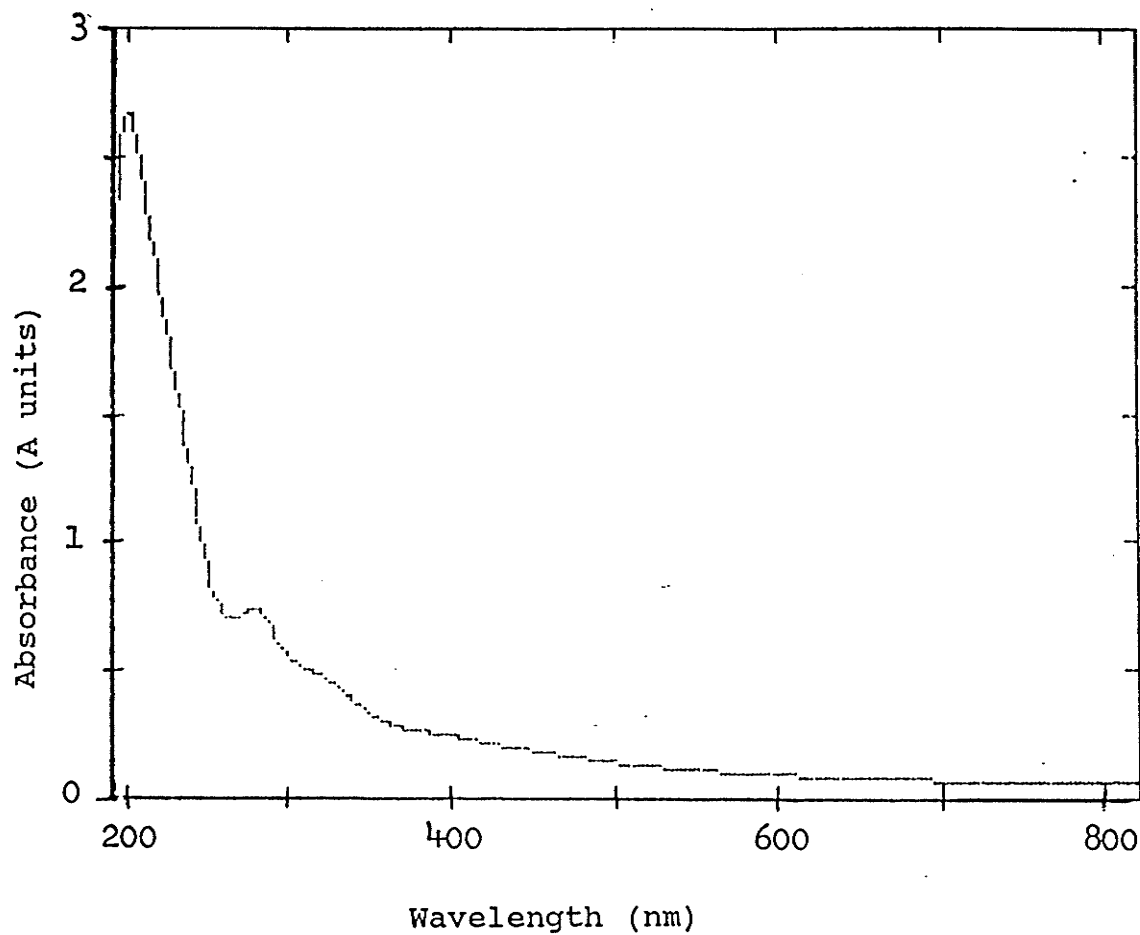


Figure 2 Spectroscopic scanning of fresh apple juice
from 190 to 800nm

compounds and proteins).

3.1.2 pH and Buffer Capacity

The determination and control of pH in a system, is of great importance to the food industry. Chemical, enzymatic and microbiological changes in the product during processing depend upon its pH value. Furthermore, the ability of the system to resist change in pH is directly related to the buffer action of that particular system. Hence the importance of studying and interlocking both parameters during processing, in order to achieve optimum pH control.

A pH value of 4.2 was found in the fresh apple juice. This value correspond to that of a mild acid fruit (3.5-4.5) as classified by Joslyn in 1975. The titration curve for FAJ was also determined and the results are shown in Figure 3. Hulme (1970), reported malic acid as the predominant acid in apple tissue and it accounts for 80 to 90 percent of the total acid present in the ripe fruit. The total acid in apples reported as malic acid, range from 0.2 to 1.27 percent (Hulme 1970).

The pKa values for malic acid are 3.8 and 5.11 (Joslyn 1975), and this acid is expected to play an important role in the buffer capacity of not only the apple juice but the recycled blanching water as well. The buffer capacity of fruit juices has been ascribed to phosphates, carbonates and organic acids; commonly malic,

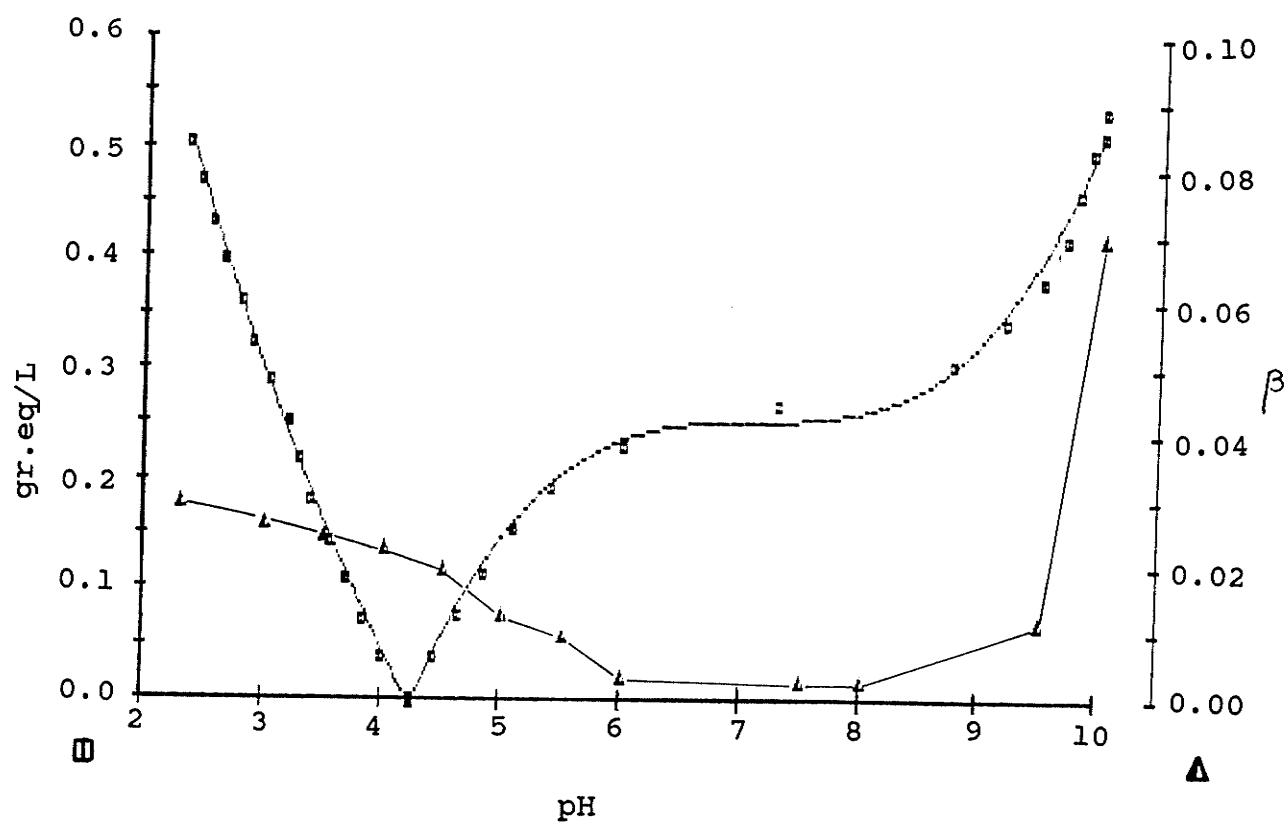


Figure 3 Titration curve (gr.eq/L) and Buffer Index (β) of apple Juice

citric, oxalic, tartaric and some amino acids.

In Figure 3 the buffer capacity or buffer index (β) of apple juice is plotted against pH. The curve shows two plateaus, which indicates that various weak acids with very close individual pK values are involved. The values reported for malic acid, 3.48 and 5.11, fall in the plateaus found in the pH range from 2.5 to 6. The formation of plateaus is common in complex juice mixtures and have been also observed in vegetable juices (Joslyn, 1975).

3.2 BLANCH WATER RECYCLED WITHOUT PURIFICATION

The study of the chemical interactions between Apple Slices (AS) and Blanch Water (BW) with the water being reused many times on sequential lots of tissue, was carried out under controlled conditions. The blanching temperature and contact time were 98 °C and four minutes respectively, the water:tissue ratio was 10:1. Several factors such as Soluble Solids (SS), pH, Turbidity (T), Spectroscopic measurements at 280nm and 450nm, Phenolic Compounds (PC) and Standard Plate Counts (SPC) were monitored during recycling.

The recycled blanch water in this initial study was not significantly purified during reuses, and build up of undesirable odor and color was observed, not only in the RBW but in the blanched apple slices. Foaming in

noticeable amounts, appeared after approximately eight recycles.

3.2.1 Soluble Solids

Soluble solids levels were determined from the degree Brix obtained by the Abbe Refractometer. The changes in SS in the blanch water were monitored during recycling and the results are shown in Figure 4. The sections A and B of the curve (0-57 and 58-94 recycles) were obtained by recycling the blanch waters, which were initially distilled water and a simulated solution respectively.

The simulated recycled blanch solution was prepared from apple juice concentrate and diluted until the level of SS was similar to that found in the RBW after 57 recycles (12.2%). Fresh lots of apples of unavoidably different soluble contents were used in sections A and B (12.5% and 15% respectively) causing a sharp increase in the SS level of the RBW and SRBS due to the large concentration gradient found in the initial stages. However, both curves seem to follow the same pattern, and seem to come close to equilibrium conditions where the concentration gradient is expected to be about zero and the level of SS in the recycled blanch solution will remain almost constant.

In general, this Figure shows that the percent of soluble solids increased with each recycle, and within the range of this experiment, the equilibrium was not reached.

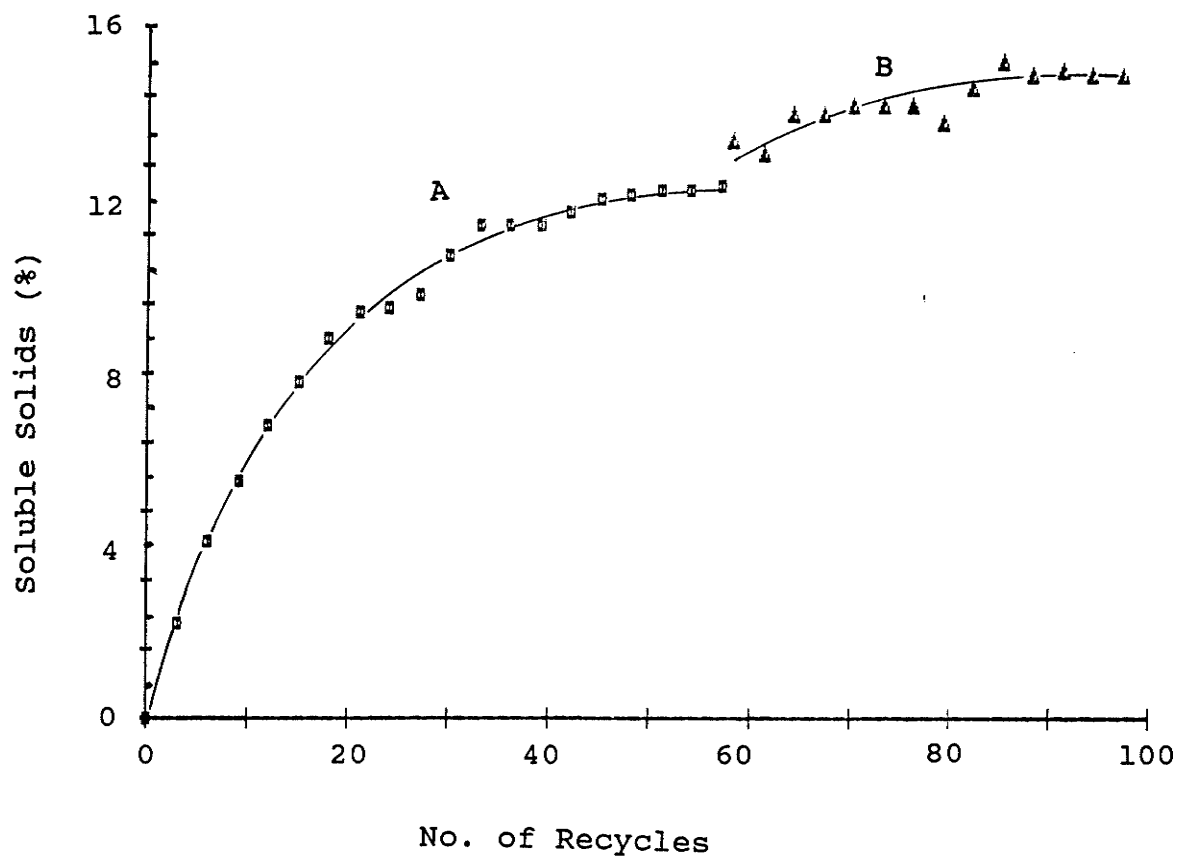


Figure 4 Variations in the soluble solids levels during blanch water recycling. Curve A used distilled water as the initial blanch water (zero recycle) and apple slices with 12.5% SS; curve B used a simulated recycled blanch solution (12.2%SS) at the 58th recycle and apple slices with 15.5% SS

However, by comparing the slopes at several points of both curves it could be observed that the rate of increase of SS in the recycled blanch water is reduced as recycling progresses, as expected. In section A, it goes from 0.83%SS/recycle in the initial stage (0-6 recycles) to 0.02%SS/recycle in the latter stage (51-57 recycles); which indicates that over 95% of the SS lost in the initial stage, are retained in the blanched apple slices, when the level of SS in the blanch solution (12.2%) is close to that found in the fresh apple (12.5%). The same phenomenon is observed in section B of the graph. However the difference between the rates in the initial and latter stages (0.08%SS/recycle and 0.01%SS/recycle respectively) is considerably lower because the relatively high level of SS in the initial blanch solution (12.2% at recycle 58).

3.2.2 pH

pH was monitored during recycles of the blanch water (0 to 57 recycles), and the results are shown in Figure 5-A. From the graph it can be observed that pH in the RBW decreased rapidly after the first recycle, going from 5.40 to 4.40. After this, pH slowly decreased until a value of 4.25 was reached (recycle 57).

The behaviour of the pH through recycling may be explained if the following factors are taken into consideration : a) the higher the concentration gradient

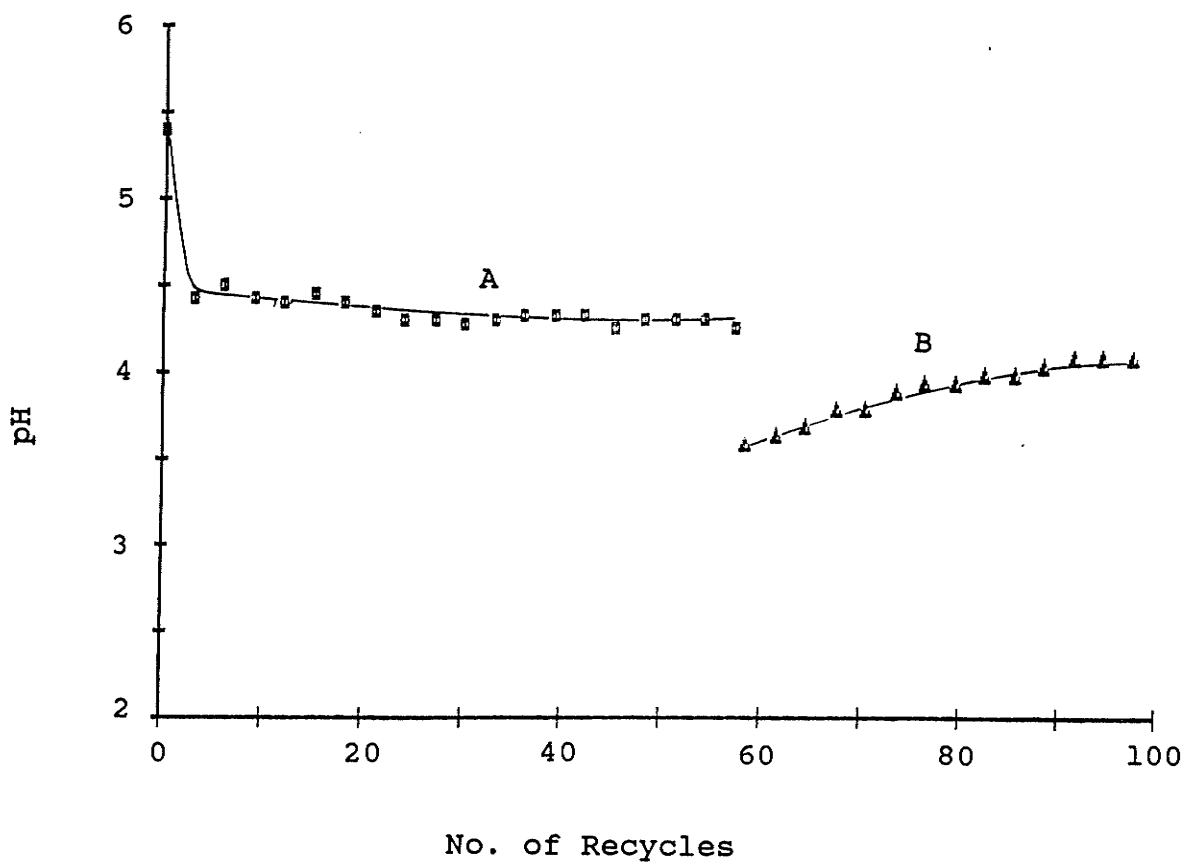


Figure 5 Variations in the pH during blanch water recycling. Curve A used distilled water as the initial blanch water (zero recycle) and apple slices with 12.5% SS; curve B used simulated recycled blanch solution (12.2% SS) at the 58th recycle and apple slices with 15.5% SS

between apple slices and the blanching water, the higher will be the removal of soluble solids; including organic acids from the apple tissue; b) after several recycles RBW has a higher concentration of other water-soluble components along with the weak organic acids, that will increase the buffer capacity of the RBW. This increase in the buffer capacity of the RBW will allow the pH of the system to remain virtually unchanged during subsequent recycling, as can be seen from Figure 5-A.

Since there are no significant changes in pH during recycling of RBW, adjustment of the pH was not required. Furthermore, the pH values obtained after recycling, range from 4.2 to 4.3, which is very close to the original pH of the apple tissue. Hence, the value of 4.2 was selected as a reference for the design of the most adequate treatment of the RBW during recycling.

When simulated recycled blanch solution from apple juice concentrate, was used instead of RBW, after 57 recycles, the system had a low initial pH (3.6), which was retained in order to avoid excessive changes in the chemical make up of the apple juice solution. This product's lower pH was probably due to the higher acidity of the apples used in the commercial production of apple juice concentrate, along with perhaps added acid to keep that pH low.

Figure 5-B shows the pH changes of the SRBS solution after each recycle (58-94). In the first stage (58-67

recycles) the rate of pH increase was 0.023 pH units/recycle. Whereas in the last stages (88-94 recycles) the rate was only 0.002 pH units/recycle. This decreased rate should be expected if the system is close to a steady-state or equilibrium.

3.2.3 Phenolic Compounds

The changes in phenolic compounds concentrations in the RBW during recycling are shown in Figure 6, where sections A and B, as defined in section 3.2.1, are also present. The build up of PC in the RBW is greater in the initial stages of recycling than after several recycles. The rates of increase for the initial and the last stages of section A are 0.083 and 0.014(mg/mL)/recycle respectively. In section B, the level of PC is originally high (1.58mg/mL), therefore, any change in PC levels, would be mainly associated with an increase in the degradation products rather than leaching, and this could account for the linear behaviour of the curve obtained. The slope of curve B is 0.024(mg/mL)/recycle.

A secondary study was carried out to determine if the increase in PC was due to PC being leached from the apple slices or by degradation products generated during heating. This study showed that some of the degradation products which were being produced during heating of a simulated solution are detected as "PC" by the Folin-Ciocalteu method. The rate of formation of this "PC" is

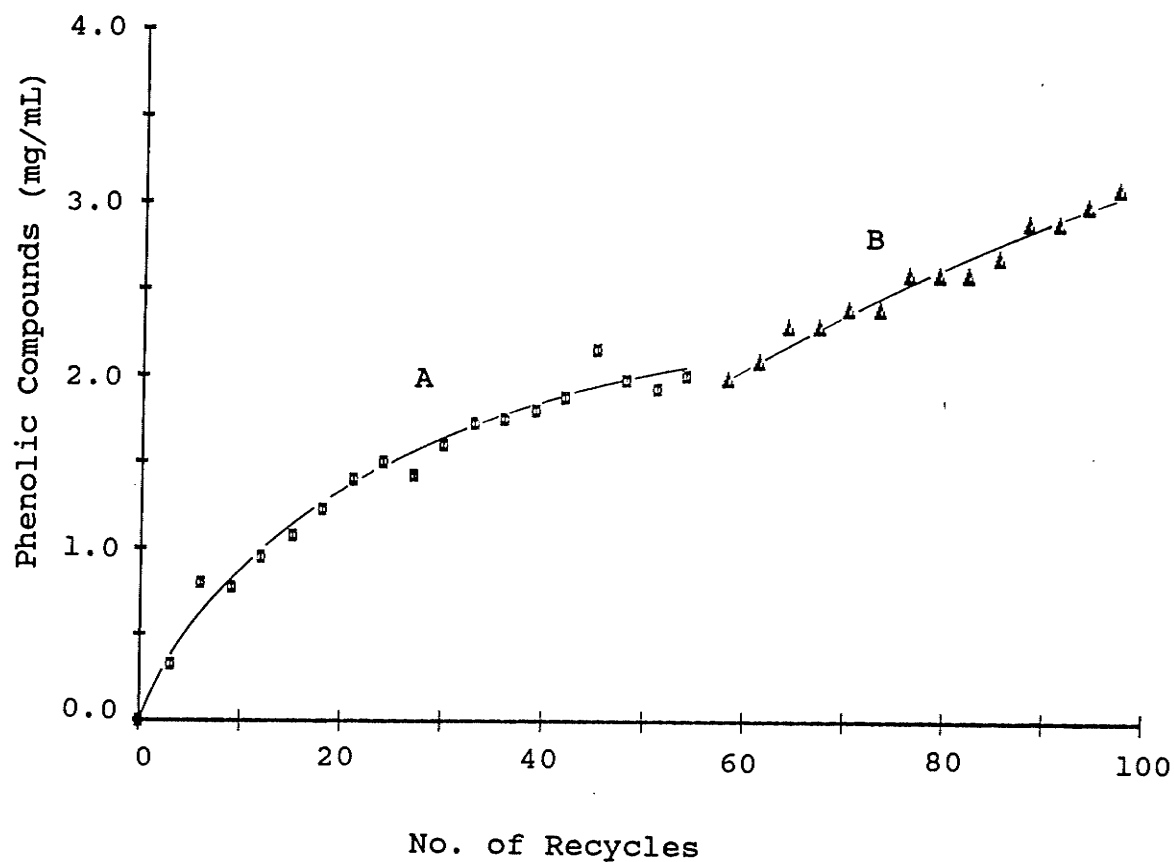


Figure 6 Variations in the phenolic compounds levels during blanch water recycling. Curve A used distilled water as the initial blanch water (zero recycle) and apple slices with 12.5% SS; curve B used a simulated recycled blanch solution (12.2% SS) at the 58th recycle and apple slices with 15.5% SS

0.03 (mg/ml)/hour, when the initial PC concentration is 1.6 mg/ml (see degradation studies section 3.4.2 for more details).

It must be expected that when the level of soluble solids including PC, increases, the rate of formation of "PC" will also increase. Therefore, it is possible that the level of PC being measured after each recycle will be a combination of the PC being leached plus the "PC" being formed during heating, and the higher the soluble solids content in the solution the higher this total PC value will be.

The degradation products that are more likely to interfere with the Folin-Ciocalteu test for PC, are reductones (diketones) which are formed during the Maillard reaction, as well as sugar degradation. These have been previously accused of interfering with this determination (Cornwell and Wrolstad, 1981).

3.2.4 SPC Counts

The SPC Counts for recycled blanch water and blanched apple slices after 3, 6, 9 and 12 recycles were negative. This result was expected for this particular study; since, one of the purposes of the blanching is the reduction, by heat, of the bacterial load, and the apple slices being used are virtually sterile but for some minimal handling and airborne contamination.

3.2.5 Turbidity

The turbidity of the recycled blanch water was measured after each recycle (0-54 recycles) and the results are shown in Figure 7. This figure shows linear increases in the T values for the first stage of recycling (1-18 recycles) and the rate at which turbidity increases is 7.14 JTU/recycle.

After 18 recycles, the turbidity increases at a lower rate than that of the first stage. In the last stage (51-57 recycles) the rate of increase is 0.70 JTU/recycle. There was a reduction in the dispersal of insoluble solids and the leaching of soluble solids from the apple slices, when the system was close to steady-state conditions.

These results are supported by the results from the study carried out on simulated systems (see section 3.3.3), where rates of change in the turbidity of the blanch solution were reduced, with any increase in the percentage of soluble solids in the blanch solution.

3.2.6 Spectroscopic Measurement at 280 nm and 450 nm

The SRBS (12.2% SS) was submitted to a spectrophotometric analysis in the UV and Visible region (190-800 nm). The results are shown in Figure 8. Two major bands (200 and 280nm) and a shoulder (315nm) were observed.

The spectra for the simulated system is very similar to that obtained for the apple juice (see Figure 2), which indicates that similar compounds are present in both

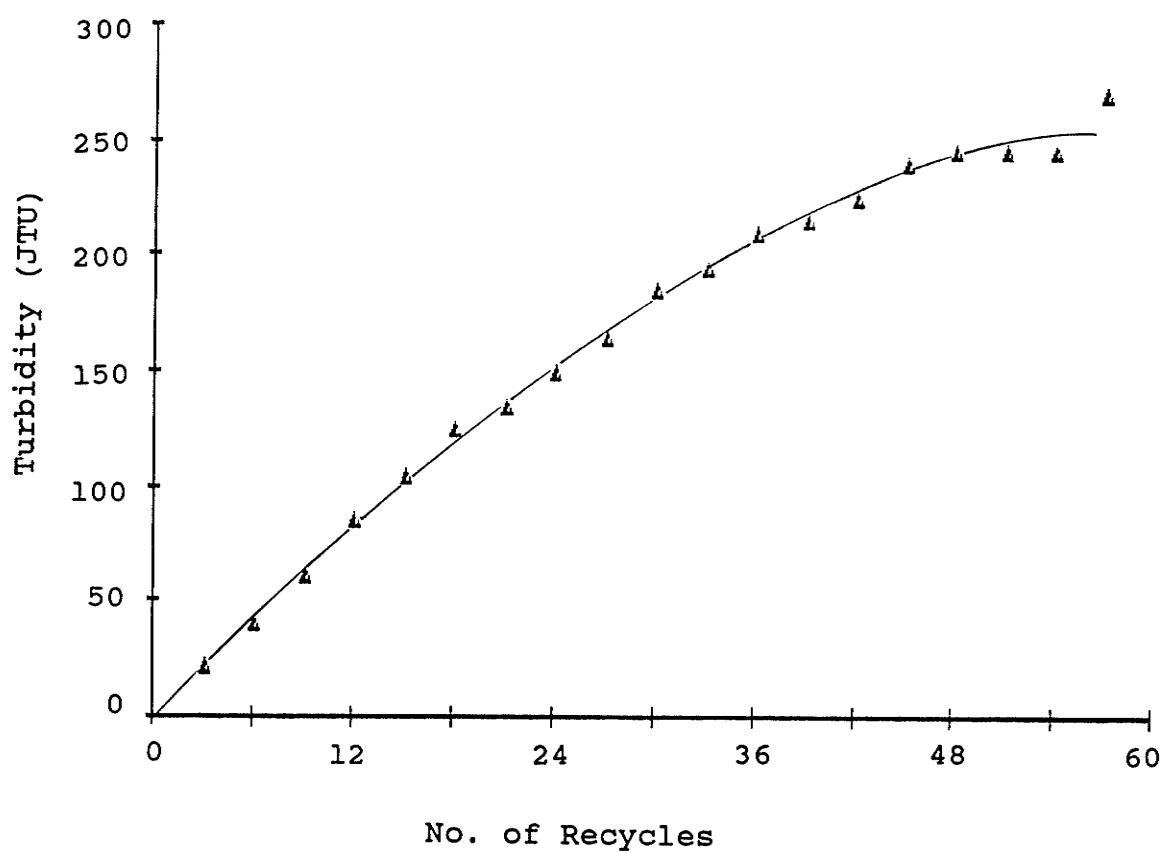


Figure 7 Variations in the turbidity during blanch water recycling

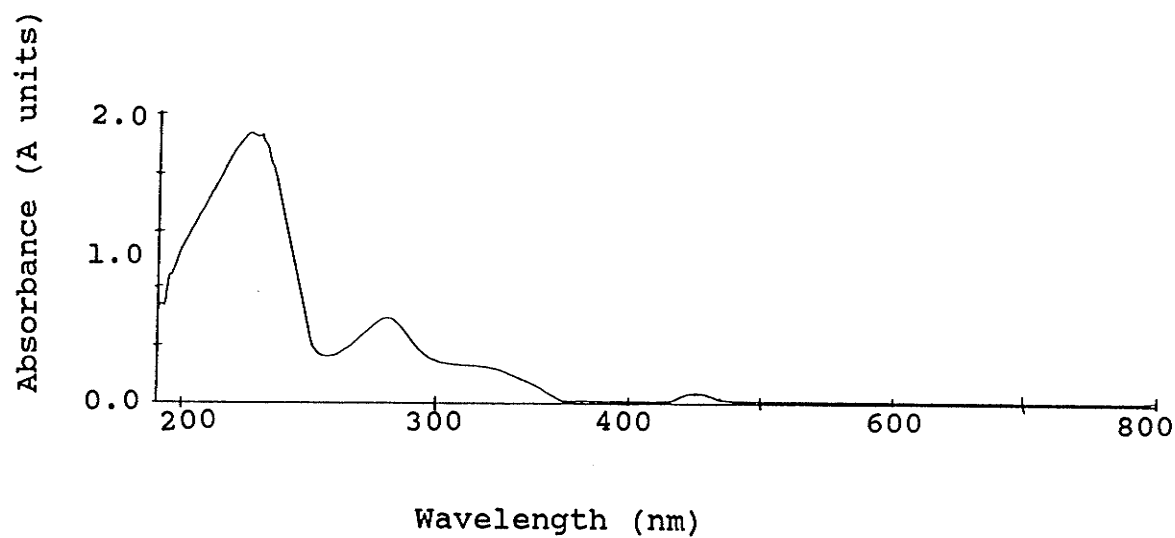


Figure 8 Spectroscopic scanning of simulated recycled blanching solution (12.5% SS) from 190 to 800nm

solutions. The only apparent difference is the intensity of the bands with relation to each other. This could be caused by raw material variations and by the generation of unsaturated compounds (e.g. furfural, premelanoidins and diketones), caused by heat degradation in the simulated recycled blanch solution. The latter factor may explain the increase in the intensity of the bands at 280 and 315nm, with relation to the band at 200nm.

In the degradation studies (section 3.4), the presence of a band at 450nm was also observed. This was associated to the presence of coloured compounds generated mainly by caramelization and to certain extent, to Maillard reactions and Strecker rearrangements occurring during heating. Since the bands at 280 and 450nm were mainly associated with compounds either being leached from the apple tissue and/or generated during heating, they were selected as the bands to be monitored during recycling of the blanch water.

Absorbance changes of the blanch solution at these two wavelengths (280 and 450nm) were monitored during recycling and the results are shown in Figure 9. It is apparent that the absorbance at 280nm, in the first stages, changes more rapidly than in the last stages, which could be associated with the rapid increase in solids leached from the apple tissue into the blanch water plus the degradation compounds being generated during heating. In the last stages, the solids being leached are

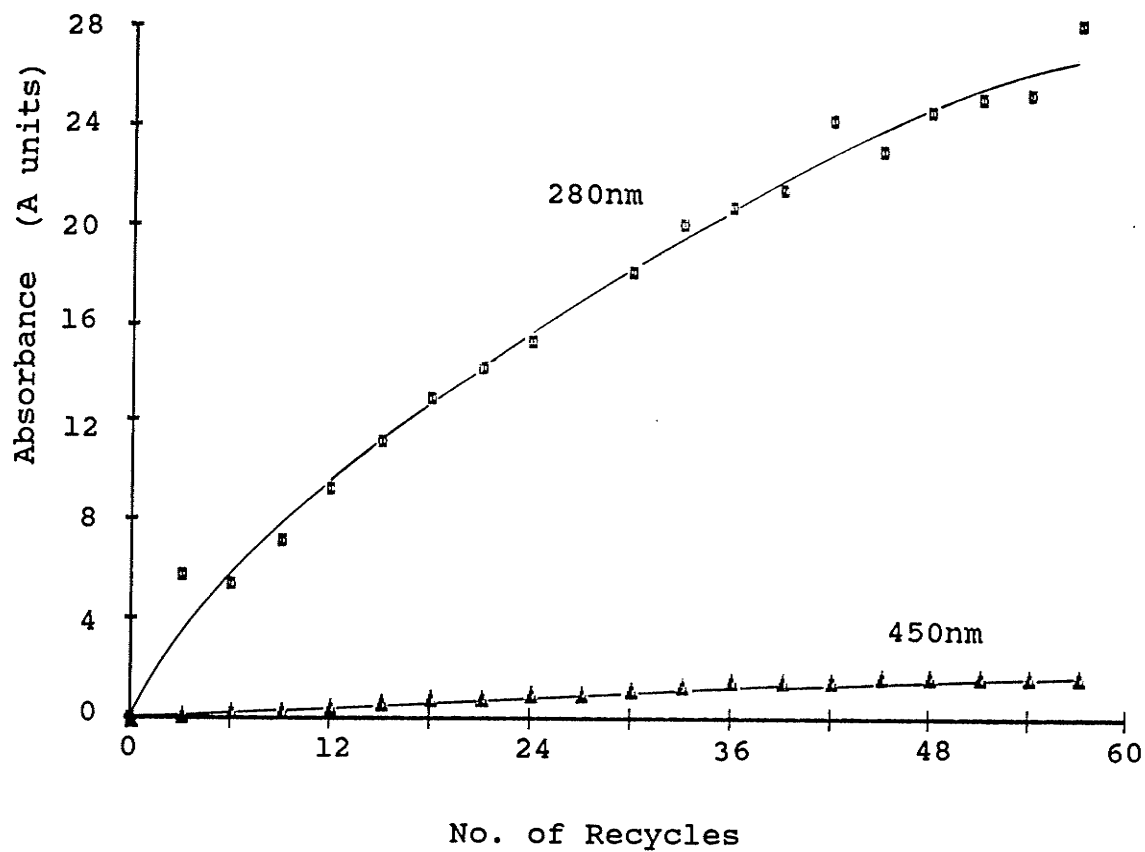


Figure 9 Variations in the absorbance values of the blanch water, at 280 and 450nm, during recycling

minimal and the increase in absorbance in both wavelengths will be mainly associated with the degradation products. The absorbance at 450nm increases steadily as recycling progress, due to the constant increase in the level of coloured compounds generated during degradation.

3.2.7 Sensory evaluation of appearance of blanched apple slices

Apple slices blanched in continuously recycled water are shown in Figure 10-A. It is clear that the blanched AS from the latter stages (51 and 54 recycles) are more coloured than those from the initial stages (0, 3 and 6 recycles). Furthermore, sensory studies on the appearance of those blanched AS show that the degree of "liking" significantly decreases with recycling, and it was mainly associated with the increased coloration (see Figure 10-B). The analysis of variance and the Tukey's test are shown in Appendix V.

These results show that recycling of blanch water without purification can adversely affect the quality, especially the appearance of blanched apple slices.

3.3 BLANCHING OF APPLE SLICES IN SIMULATED BLANCH WATER SYSTEMS

Apple slices were blanched in 0, 5, 10, 15 and 20 percent soluble solids solutions and the results are as follow:

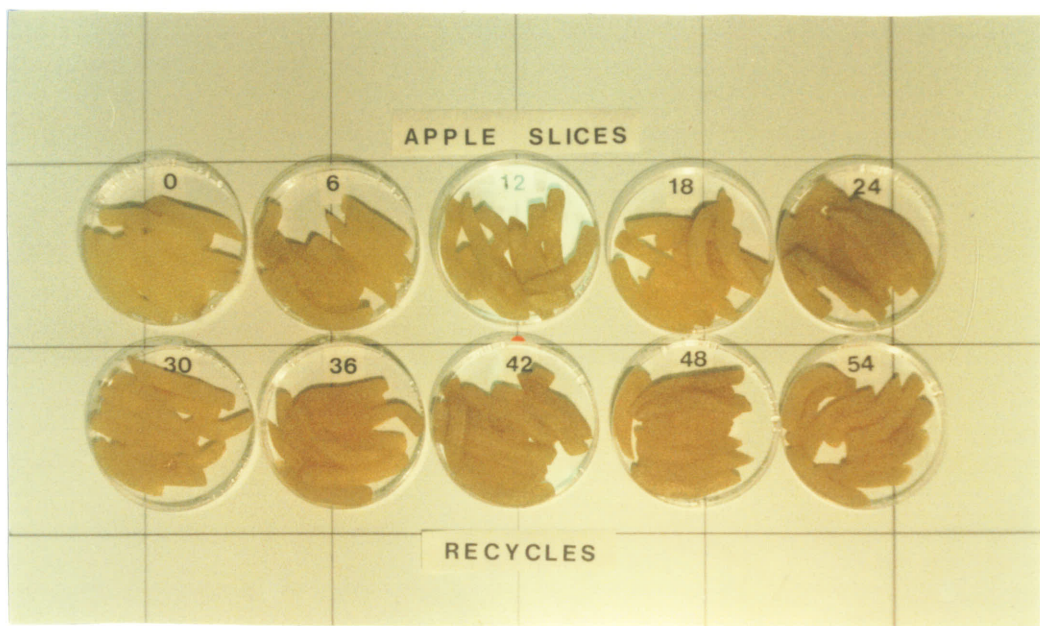
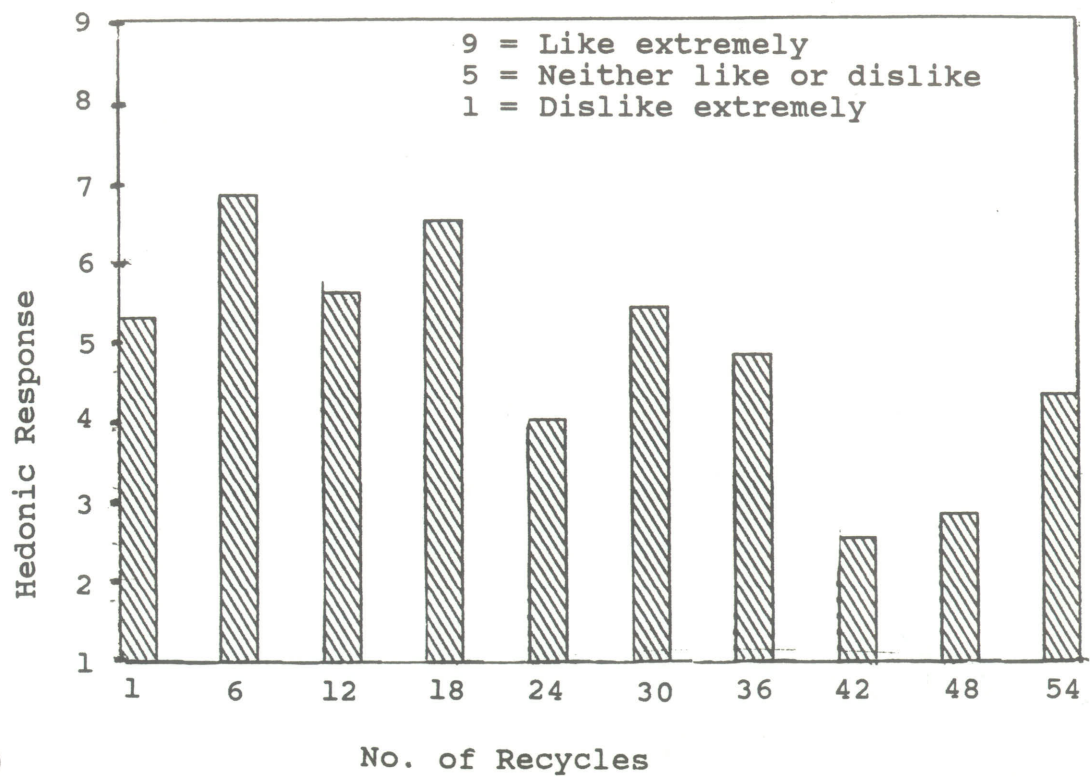


Figure 10 Apple slices blanched in recycled blanch water for four minutes at 98°C. a) Hedonic responses for appearance and b) Photograph

3.3.1 Yield

The yields of blanched apple slices obtained with each of the blanch solutions were determined, and the results are shown in Figure 11. It was observed that as the soluble solids in the blanch solution increased, the yields decreased. Although the decrements were minimal in general, the yield at 0% (87.8) is significantly different (at the 5% level) from those obtained at 10, 15 and 20% (85.3, 85.6 and 85.5% respectively). The ANOVA is shown in Appendix VI.

3.3.2 Total Solids in the raw and blanched apple slices

The total solids difference (ΔTS) between the unblanched and blanched AS for each blanch solution are shown in Figure 11. For the samples blanched in the solutions with 0% and 5% SS, the ΔTS values were negative, indicating that SS are being leached from the AS into the blanch solution. The ΔTS values for the remaining samples were positive indicating migration of SS from the blanch solution into the apple slices. The latter would be expected only when the level of SS in the blanch solution is higher than the value found in the unblanched AS. In Figure 11, although the level of SS in the blanch solution (10%) is below the equilibrium value (12.5%), the ΔTS of the AS is positive. This condition, is caused by slight dehydration of the blanched apple slices during the two minutes of air cooling. If dehydration during

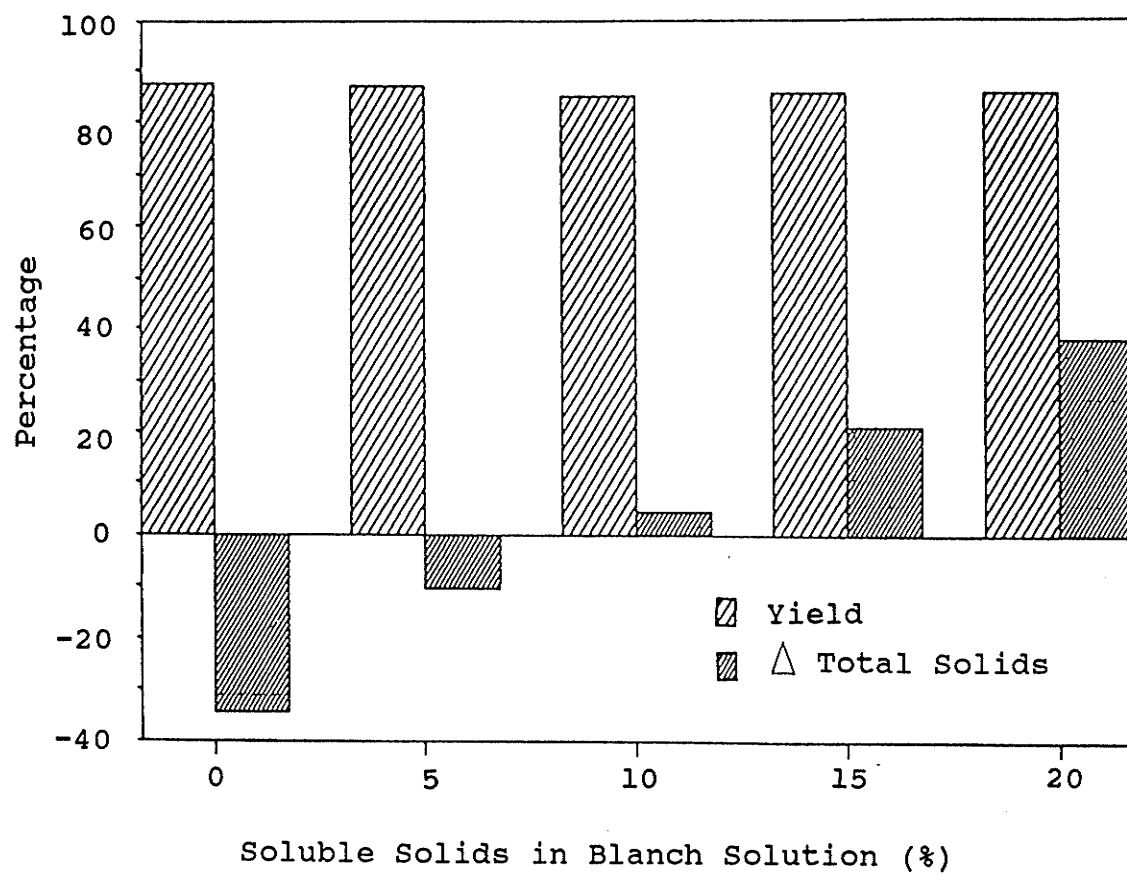


Figure 11 Yields and changes in Total Solids (Δ TS) levels of apple slices blanched in various simulated blanch solutions

cooling is eliminated, increased total solids in the blanched AS when compared to the unblanched ones, would be expected when the level of SS in the blanch solution is higher than the level found in the unblanched apple (12.5%).

3.3.3 Changes in Total Residue (ΔTR) and Turbidity (ΔT) in the blanch solution.

Changes in the total residue of the blanch solutions are shown in Figure 12. Any increase in the percentage of SS in the blanch solutions seems to reduce the rates of removal of solids from the AS into the blanch solution. The maximum leaching occurred at 0%, where a ΔTR increase of 0.56% in the blanch solution was observed. This percentage represents an approximate solids loss of 5.6g per each 100g of fresh apple slices being blanched, with major quality/economic implications.

When the level of SS in the blanch solution increased, the TR changes in the blanch solution during blanching were decreased. When the level of SS in the blanch solution was 20% (higher than equilibrium conditions of 12.5%), the ΔTR was negative. This change indicated loss of solids in the blanch solution, which is probably caused by diffusion of SS from the solution into the apple slices, in addition to the osmotic dehydration of the apple slices, which draw water from the apple tissue into the blanch solution. These two mechanisms are expected when the level of SS in the blanch solution is

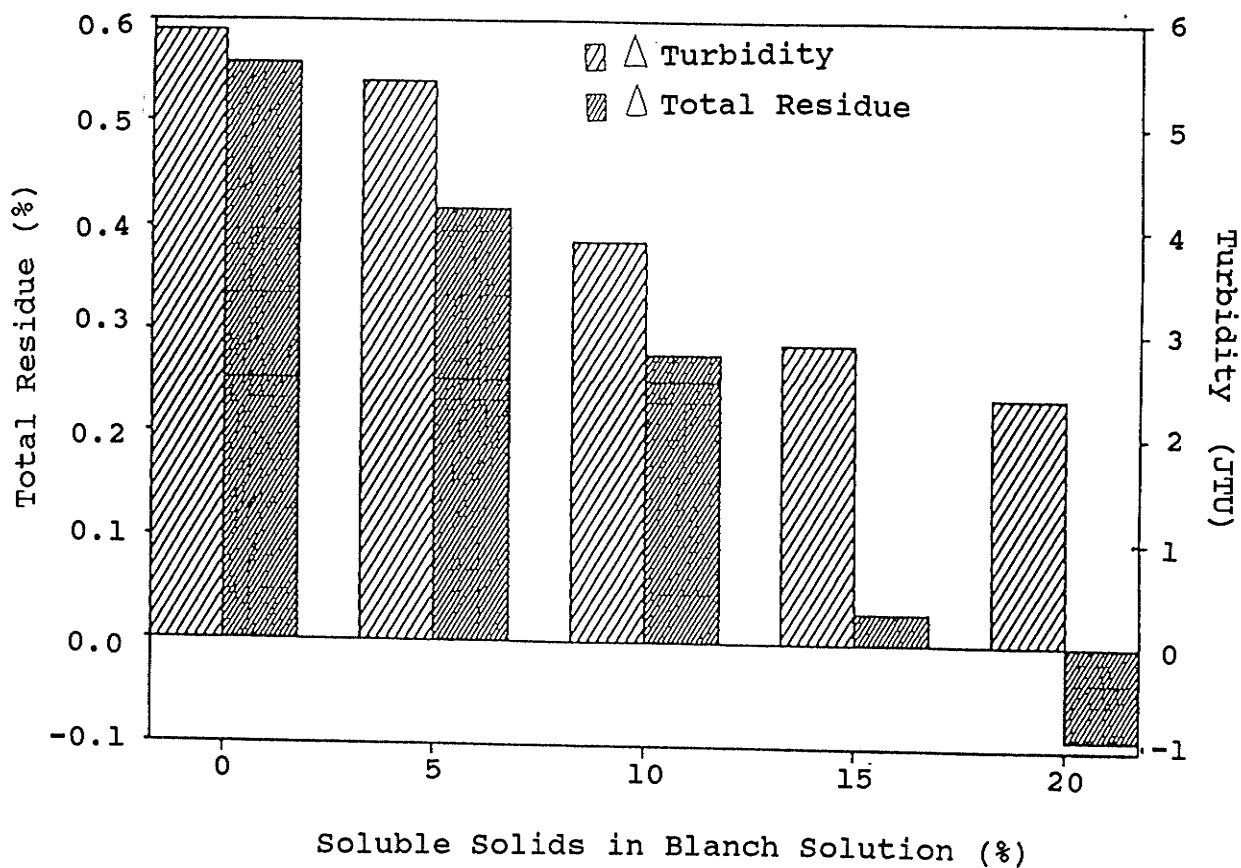


Figure 12 Changes in Turbidity (ΔT) and Total Residue (ΔTR) of the various simulated blanch solutions during blanching

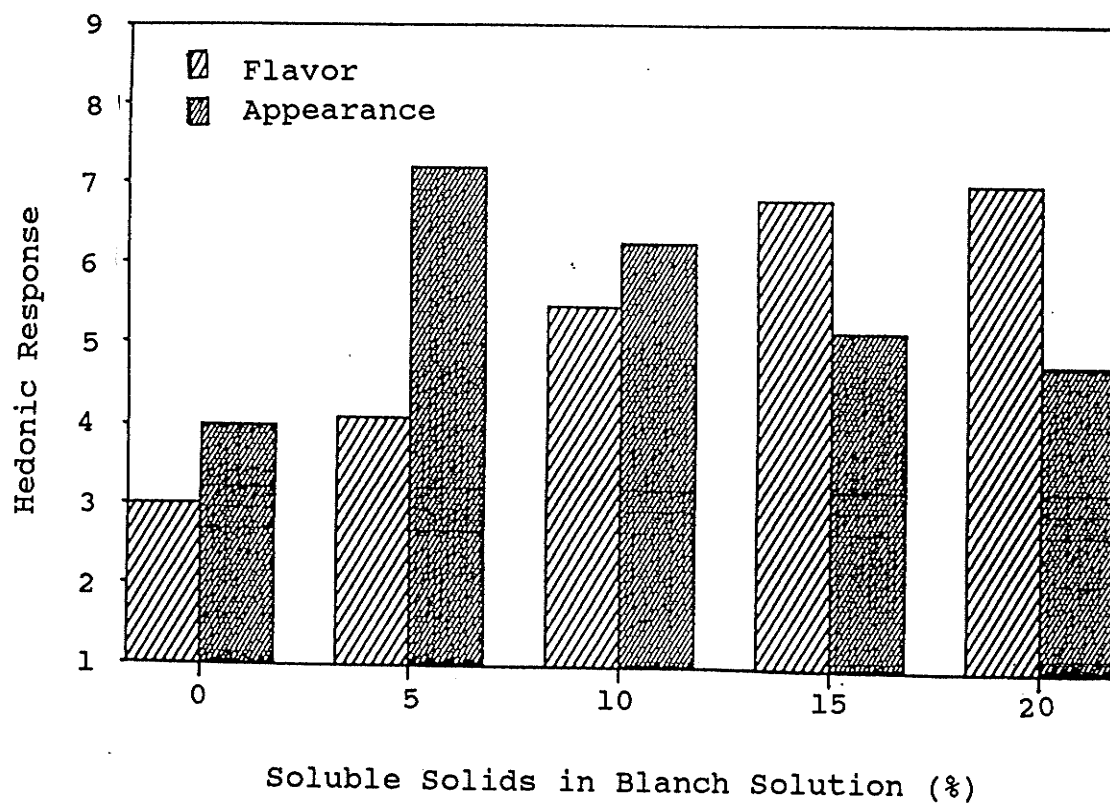
significantly higher than that found in the apple slices.

Changes in turbidity during blanching were monitored too, and the results are shown in Figure 12. It is clear that with any increase of the SS level in the blanch solution, the changes in T will be significantly decreased. When the blanch solution had 0% SS, the ΔT was 5.9JTU whereas at 20% SS the ΔT was only 2.4JTU. This seemed to show that the suppression of the leaching of higher molecular weight substances (e.g. starches, pectins, etc.), that could affect turbidity readings, by greater SS levels, was taking place.

3.3.4 Sensory Studies

The sensory evaluation for the apple slices blanched in the various simulated solutions was carried out and the results of flavor and appearance are shown in Figure 13. The results showed that any increase in the level of SS in the blanch water increased the degree of "liking" of the blanched apple slices. Significant differences in flavor (at the 5% level) were found between samples (see Appendix VII for more detail). The mean hedonic responses ranged from dislike moderately (3) to like moderately (7) for the samples blanched in solutions with 0% and 20% SS respectively.

The means for appearance decreased as the level of soluble solids increased in the blanch solution, and were mainly related to color differences. The blanch solutions



9 = Like extremely, 5 = Neither like or dislike and
1 = Dislike extremely

Figure 13 Hedonic responses for flavor and appearance of apple slices blanched in various simulated blanch solutions.

were prepared from apple juice concentrate which had a high level of coloured compounds. Therefore, the higher the SS in solution, the higher the color levels in the blanch solution, along with higher levels of coloured degradation products generated during blanching.

This work showed that in commercial practice, clean cull fruit could be used to prepare the start-up blanching solution so that virtual solid concentration equilibrium could be reached immediately, and then easily maintained.

3.4 DEGRADATION STUDIES IN SIMULATED SYSTEMS

3.4.1 Simulated systems of Sugar Mixtures (SM)

Four SM were studied, and their degradation curves are shown in Figure 14, where each curve corresponds to a particular sugar concentration. It can be observed that changes in the concentration of the sugars in the SM alters the rate of the degradation and yields of degradation or decomposition products (based on Absorbance readings at 280nm) which may be increased 2 to 6 times when the concentration of sugars is only doubled. For example, the concentration of sugars in sample C is double of that in sample D and their absorbance at 280nm after three hours are 6.5 and 20 respectively.

A SM which was expected to have a similar composition to that found in apple juice, was also studied. The mixture had: 1.7% glucose, 5.0% fructose, 2.5% sucrose

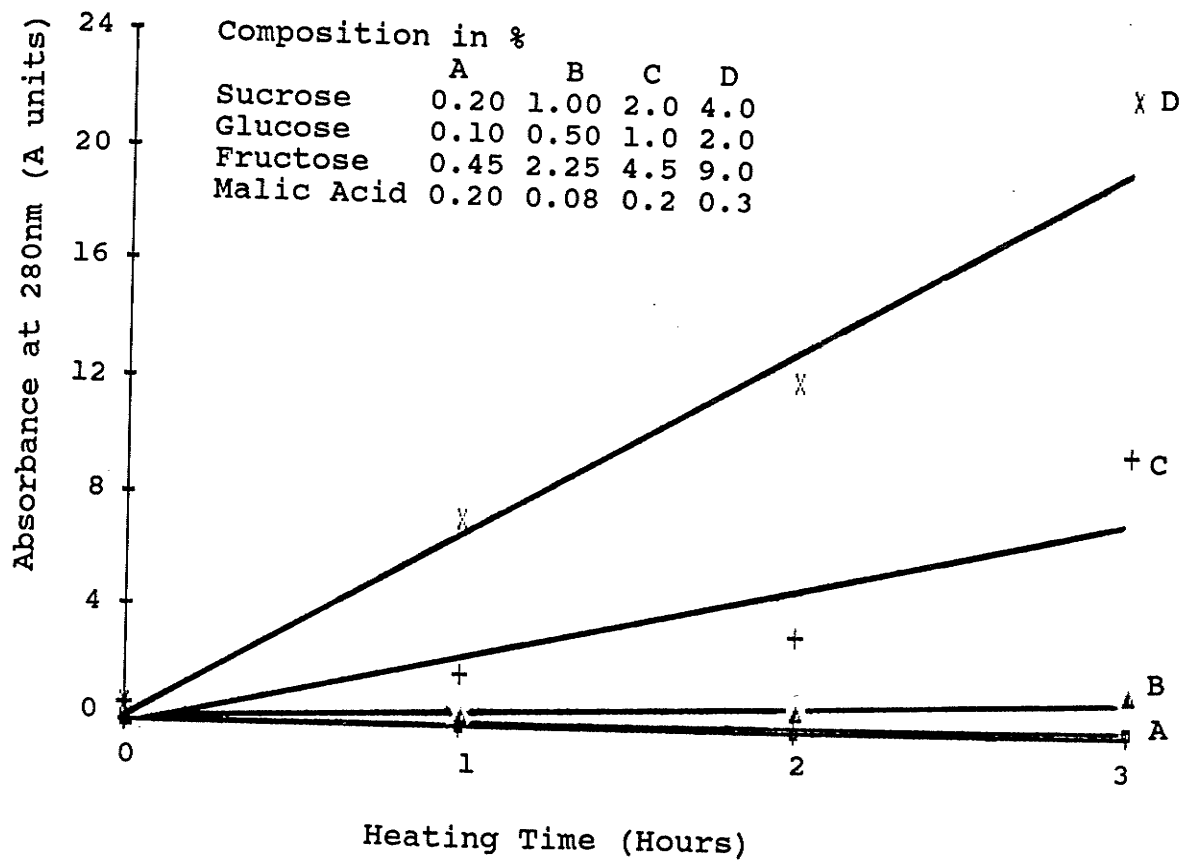


Figure 14 Degradation curves of various sugar mixtures heated at 98°C

and 0.27% malic acid. The results are shown in Figure 15. The generation of decomposition products was monitored by Absorbance readings at 280nm, and the rate of degradation was 8.33 A units/hour.

The decomposition products formed during the heat-treatment of SM were strictly the product of sugar degradation reactions, namely primarily caramelization reactions.

3.4.2 Simulated recycled blanch solution

A simulated recycled blanch solution (12.2% SS, from apple juice concentrate), was heat degraded at 98°C and the degradation curve is shown in Figure 16-A. The level of phenolic compounds and the degradation products, were plotted against the heating time. The visual color deterioration is shown in Figure 16-B.

Figure 16-A showed that the level of phenolic compounds increased at a rate of 0.03mg/mL/hour and this was mainly associated with the formation of reductones, which will interfere with the PC test, rather than an increase in the PC levels. The formation, during heat degradation, of compounds that will interfere with the PC test had been previously proposed by Cornwell and Wrolstad in 1981.

The rate of formation of decomposition products, expressed as absorbance at 280nm, was 13.80 A units/hour. The degradation mechanisms in SRBS are more complex than

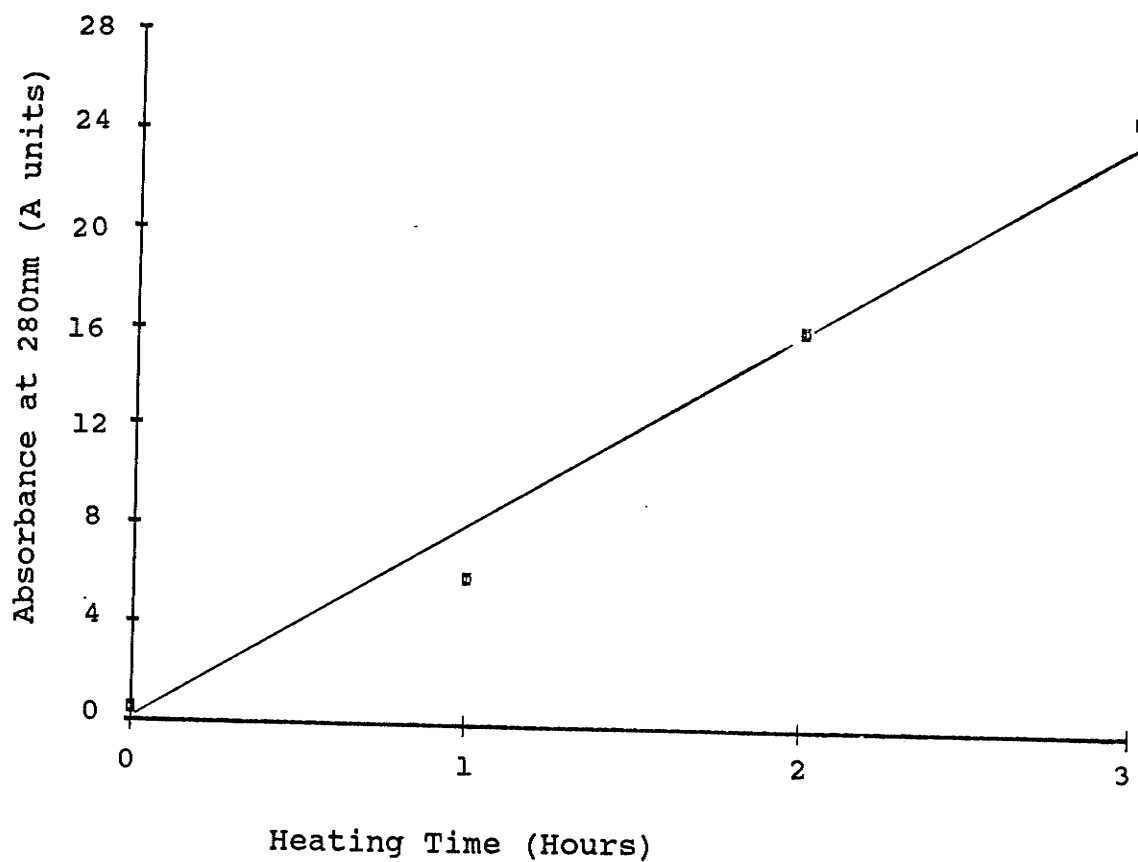


Figure 15 Degradation of a sugar mixture with a simulated apple composition, heated at 98°C. Composition: glucose 1.7%, fructose 5.0%, sucrose 2.5% and malic acid 0.27%

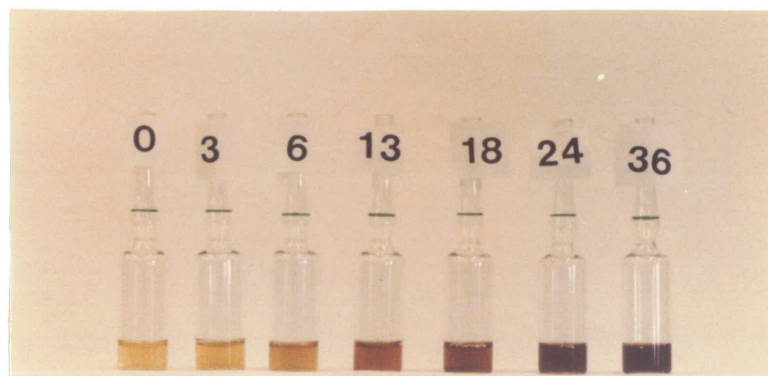
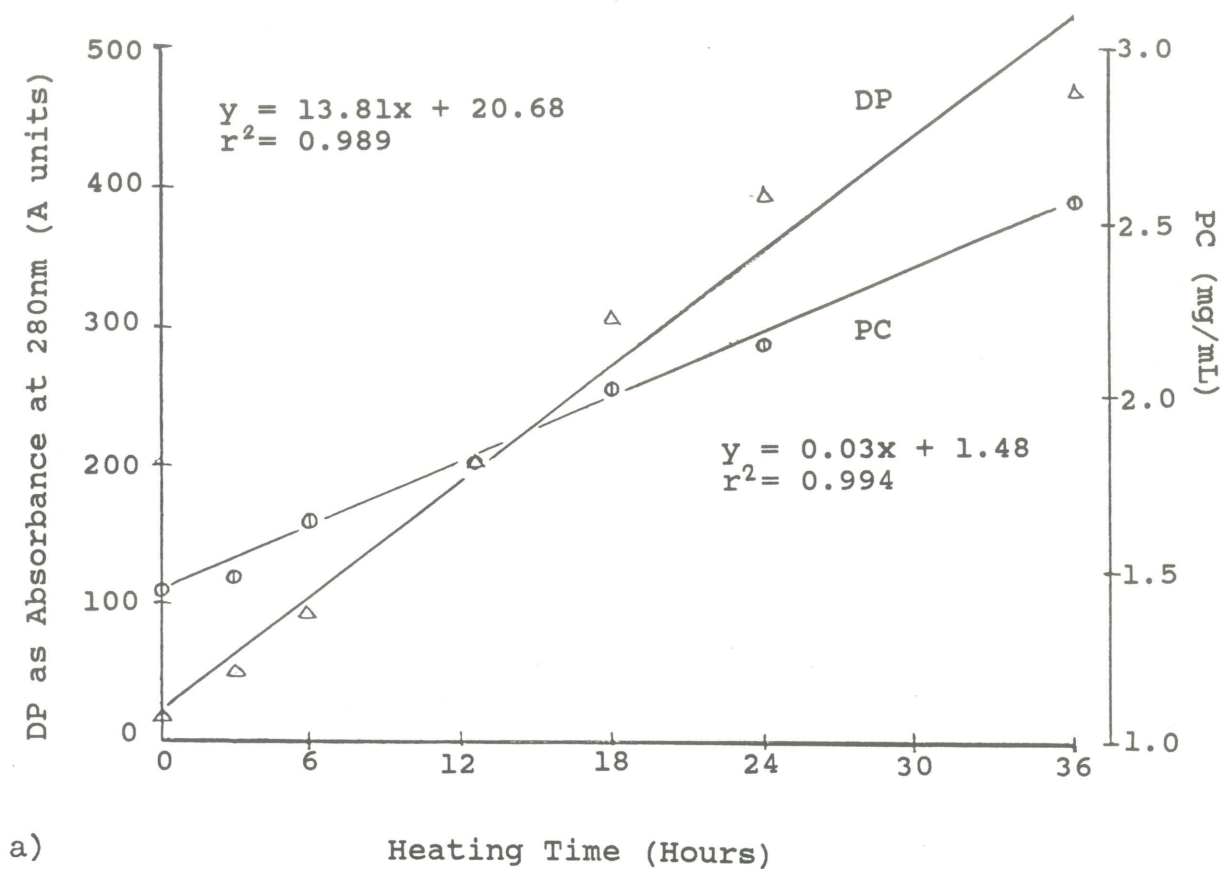


Figure 16 Degradation of a simulated recycled bleach solution (12.2% SS) heated at 98°C. a) Degradation curves of phenolic compounds and decomposition products; b) Photograph

in the SM due to the large variety of components found in the re-constituted apple juice concentrate that has been prepared by thermal evaporation under vacuum. Therefore, in addition to caramelization, Maillard reactions and Strecker rearrangements are present.

Figure 16-B showed the visual degradation of SRBS after various degradation times. From this picture, it is obvious that when the level of SS in the solution is relatively high (12.2%), the heat degradation would render the unpurified cyclic blanch solution useless after an hour or more of such heat treatment. The main problems would be the generation of off-flavours, off-odours and coloured compounds which would directly affect the quality of the blanched product, unless they are adequately dealt with continuously.

3.5 ADSORPTION STUDIES

Adsorption from solutions is rather complex and often the chemical nature of the impurity is unknown. Therefore, it is normally necessary to investigate the specific effects of powdered activated carbon treatment on the actual solution. Apple blanch water is an extremely complex mixture and the degradation products generated during blanching make it even more complex. There is, no specific information in the literature about those products. A less complex mixture similar to apples in

sugar/acid composition was used, to study the generation of the decomposition products and their removal with PAC.

3.5.1 Degraded SM

3.5.1.1 Comparison of three different PAC samples on the adsorption of decomposition products from SM

Three types of PAC: Hydrodarco H (HDH), Darco KB (DKB) and Norit 4N, were tested for the removal of DP, from SM.

The curves for rate of adsorption, at 80°C, of these three PACs are shown in Figure 17. It was observed that the maximum adsorption efficiency that can be obtained varies with each one of the PACs. PAC-Norit adsorbed 90% of DP after two minutes of contact time and reached equilibrium after ten minutes; PAC-HDH and PAC-KBD showed a maximum adsorption efficiency at five and two minutes respectively. In case of PAC-HDH the maximum adsorption was followed by a decline that could be due to the formation of non-readily adsorbable coloured compounds during the PAC treatment. The low-cost PAC-HDH could contain traces of iron compounds from its manufacture, which would catalyze sugar degradations, producing colored compounds. This is very likely to occur when the activation process leaves metallic residues in the PAC or when the metal is present in the raw material before activation (Benefield et al. 1982).

The formation of coloured compounds was monitored at 450nm, and the results are shown in Figure 18, where

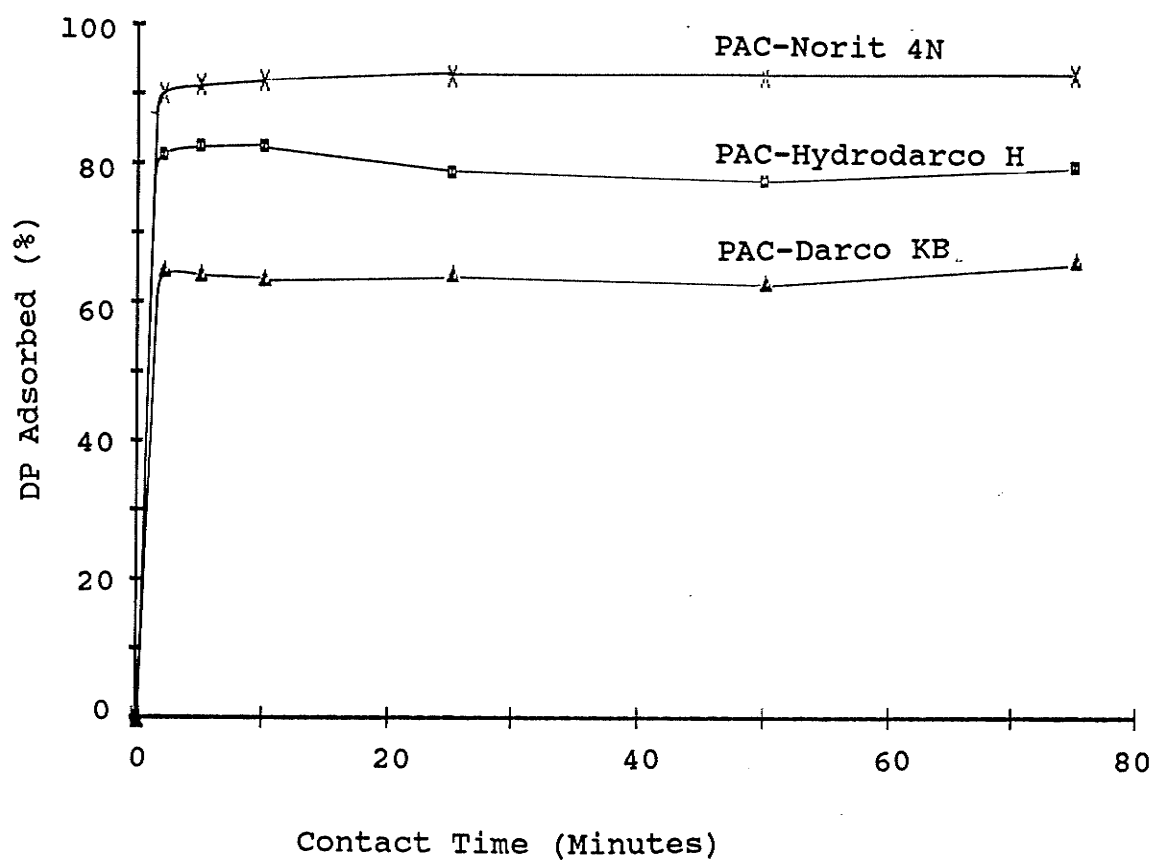


Figure 17 Curves for the rate of adsorption of decomposition products at 80°C for three powdered activated carbons, using a degraded sugar mixture with 1% PAC

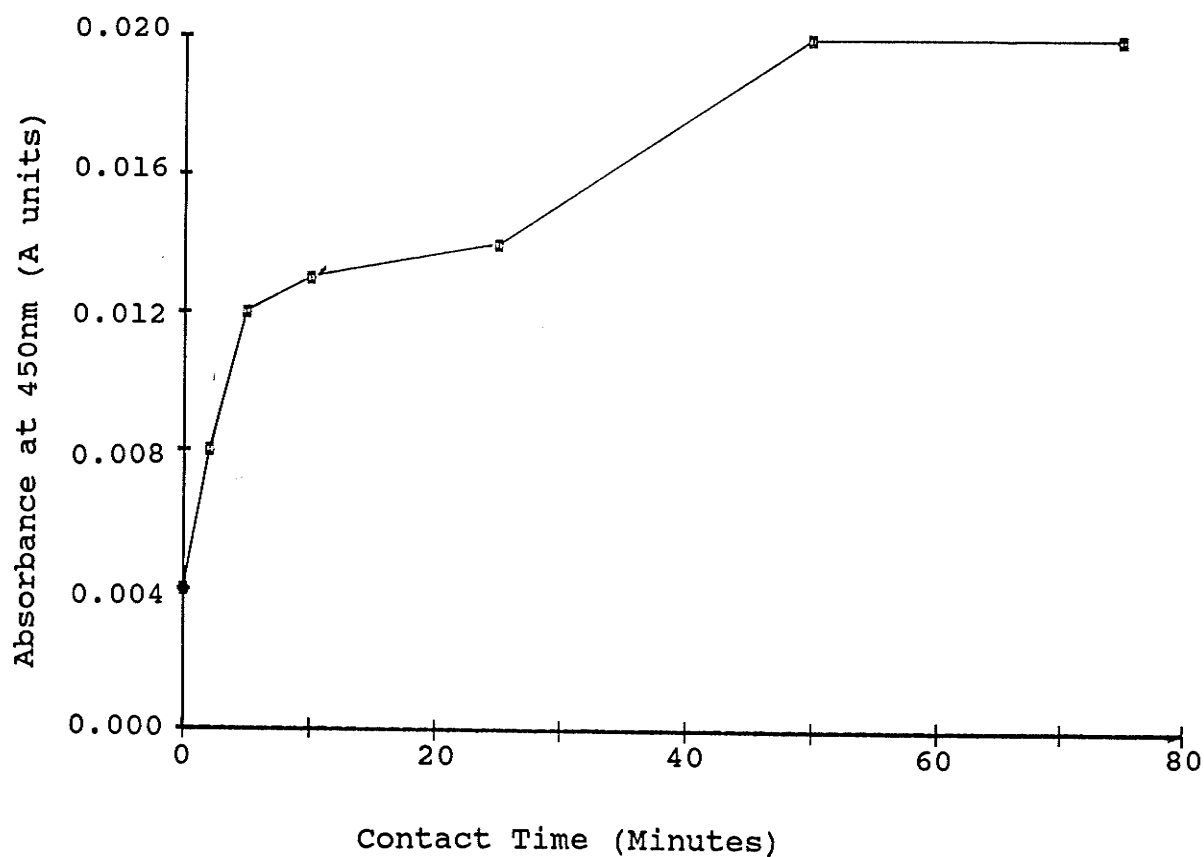


Figure 18 Absorbance changes at 450nm, for the sugar mixture, after treatment with 1% PAC-Hydrodarco H at 80°C

Absorbance at 450nm is plotted against contact time. This phenomena was observed only in the case of PAC-HDH, which is a low-cost PAC made by a special heat/steam activation process.

PAC-DKB is a chemically activated carbon and it showed only a very small fall in the adsorption capacity after two minutes of contact time (see Figure 17) but color was not present. The different activation process, along with a more likely low-cost raw material used for HD, compared to DKB, could be the main reasons for their particular behavior. PAC-Norit 4N showed the highest adsorptive capacity, without any apparent secondary effects.

Figure 17 shows that a maximum of 65, 83 and 92 percent of the decomposition products were removed from the SM, when PAC-HD, PAC-DKB and PAC-Norit 4N were used. PAC-Norit 4N seems the most suitable PAC for the efficient removal of DP in the SM and it was used for the major studies to follow.

3.5.1.2 Adsorption properties of PAC-Norit 4N

The adsorption of the decomposition products in several SM solutions by using various dosages of PAC was studied, at 50 °C. Four SM solutions were heat-treated during 0, 1, 2 and 3 hours respectively, before PAC adsorption. Each one of those solutions was treated with 0.0, 0.2, 0.5 and 1.0% PAC, and the results are shown in

Figure 19. The curves showed that when the levels of DP in solution were low, adsorption was poor and desorption and/or generation of products that absorb at 280nm seems to take place.

3.5.1.3 Adsorption Isotherm Evaluation

A Freundlich adsorption isotherm was obtained for the heat-treated sugar mixture solution. The object of this experiment was to evaluate the performance of the PAC-Norit 4N in the removal by adsorption, of the decomposition products generated during the heat treatment. The experimental data were evaluated using the Freundlich adsorption isotherm equation (see Section 2.3). The graphical representation of the experiment is shown in Figure 20.

The ultimate calculated capacity of the PAC-Norit for the SM solution under study, was 6000A units/mg of PAC. This ultimate capacity (x/m) or optimum adsorption value, represents the amount of DP adsorbed when the carbon is in equilibrium with the HT-SM solution with an original maximum DP concentration of 2,230 A units/L. It was calculated by extrapolation of the adsorption isotherm (2,230 A units/L describes any solution with an absorbance of 2.23 at 280nm).

The fact that the isotherm has a steep slope (2.47) indicates that its adsorptive capacity increases at higher equilibrium DP concentrations over that at lower

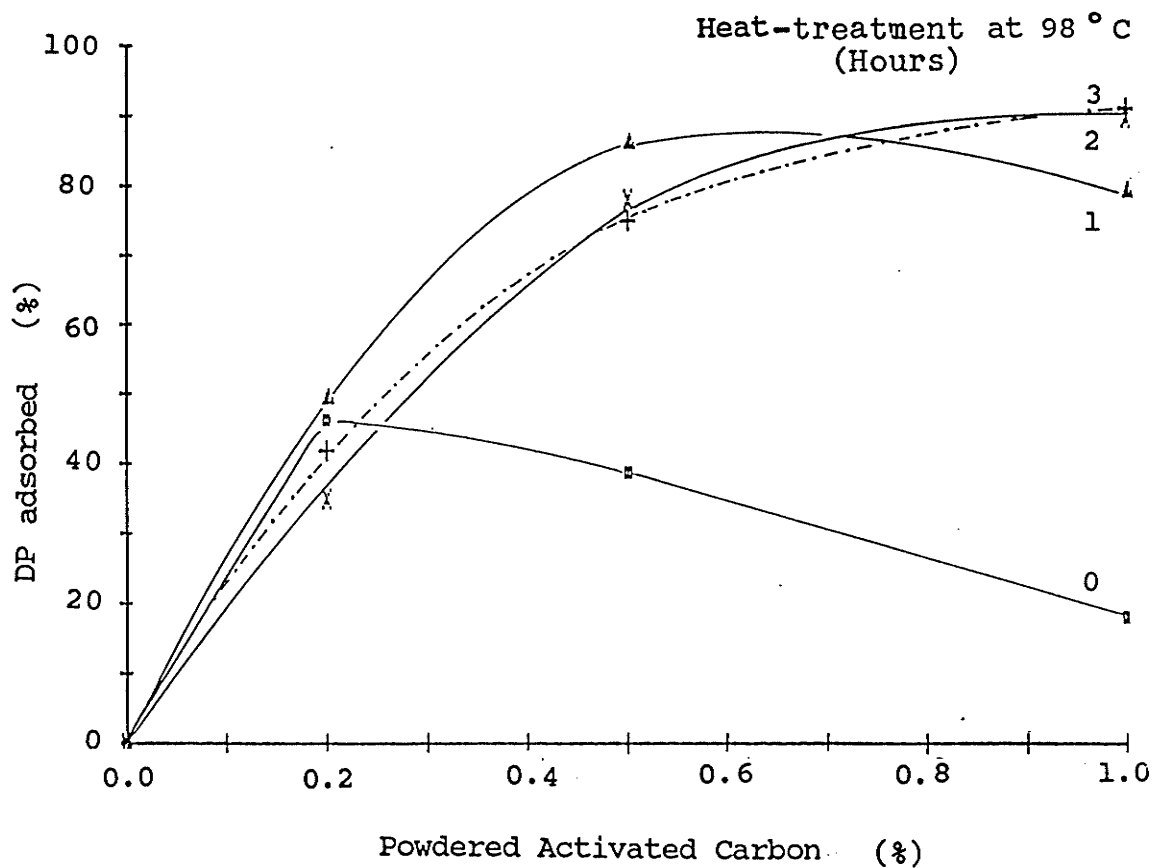


Figure 19 Adsorption of decomposition products in several heat-treated SM solutions, by using various dosages of PAC-Norit 4N, at 50°C

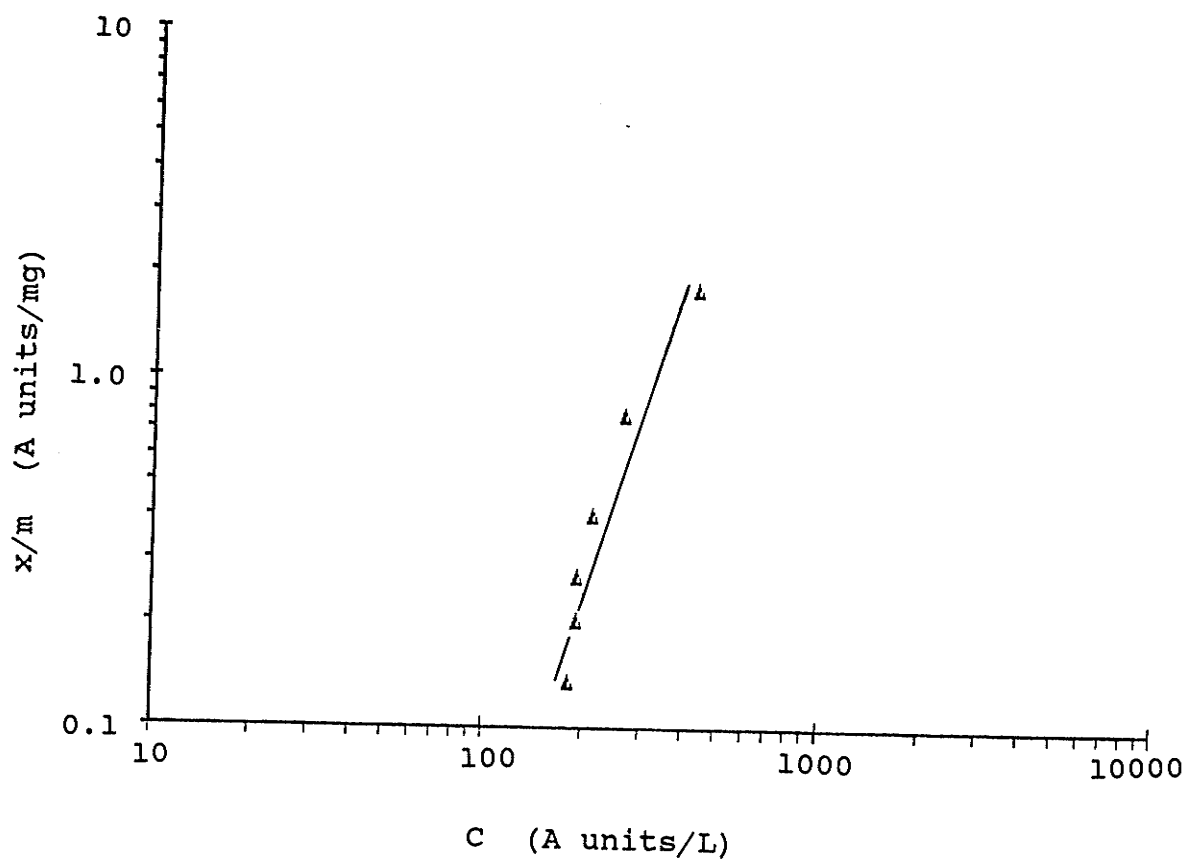


Figure 20 Adsorption isotherm for the heat-treated sugar mixture at 80°C

concentrations. This also indicates the difficulty in removing final traces of DP from the SM solution. These results showed that a maximum of 94 % removal of DP could be achieved by the adsorption treatment, and this was sufficient in practice, for good quality control.

3.5.2 Simulated Recycled Blanch Water

3.5.2.1 Optimum pH

The pH in the SRBW can greatly affect the adsorption of DP and phenolic compounds present in the solution. In order to find the optimal pH for PAC treatment, SRBW solutions, with modified pH values, were treated at 80°C with 0.5% PAC-Norit 4N, and the results are shown in Figures 21 and 22.

Figure 21, shows the percentage of DP and PC adsorbed versus the pH of the SRBW. The adequate range for optimum DP and PC adsorption seems to be from pH 2.5 to 5 (over 80% of the DP and PC was removed). At pH 3, removal of approximately 85% of DP can be obtained. However, any change in the pH of the SRBW solution (4.2), would require the addition of large amounts of acid or base, due to its buffer capacity, causing severe and undesirable modifications in its overall characteristics and behavior throughout recycling.

Spectrophotometric measurements at 450nm are shown in Figure 22. Effective removal of coloured compounds was carried out when the pH was between 2 and 5. The

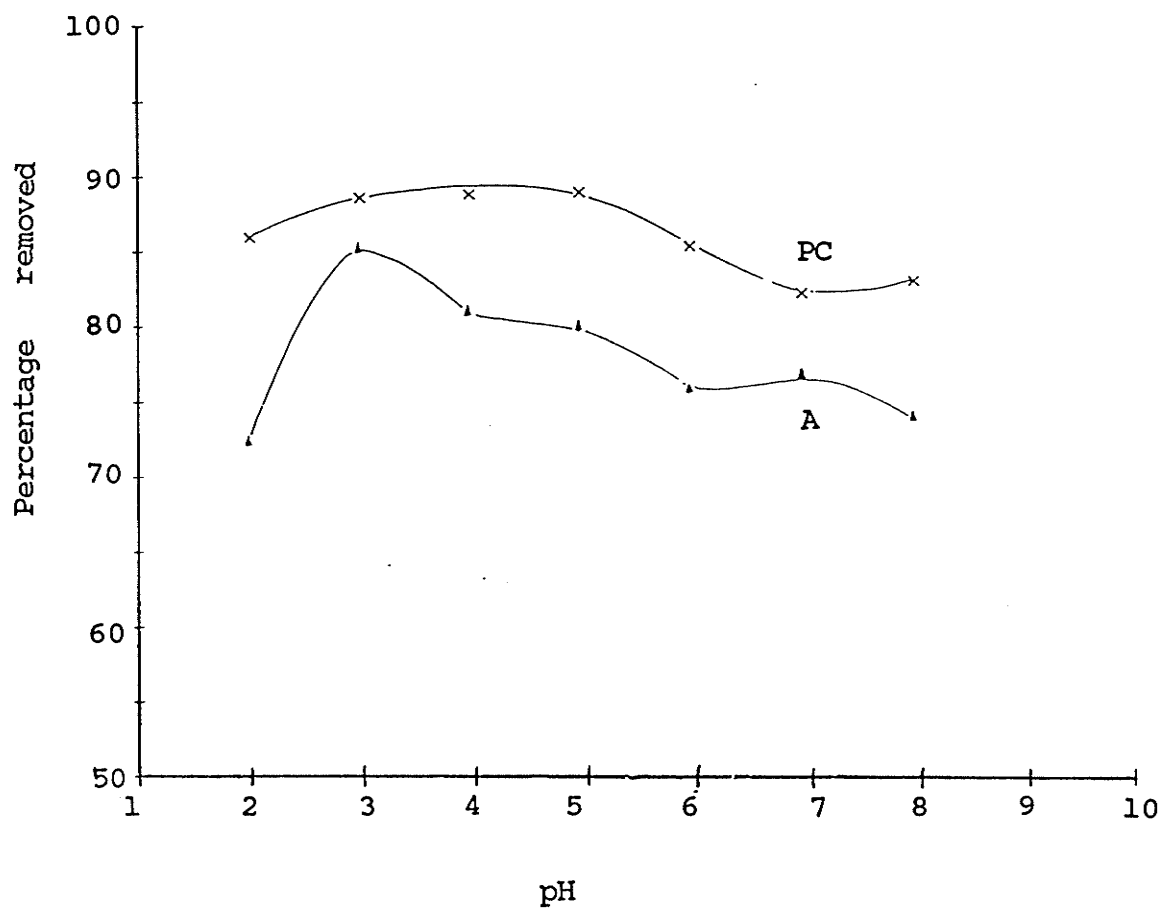


Figure 21 Optimum pH for powdered activated carbon adsorption of the phenolic compounds and absorbance at 280nm, present in the simulated recycled blanch water. SRBW solutions were treated at 80°C with 0.5% PAC-Norit 4N for five minutes

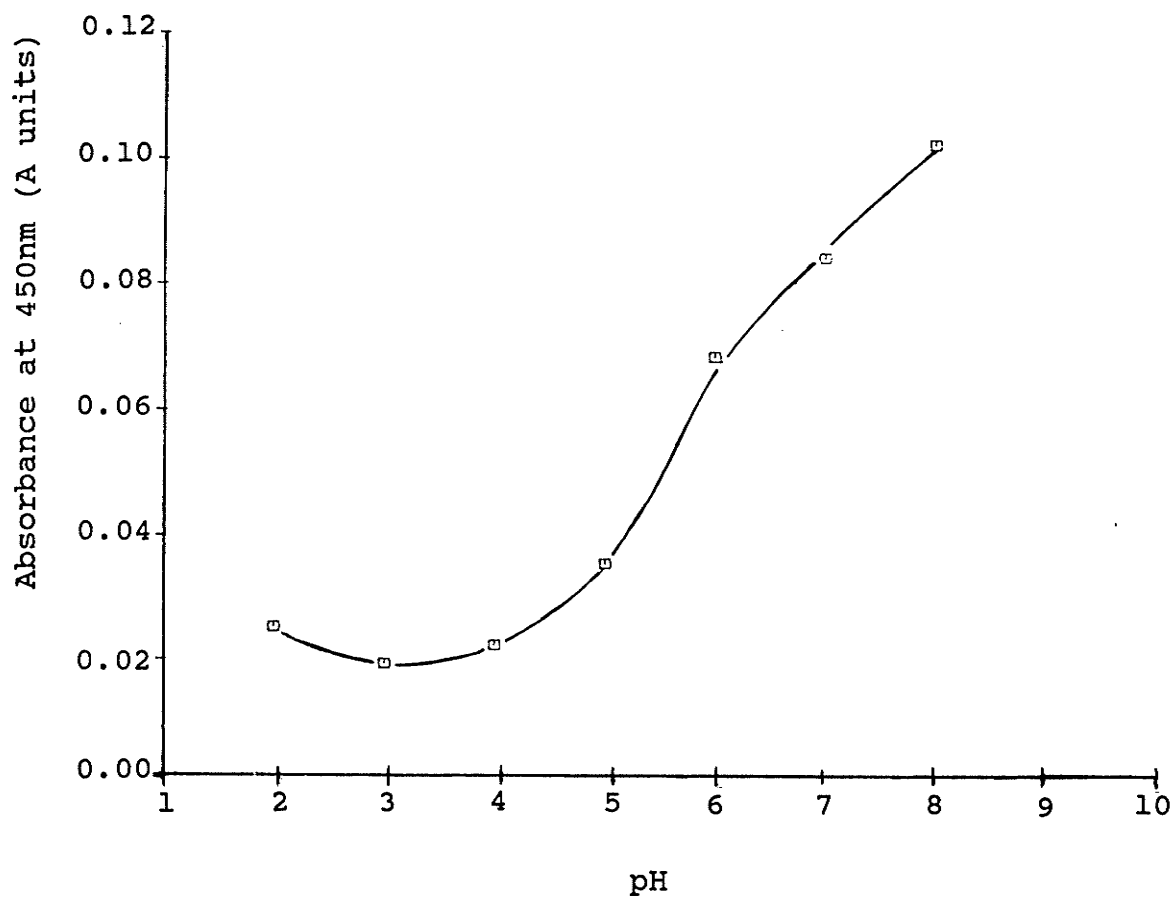


Figure 22 Absorbance changes at 450nm, for the simulated recycled blanch water, after treatment with 0.5% PAC-Norit 4N at 80°C for five minutes

absorbance at 450nm of the original SRBW was 0.053, and after PAC adsorption, it ranged from 0.024 to 0.034 for pH 2 and 5 respectively, with an optimum of 0.018 at pH 3. The expected absorbance at pH 4.2 is 0.022, which represents a reduction of 58% of the coloured compounds from the original solution.

It was concluded that adequate PAC adsorption of DP and PC and coloured compounds, from the SRBW solutions, could readily be achieved without pH modifications, by intermittent adsorptive-filtration treatments, when necessary. Rates of possible removal, far exceeded potential rates of generation of the undesirable compounds, during recyclic use of the blanch waters, thus insuring its possible exhaustive reuse in commercial practice.

3.5.2.2 Rate of Adsorption

SRBW was treated with various concentrations of PAC at 50°C and the results are shown in Figure 23. The initial concentration of phenolic compounds in SRBW was approximately 0.06%. Figure 23 confirmed that the lower the PAC level used, the longer the time that will be required to achieve equilibrium. At 0.3% PAC, 82% of PC were removed after 40 minutes; at 0.2% PAC, 62% of PC were removed after 40 minutes; and at 0.1% PAC only 40% of PC were removed after a contact time of 50 minutes. Moreover, at this low level of PAC (0.1%) the rate of adsorption

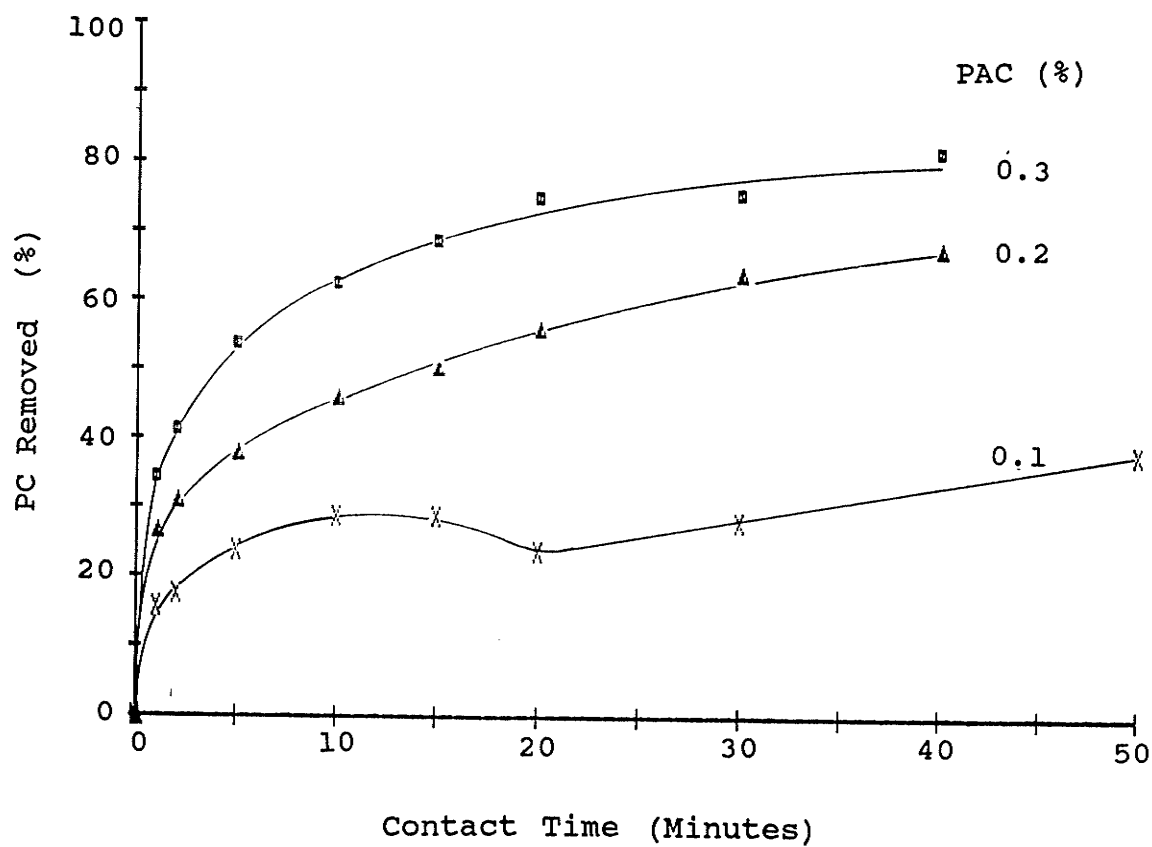


Figure 23 Simulated recycled blanch water treated with various concentrations of PAC-Norit 4N at 50°C

curve showed a distinct drop at 20 minutes . This apparent desorption of the PC from the PAC was also observed when SRBW solutions at various pH values were treated with 0.1% PAC (see Figure 24). The major difference, between the curves, seems to be a shift of the depression found between 8 and 25 minutes. The adsorption of PC after 50 minutes ranged from 35 to 55% depending upon the pH of the solution (similar behavior to that observed in section 3.5.2.1).

The rate of adsorption at 80°C was also studied and the results are shown in Figure 25. The percentage of PC and DP removed from SRBW by PAC (1% level) are plotted against contact time. It was observed that over 95% of PC and over 90% of DP were removed from the SRBW after one minute of contact time with PAC.

Equilibrium in both cases seems to be reached within the first five minutes. Close to 95% PC and 91% DP were removed from the ABW after one minute of contact time with PAC. The ultimate levels of PC and DP removed were 96% and 92 respectively. The need for prompt, brief, efficient contact with the PAC, was obvious from these results.

3.5.2.3 Adsorption Isotherm for SRBW

The adsorption isotherm was obtained for the SRBW (simulated solution after six recycles) and its graphical representation is shown in Figure 26. The isotherm obtained is non-linear and exhibit a well-defined

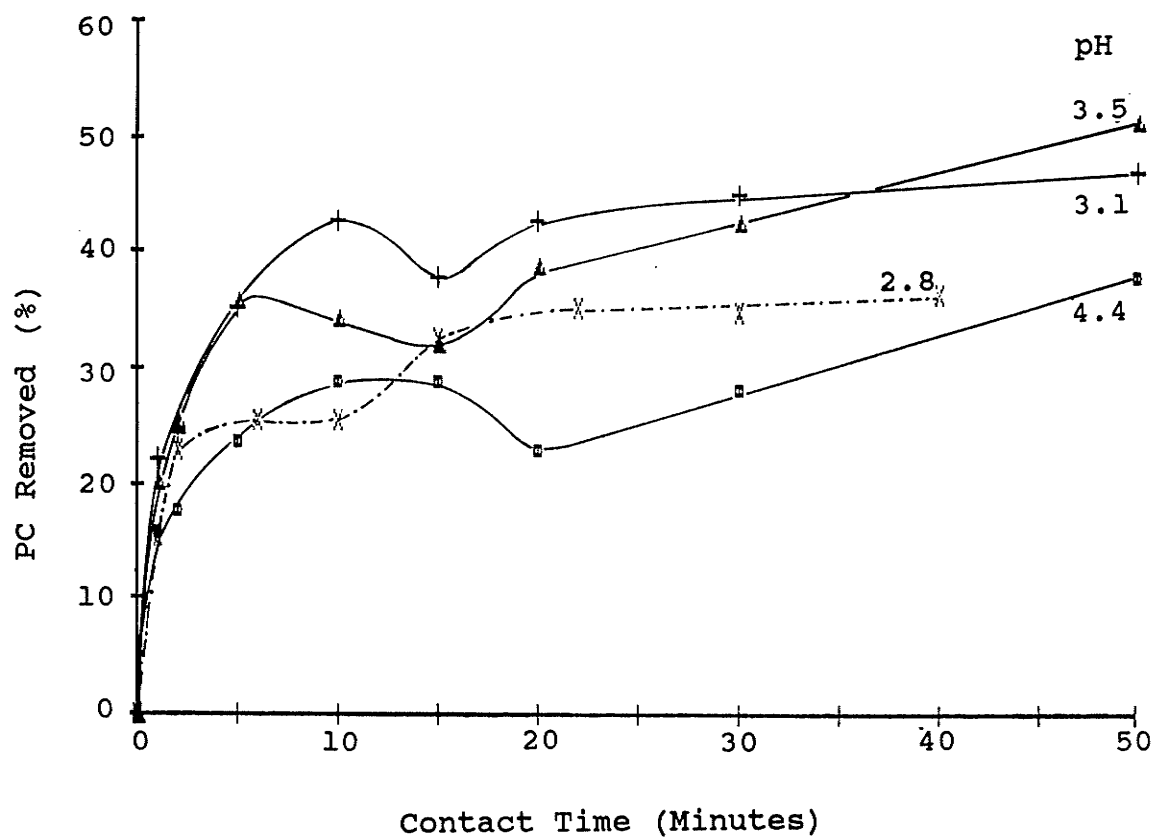


Figure 24 Simulated recycled blanch water, at various pH values, treated with 0.1% PAC-Norit 4N at 50°C

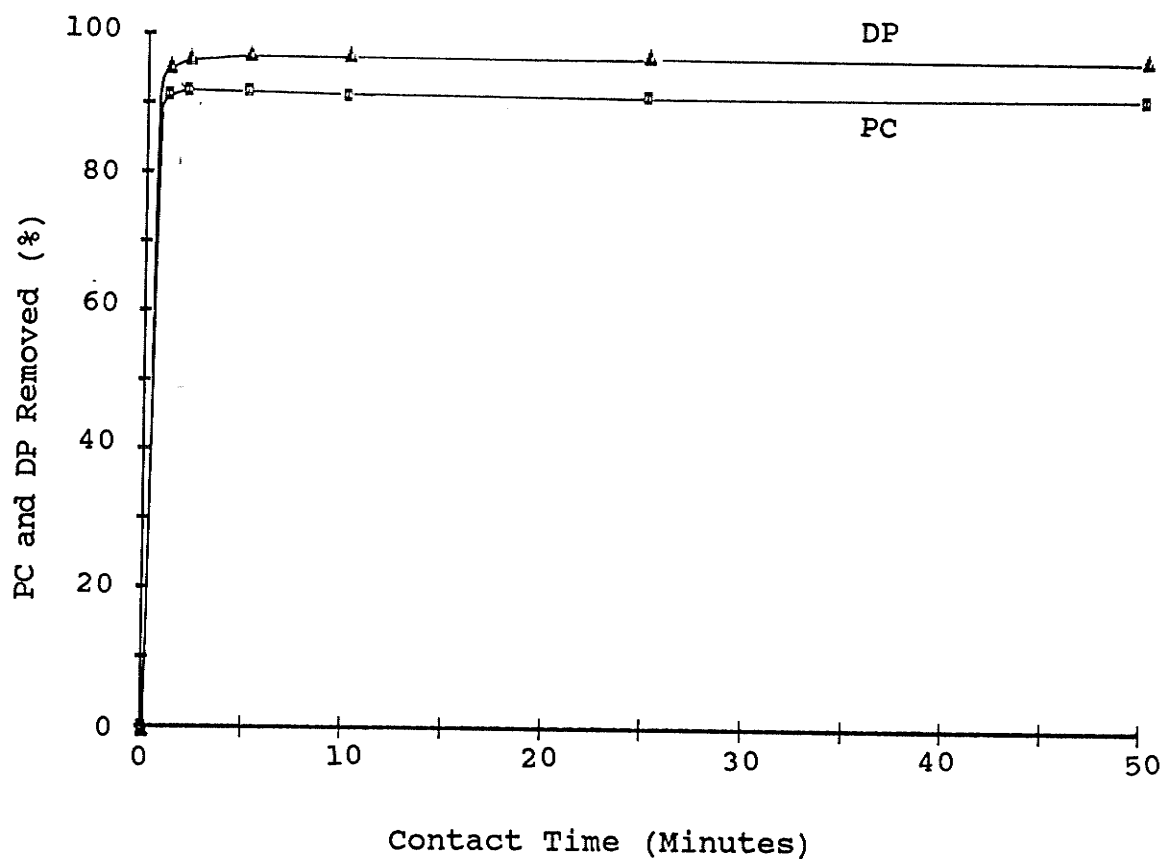


Figure 25 Rate of adsorption of decomposition products and phenolic compounds, from simulated recycled bleach water, with 1% PAC-Norit 4N at 80°C

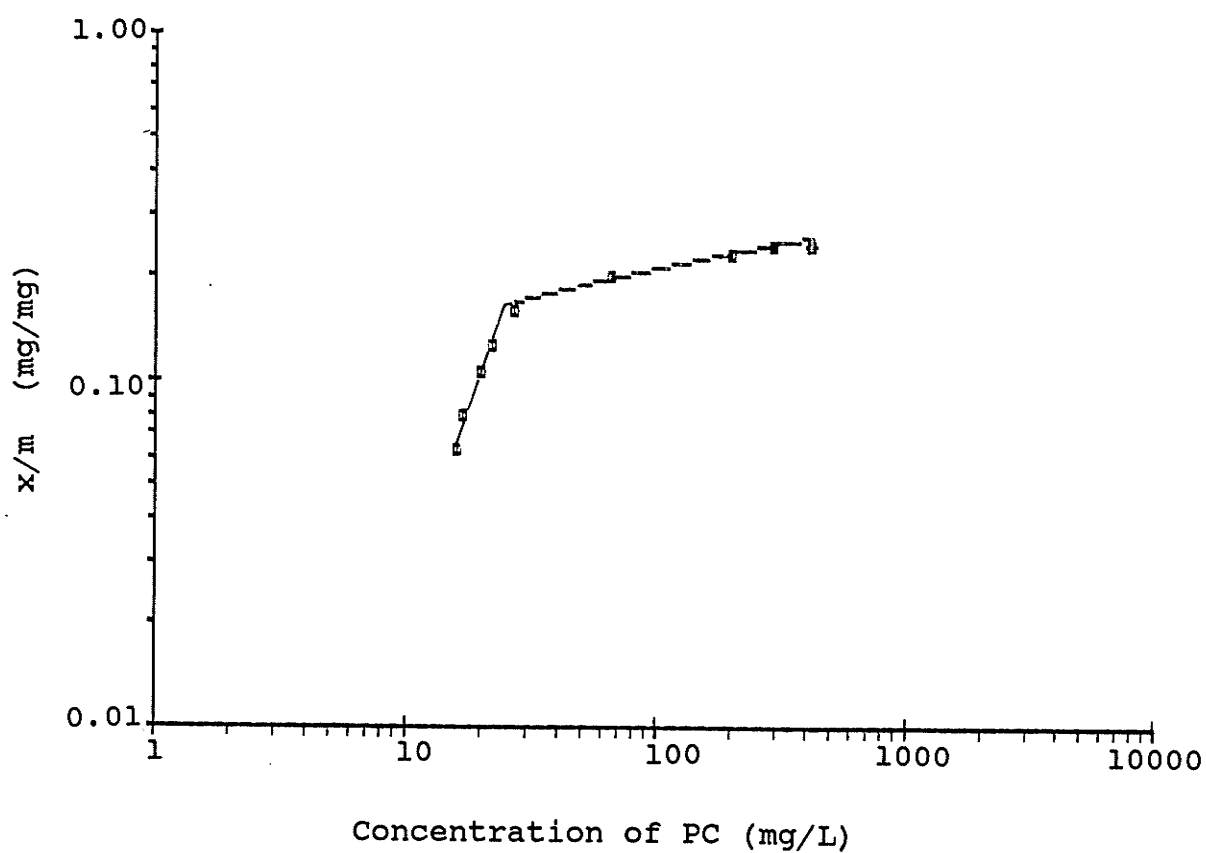


Figure 26 Adsorption isotherm for the simulated recycled blanch water at 80°C

breakpoint. This is caused by the presence of several compounds, which are not equally adsorbable, in the complex apple extract.

The upper linear portion of this isotherm indicates the removal of readily adsorbable material, whereas residual material remaining at the breakpoint is not as easily adsorbed by the carbon. Additional removal by adsorption may be feasible below that breakpoint. However, the fairly steep slope indicates that the breakpoint at 25mgPC/L, may represent the minimum concentration of PC removal that can be economically achieved by adsorption. But it seemed to be sufficient, in practice.

The ultimate capacity of the PAC-Norit for this SRBW solution was 0.27mg PC/mg of PAC. The PC concentration in the untreated SRBW was 656mg PC/L. This would require at least 2500mg PAC/L for removing most of the PC in a volume of SRBW. But this does not need to be fully removed, but only reduced steadily, to a satisfactory level (see section 1.4.3 for further details).

PAC-treatment of the blanch solution every six recycles will significantly reduce the PC levels, to allow extended recycling of the blanch solution. The PC test, as previously explained, detects not only the phenolic compounds in solution, but most of the degradation products (DP) too. Therefore, the adequate reduction in the level of PC, when necessary, would indicate reduction in the levels of PC and other undesirable degradation

products, which have been associated with off-odours and off-flavours, to make possible the prolonged recycling of the blanch water.

3.5.3 MICROSCOPIC OBSERVATIONS OF PAC IN SELECTED SOLUTIONS

3.5.3.1 Filtration performance.

During the adsorption experiments, the PAC was removed by filtering the solution through a glass fiber filter. In the case of SRBW a gray "haze" was observed in the filtrate, and when this filtrate was held at 4°C for 24 hours, traces of a "blackish sediment" were apparent. This problem arose when SRBW was being used, but not with the SM solutions. SRBW was treated with PAC at several temperatures and the Turbidity (T) of the filtrate was determined. The results are shown in Figure 27. Turbidity increased with any increase in the temperature of adsorption.

When a membrane filter with a pore size of 0.45 μm was used to remove the PAC from the SRBW, the gray haze problem disappeared. This indicated that the haze problem was more likely to be produced by small suspended PAC-particles, between 0.45 and 1.2 μm in size. The presence of such PAC-particles is possible, according to the specifications for PAC-Norit 4N given by the manufacturer (see Appendix III) which indicates that 20% of PAC

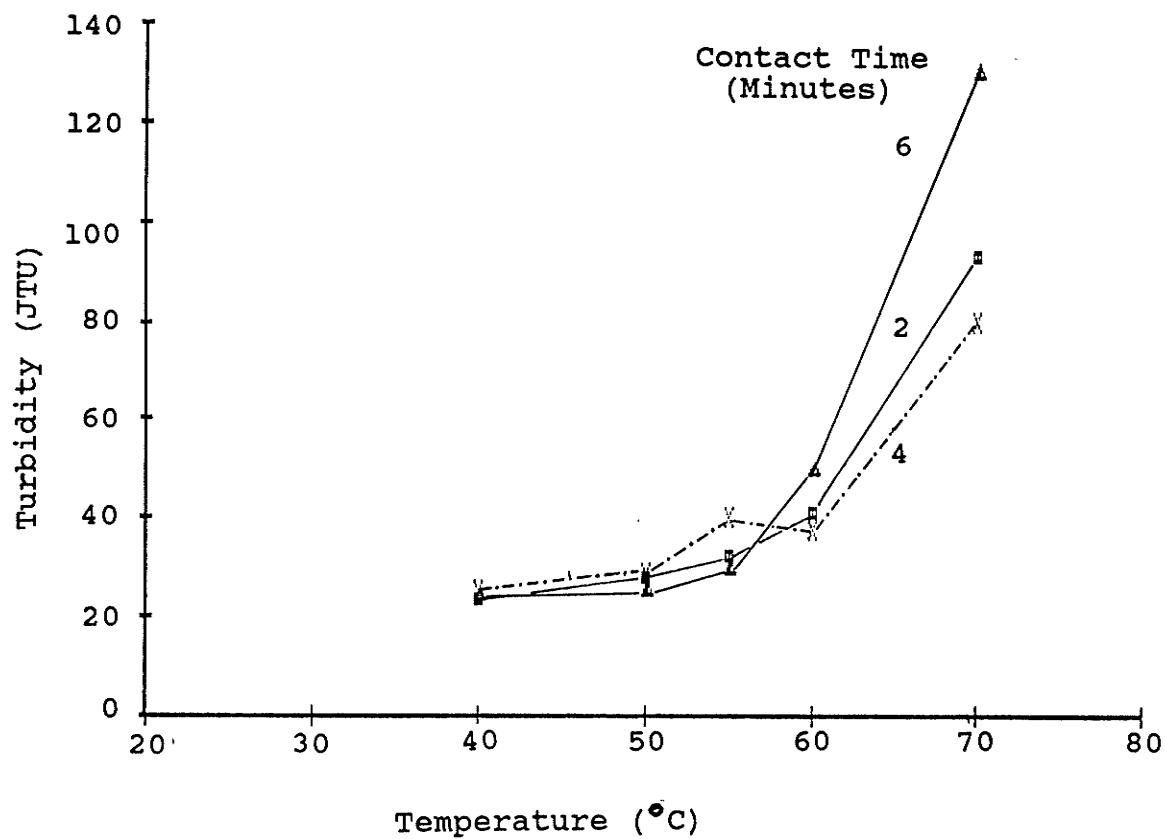


Figure 27 Turbidity changes for PAC-treated simulated recycled blanch water at various temperatures

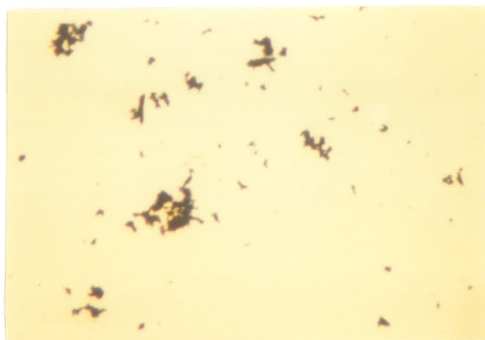
particles are under $10\mu\text{m}$. However, the unusual fact was that the gray haze problem was not present when PAC was used on the SM solutions, instead of SRBW.

3.5.3.2 PAC in SRBW and SM solutions at various pH values.

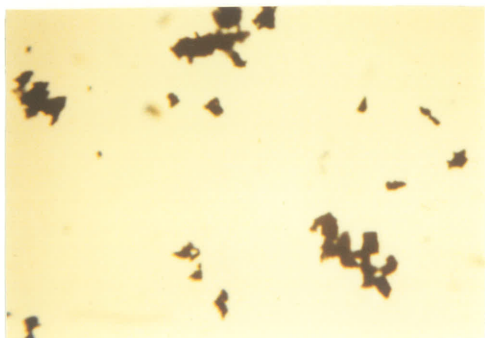
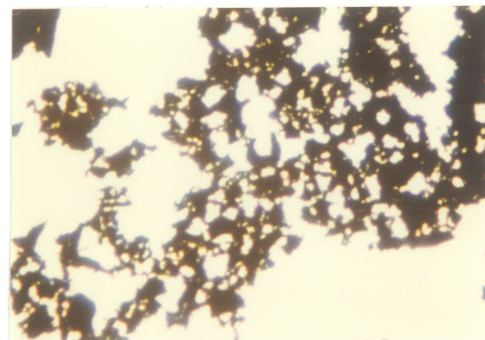
Microscopic observations were carried out for both systems before filtration and the results are shown in Figure 28 and Figure 29. Figure 30 shows the "black sediment" present in the filtered SRBW samples. A sample of this sediment under the microscope appears as a collection of uniformly sized PAC particles. Figure 28 shows the PAC-SRBW system at different magnifications and two different pH values, 3.8 and 4.2. In each case, all the particles seem to be dissociated and aggregates are not observed, but instead a large number of small particles of non-uniform size are present (See Figures 28-b and 28-d).

Figure 29 shows the PAC-SM system at different magnifications and three pH values 2.7, 3.8 and 4.2. When comparing the results in Figure 28 with those in Figure 29, it can be noted that the PAC in the SM seems to have a tendency to form three-dimensional complex aggregates, particularly at pH 3.8 followed by those at pH 4.2 (see Figures 29-d and 29-g). SM at pH 2.7 showed less aggregation than those at 3.8 or 4.2. This could be explained based on the electronegative character of PAC.

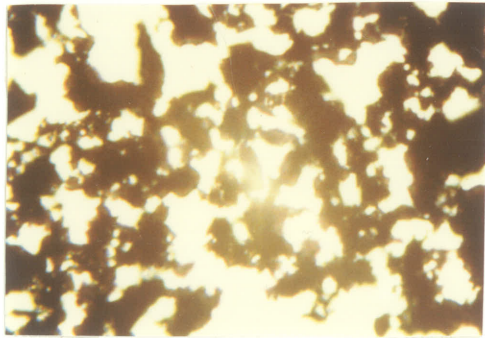
It seems that in both systems the pH has little



108X



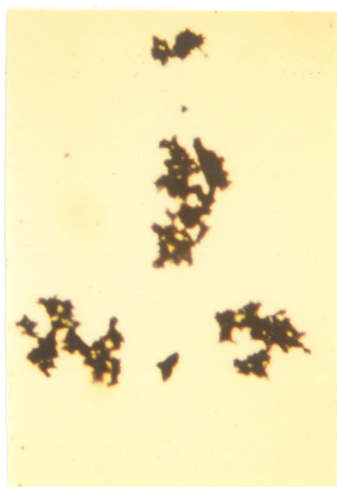
256X



pH 2.7

pH 3.8

108X



256X

pH 4.2

Figure 28 Microscopic observations for a PAC-SM mixture system

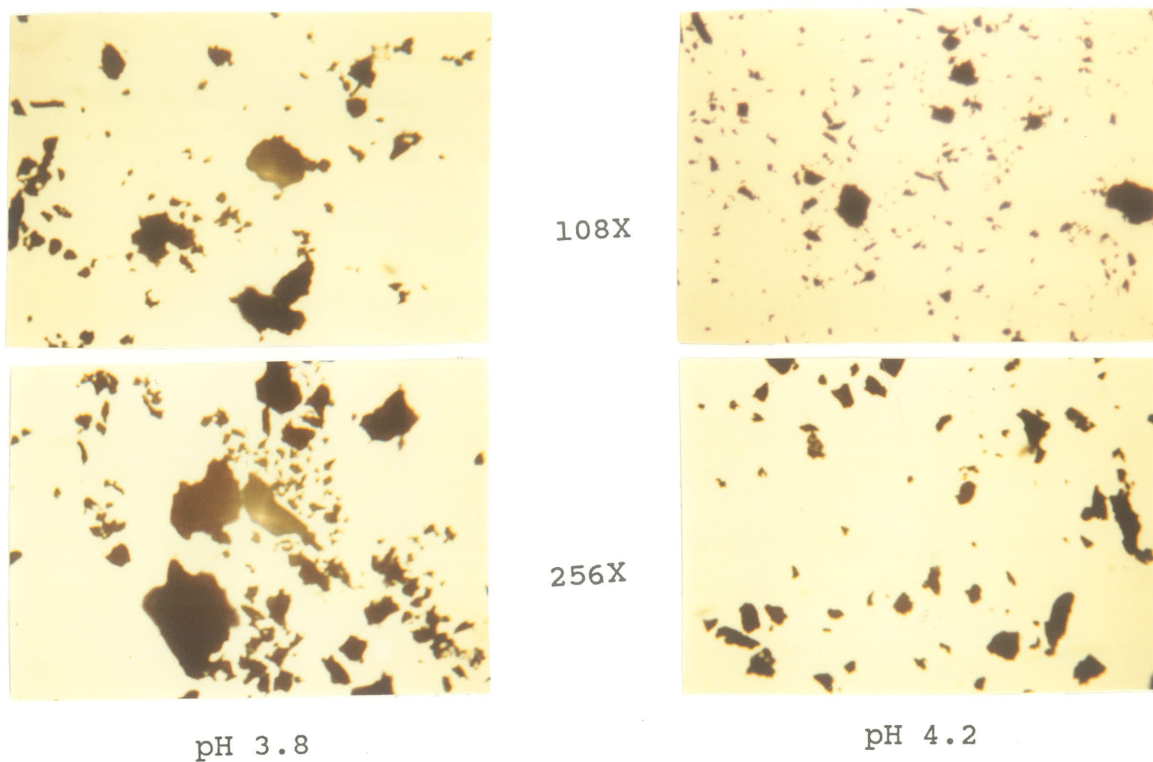


FIGURE 29 Microscopic observations for a PAC-simulated recycled blanch water system

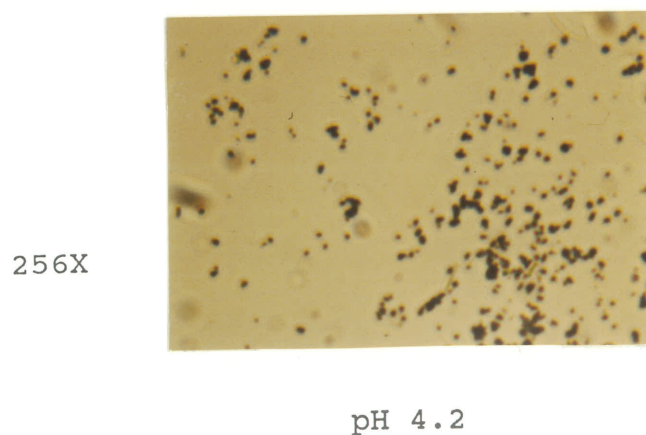


FIGURE 30 Microscopic observations of the "black sediment" present in the filtrated PAC-treated simulated recycled blanch water

effect on the formation of aggregates. Other factors must largely be responsible for this phenomena, which could complicate the recycling of pAC-treated blanch waters. A few common factors were investigated, as possible causes.

3.5.3.3 PAC in SRBW at different NaCl concentrations (0.01-2%)

The PAC in the SRBW with 0.01, 0.1, 1.0 and 2% NaCl showed little aggregation under the microscope. At 2% NaCl the particles of PAC were slightly more aggregated than in the other cases, however, turbidity measurements of the filtrate showed no variation and remained at 21 JTU in all cases.

3.5.3.4 PAC in Acetic Acid/Acetate (AAA) buffer solutions at several pH values (3.4-5.9)

The PAC in AAA Buffer solutions formed small 3-D like aggregates in all cases. The pH, for the range studied, seems to have little effect on the de-aggregation process.

3.5.3.5 PAC in AAA buffer solutions (pH 3.4, 4.3 and 5.9) with protein, starch and pectin

a) The level of protein (as egg white) was 0.85% in each case, and the results from the microscopic observations showed that the higher the pH, the larger the particles of PAC present in the solution (fewer smallest and small chunks were observed), however, no 3-D aggregates were observed. When the pH of the solution was 3.4, the added protein formed a clear precipitate (most likely denatured protein). The PAC in this system was

easily separated by filtration . At pH 4.3, the protein present in the solution caused excessive foaming and dispersed the PAC particles to give a "smudgy" appearance to the solution and caused slow sedimentation. At pH 5.9, PAC formed large aggregates, visible to the naked eye, the dusty appearance was not present, and sedimentation to leave a clear solution behind, occurred in less than ten minutes.

b) The starch level used was 1% , and in all the cases, the PAC in the solution formed a "dusty-slimy" film in the bottom of the flasks and after several hours of settling, the solutions were fairly clear with a very pale bluish gelled starch coloration. Under the microscope, chunks of PAC were observed. The higher the pH values, the fewer the small particles present.

c) The pectin level used was 0.2%, and upon PAC addition a large amount of suspended PAC particles was observed in the solution. Even after filtration, large amounts of suspended particles could be observed in the filtrate. The microscopic observation of the solution , before filtration, showed large quantities of small PAC particles with only a few medium and large ones, and no aggregation was observed. The PAC in the solution slowly formed a "dusty-slimy" film in the bottom of the flask, after several hours of settling. However, the supernatant solution retained a grayish coloration and was extremely

unstable, since any small disturbance would bring the PAC back into suspension.

3.5.3.6 PAC in SABW and SABW after pectinase treatment

PAC was added to a simulated recycled system (pH 4.2, 3.5% soluble solids) as well as a similar solution previously treated with pectinase (0.01% pectinase, 4.5 hours at 50°C). After filtration, turbidity measurements showed that the sample treated with pectinase, had a lower turbidity value (7.8 JTU) than the one untreated (18 JTU). The hydrolysis of pectin seemed to reduce the capacity of the system to de-aggregate and suspend the PAC particles.

It was concluded that pectin substances could potentially interfere with the final required clarification of PAC-treated food extracts, such as blanch waters. Appropriate treatments might include pectinase treatments prior to PAC-contacting, followed by a final microfiltration step.

3.6 SENSORY EVALUATION OF APPLE SLICES BLANCHED IN SIMULATED AND PAC-TREATED SOLUTIONS

Sensory studies were carried out on the apple slices blanched in the following solutions: a) Distilled Water (Water), b) Fresh Apple Juice (FAJ), c) Simulated Recycled Blanch Solution from concentrate (SRBS), d) Degradated or Heat-Treated SRBS (DSRBS) and e) PAC-

Treated DSRBS (PAC-DSRBS). The level of soluble solids in all the solutions was 12.5% except for distilled water where the level was 0%.

Summaries of the analysis of variance (ANOVA) for flavor and appearance of the blanched apple slices are presented in Appendix VIII and IX respectively. The F** values indicate significant differences at the 1% level and the Tukey's tests reveal where those differences are.

Both ANOVA results show significant differences: a) between treatments and b) between judges, along with interactions c) between treatments and judges, and d) between judges and replicates. This can be interpreted as follows: a) That there are significant differences in flavor or appearance (at the 1% level) between AS blanched in the different solutions. b) The judges differ significantly in their scores; probably because they were differentially responsive to the apple flavor or appearance. c) The significant interaction between the treatments and the judges, was mainly associated with variations in the order of "liking" of the various treatments by judges. d) A significant interaction between judges and replicates was also present and it was associated with variations in the trend for scores over judges when replication was added.

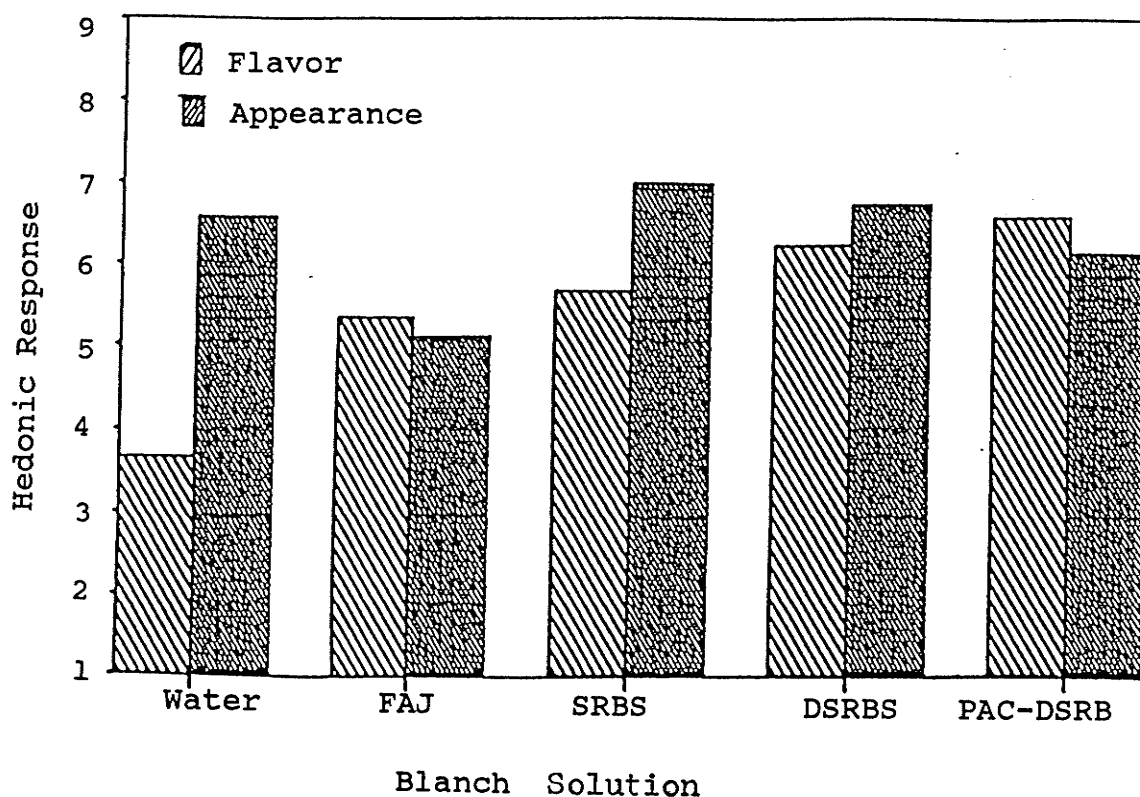
In 1986, O'Mahony, conceptualized interaction as lack of consistency and pointed out that it is expected during hedonic studies, since the panelists are unlikely to agree

on the degree of liking for each treatment. In spite of this interaction, the ANOVA showed a trend, which was followed by the majority of the panelists, and it was that the apple slices blanched in water, were rated as the most disliked, whereas the ones blanched in PAC-DSRBS were the ones rated as the more liked.

The hedonic responses for flavor and appearance of the blanched apple slices are shown in Figure 31. They indicate that the use of PAC did not diminish the degree of liking of the apple slices. The score for flavor, assigned to the apple slices blanched in PAC-DSRBS, was the highest of all the samples tested (6.59). Most of the panelists commented that this sample had a well balanced and fresh apple flavor. The reason for the fresh apple flavor, could be that the PAC treatment removed most of the off-flavor compounds, which will be present in most of the other solutions; therefore, allowing the panelists to more easily detect the normal apple flavor, which was well- retained.

The apple slices blanched in distilled water were given the lowest flavor score (3.68); which was significantly different (at 5% level) from that of AS blanched in PAC-DSRBS (6.59). A large number of panelists commented that the AS had a bland poor apple flavor.

Figure 31 shows that the flavor scores for the remaining samples fall in between the one for the AS



9 = Like extremely, 5 = Neither like or dislike and
1 = Dislike extremely

Figure 31 Hedonic responses for flavour and appearance of apple slices blanched in various solutions.
FAJ = Fresh apple juice
SRBS = Simulated recycled blanch solution
DSRBS = SRBS after 1 hour reflux at 98°C
PAC-DSRBS = DSRBS treated with 1% PAC for 5 minutes, at 90°C

blanched in Water and the one for AS blanched in PAC-DSRBS.

The hedonic responses for appearance of apple slices (Figure 31 and Appendix IX) were mainly associated with color. However, there were not significant differences between the samples blanched in water and those blanched in the other solutions, except for the one blanched in FAJ; which showed a pinkish coloration, and was significantly more disliked (at the 5% level) than the rest.

CONCLUSIONS AND RECOMMENDATIONS

1) During closed-loop blanching:

a) Leaching of Soluble Solids (SS) from the apple slices into the blanching water, was more severe in the initial stages of recycling than in the latter ones, due to the higher concentration gradient versus almost equilibrium.

b) The pH will remain almost unchanged because of the buffer capacity exhibit by the SS leached into the blanch water.

c) The increase in the absorbance at 280nm is reduced with recycling, however, absorbances at 280 and 450nm, do not reach equilibrium during recycling. This is expected since they are associated with the intermediate products generated during the caramelization of sugars, and the Maillard reactions.

2) The data obtained during microscopical observations indicate that:

a) Effective removal of PAC depend largely upon the composition of the solution and was mainly associated with the ability of PAC to maintain and form aggregates.

b) PAC dispersion (de-aggregation) occurred when pectin was present in the solution and to a lower extent in the presence of protein (egg white) and starch.

c) The use of pectinase, improved the PAC removal by reducing the level of suspended PAC particles during filtration through a $1.25\mu\text{m}$ glass filter. d) PH changes (3.4-5.9) and the presence of NaCl (0.01%-2%) had little effect on PAC aggregation/de-aggregation.

3) The data obtained during degradation, adsorption and sensory studies of the simulated systems, indicated that:

a) The closed-loop blanching of apple slices is technically feasible.

b) The routine filtration of the recycled blanch water, through coarse and fine filter media, with the periodic use of PAC to adsorb the undesirable soluble compounds, would be the best approach.

c) Modifications to the pH of the apple blanch water are not necessary, since its natural pH (4.2) falls in the range for optimum PAC adsorption, with least unit needs for PAC dosages, and contact times.

4) The data obtained during blanching of apple slices with various solutions indicated that with any increase in the SS level of the blanch water:

a) The yield decreased and the total solids content of the blanched apple slices increased.

b) The changes in turbidity and total residue in

the blanch water decreased.

c) The degree of liking changed from dislike slightly to like moderately.

5) The blanch water can be recycled many times, reducing the energy, water and wastewater requirements. The product will have increased total solids which means increased palatability plus higher nutritional and commercial values.

6) Immediate solids equilibrium could be achieved at the start up of the blancher, by using cull fruits to prepare the initial blanch water.

7) This model study with apples, indicates that this approach can be widely applied to other fruits, with similar benefits.

8) Further research is required to effectively implement recycling of the blanch water during fruit processing.

a) More detailed information about the degradation compounds is required in order to monitor and control the process, more accurately, through an in-line detector, e.g. a spectrophotometer system.

b) Adsorption studies of some of the most relevant degradation products, and/or some pesticides and natural

toxic compounds, should show the adequacy of PAC during the treatment of recycled blanch water, as a safety system against such microchemical risks.

c) The study of individual components, particularly minerals and water-soluble vitamins, during blanching, should prove that the recycling of blanch water will indeed improve the nutritional quality of the blanched product.

d) A study of heat-resistant microorganisms, especially moulds that may grow in some parts of the system's equipment.

e) Improvement in the PAC-contacting and PAC separation are required before the advanced PAC technology can be effectively and economically used in the industry. One possible area for this particular problem will be the use of an automatically controlled belt filter.

f) Expand the use of this water recycling blanching system to other fruits, at the Laboratory/Pilot Plant levels.

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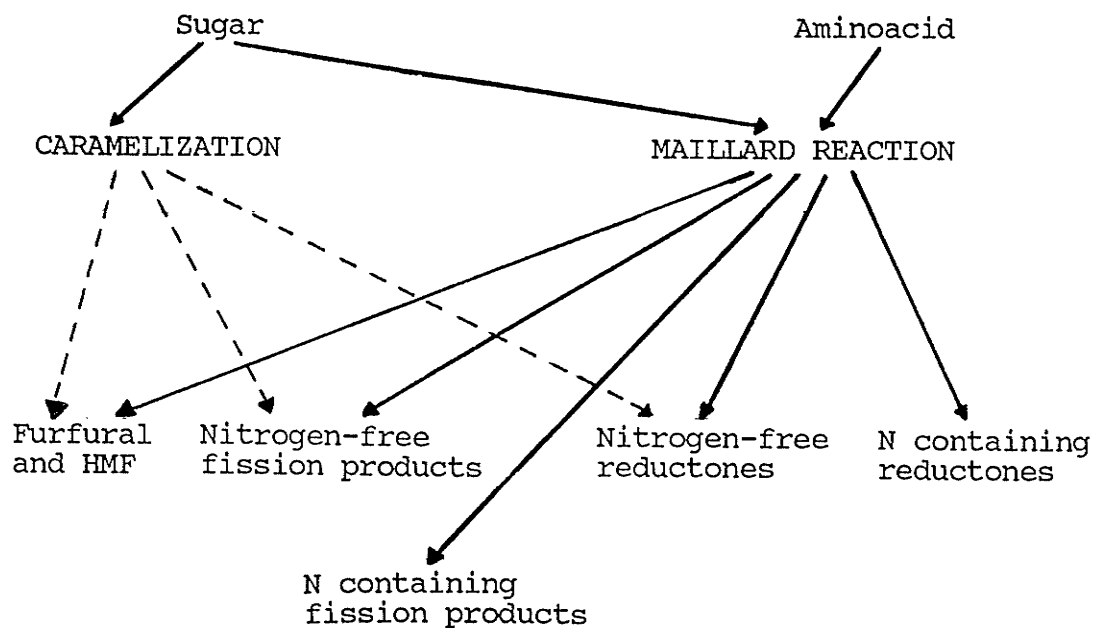
APPENDIX I

Studies published between 1976 and 1985 associated to the relative merits of steam versus water blanching.

Reference	Vegetables
Cumming et al. (1984)	Peas, Cut Beans and Carrots
Drake and Kinman (1984)	Dry Beans
Timbers et al. (1984)	Peas, Beans and Broccoli
Cabinplant a/s (1983)	Green Peas
Adams (1981)	-- Review --
Carroad et al. (1980)	Broccoli Spears
Bomben (1977)	Various

APPENDIX II

The interactions possible between caramelization and the Maillard reaction:



(Shallenberger and Birch, 1975)

APPENDIX III

NORIT PN 4 POWDERED ACTIVATED CARBON.

NORIT PN 4 is a steam activated carbon that can be used in a large range of applications, in which a carbon with a neutral reaction is required.

NORIT PN 4 is especially suitable for decolourisation of sugar and of vegetable oils and fats.

TYPICAL ANALYSIS:

Moisture (as packed) (%)	2
Molasses number (NORIT method)	525
Methylene blue adsorption (g/100 g)	11
Iodine adsorption (mg/g)	750
Total internal surface area according to B.E.T. (m ² /g)	650
Ash-content (%)	7
pH (normal range)	6-7

Particle size:

> 150 micron (mesh.100) (%)	5
> 74 micron (mesh.200) (%)	20
> 44 micron (mesh.325) (%)	37
> 10 micron (%)	80
Bulk density (tamped) (g/l)	490

NORIT PN 4 meets the requirements of foodgrade activated vegetable carbons, described in the U.S. Food Chemicals Codex. (2nd Edition, 1972.)

PACKING:

NORIT PN 4 is supplied in valve sealed multiply paper bags, containing 20 kgs of activated carbon. In order to avoid damage during transport or handling, NORIT can supply unit loads of activated carbon, shrinkwrapped on pallets or in boxpallets. It is also possible to supply this grade in bulk.

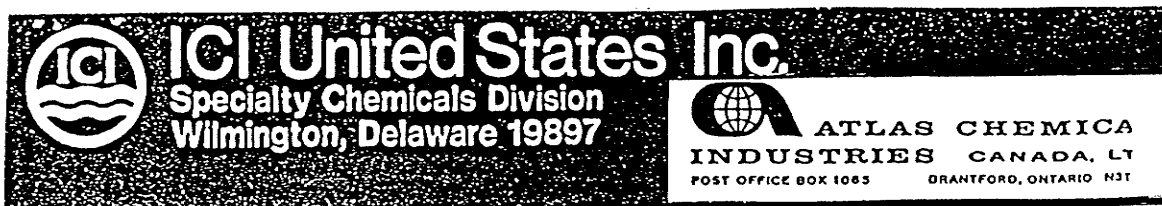


Activated carbon

P.O. Box 105, 3800 AC Amersfoort, The Netherlands
Phone 33-30454, telex 79040

20/05-77/21

APPENDIX III Continuation



POWDERED HYDRODARCO ACTIVATED CARBONS For Wastewater Treatment

HYDRODARCO H and HYDRODARCO C are low-priced, lignite-based powdered activated carbons made especially for municipal and industrial wastewater treatment.

HYDRODARCO H is suited for most powdered carbon uses. HYDRODARCO C is suited for applications where greater adsorptive capacity is needed to remove toxic compounds, dyes, detergents or refractory organics from wastewaters.

GENERAL CHARACTERISTICS

HYDRODARCO H and HYDRODARCO C are made by a special heat and steam activation process to assure optimum pore structure, pore volume and absorption of pollutants from wastewater.

Both carbons have high bulk densities, greater than 40 lbs. per cu. ft., and settle readily so that costly polymers or special equipment are not needed to trap carbon particles. Less storage space is needed for higher bulk density carbons. Both wet readily and go into suspension easily with a minimum of dusting.

TYPICAL PROPERTIES

	HYDRODARCO H	HYDRODARCO C
Particle Size, Min. % -325 mesh	70	70
Tamped Density, g/ml	0.70	0.70
Lbs./cu. ft.	44	44
Surface Area, M ² /gm	475	550
pH	10.5	10.5
Molasses RE, dry basis	40	95
Water Solubles, %	3.5	5.5

SHIPPING

HYDRODARCO H and HYDRODARCO C are available in bulk quantities, in 50-pound bags or bags in cartons.

Rev. February, 1976

**DARCO® KB POWDERED ACTIVATED CARBON
FOR PURIFICATION APPLICATIONS REQUIRING
HIGH ADSORPTIVE POWER and MINIMUM CARBON DOSAGE**

USES

Antibiotics	Pharmaceuticals
Dye intermediates	Plasticizers
Foods	Protein hydrolysates
Lactose	Sugar, liquid
Methionine	Vinegar
Molasses, blackstrap	Vitamins
Monosodium glutamate	Wine

The high bulk density of DARCO KB permits long filter cycles and reduces retention losses in the filter cake; generally, as little as one pint of liquid per pound of carbon is retained in the cake.

Moisture content (maximum as packed)	33%
Water-solubles (maximum; determined by 4 leachings with boiling water)	1%
Acid-solubles (approximate; determined by leaching with 1:1 hydrochloric acid)	2%
Ash (normal range)	3 to 6%
pH of water extract (normal range).	4.5 to 6.5
Bulk density, lbs./ft. ³ (determined by 30-minute tamping test)	26 to 32
Mesh size (approximate) through 100-mesh screen.	95%
through 325-mesh screen.	50%
Filterability (maximum; with water) 1.0 sec./ml./cm. of depth of filter cake	
Wettability	excellent

Net weight	40.0 pounds
Gross weight	41.57 pounds
Volume	2.111 cubic feet

APPENDIX IV

Type of Questionnaire used for Sensory Evaluation:

Name _____ Date _____
 Product _____

Taste these samples and check how much you like or dislike each one.

Code _____	Code _____	Code _____
<input type="checkbox"/> Like Extremely	<input type="checkbox"/> Like Extremely	<input type="checkbox"/> Like Extremely
<input type="checkbox"/> Like Very Much	<input type="checkbox"/> Like Very Much	<input type="checkbox"/> Like Very Much
<input type="checkbox"/> Like	<input type="checkbox"/> Like	<input type="checkbox"/> Like
<input type="checkbox"/> Moderately	<input type="checkbox"/> Moderately	<input type="checkbox"/> Moderately
<input type="checkbox"/> Like Slightly	<input type="checkbox"/> Like Slightly	<input type="checkbox"/> Like Slightly
<input type="checkbox"/> Neither Like	<input type="checkbox"/> Neither Like	<input type="checkbox"/> Neither Like
<input type="checkbox"/> nor Dislike	<input type="checkbox"/> nor Dislike	<input type="checkbox"/> nor Dislike
<input type="checkbox"/> Dislike Slightly	<input type="checkbox"/> Dislike Slightly	<input type="checkbox"/> Dislike Slightly
<input type="checkbox"/> Dislike	<input type="checkbox"/> Dislike	<input type="checkbox"/> Dislike
<input type="checkbox"/> Moderately	<input type="checkbox"/> Moderately	<input type="checkbox"/> Moderately
<input type="checkbox"/> Dislike	<input type="checkbox"/> Dislike	<input type="checkbox"/> Dislike
<input type="checkbox"/> Very Much	<input type="checkbox"/> Very Much	<input type="checkbox"/> Very Much
<input type="checkbox"/> Dislike	<input type="checkbox"/> Dislike	<input type="checkbox"/> Dislike
<input type="checkbox"/> Extremely	<input type="checkbox"/> Extremely	<input type="checkbox"/> Extremely

Comments:

APPENDIX V

Analysis of variance for the appearance of the apple slices blanched in recycled water

Source of Variation	df	Sum of Squares	Mean Square	F	F(tabulated)	
					5%	1%
Total	179	724.19				
Samples	9	334.36	37.15	16.50**	2.50	3.68
Judges	17	45.29	2.66	1.18	1.70	2.10
Error	153	344.54	2.25			

Tuckey's Test

The Standard Error (SE) = $\sqrt{2.25/18} = 0.35$

The Least Significant Difference (LSD) = $1.89 \times 0.35 = 0.66$

F(Tabulated) and LSD were calculated using the Tables presented by O'Mahony (1986).

APPENDIX VI

Analysis of Variance (ANOVA) for the Yield of Apple Slices blanched in various simulated solutions.

Source of Variation	df	Sum of Squares	Mean Square	F	F(Tabulated)	
					5%	1%
Total	9	9.76				
Samples	4	9.26	2.32	19.33**	3.63	6.42
Replicates	1	0.03	0.03	0.25	5.12	10.56
Error	9	0.47	0.12			

Tuckey's Test (5% level)

The Standard Error (SE) = $\sqrt{0.12/2}$ = 0.25

The Least Significant Difference (LSD) = 6.42×0.25 = 1.61

Any two sample means that differ by 1.61 or more are significantly different at the 5% level.

F(Tabulated) and LSD were calculated using the Tables in O'Mahony (1986).

APPENDIX VII

Analysis of Variance (ANOVA) for the flavor and appearance of the apple slices blanched in various simulated blanch solutions

ANOVA for flavor

Source of Variation	df	Sum of Squares	Mean Square	F	F(Tabulated)	
					5%	1%
Total	139	688.54				
Treatments	4	337.18	84.30	43.23**	2.44	3.47
Judges	13	113.74	8.75	4.49**	1.80	2.28
Error	122	237.62	1.95			

Tukey's Test

The Standard Error (SE) = $\sqrt{1.95/28} = 0.26$

The Least Significant Difference (LSD) = $2.29 \times 0.26 = 0.60$

ANOVA for appearance

Source of Variation	df	Sum of Squares	Mean Square	F	F(Tabulated)	
					5%	1%
Total	69	173.50				
Treatments	4	97.60	24.40	27.42**	2.55	3.70
Judges	13	29.50	2.27	2.55**	1.91	2.48
Error	52	46.40	0.89			

Tukey's Test (5% level)

The Standard Error (SE) = $\sqrt{0.89/28} = 0.17$

The Least Significant (LSD) = $2.39 \times 0.17 = 0.41$

F(Tabulated and LSD were calculated using the Tables presented by O'Mahony (1986)

APPENDIX VIII

Analysis of Variance (ANOVA) for the flavor of apple of apple slices blanched in simulated and PAC-treated solutions

Source of Variation	df	Sum of Squares	Mean Square	F	F(tabulated)	
					5%	1%

Total	119	375.32				
Treatments	4	52.03	13.00	6.22a**	2.46	3.51
Judges	11	108.22	9.84	4.71a**	1.88	2.43
Replicates	1	0.20	0.20	0.10a	3.94	6.90
Interactions						
TxJ	44	98.57	2.24	0.90	1.70	2.15
TxR	4	5.84	1.46	0.59	2.62	3.87
JxR	11	18.70	1.70	0.42	1.90	2.51
Error	44	91.76	2.09			

a) Calculated using combined error variance 2.09 with 103 degrees of freedom.

Tuckey's Test (5% level)

The Standard Error (SE) = $\sqrt{2.09/24}$ = 0.30

The Least Significant Difference (LSD) = 2.43×0.30 = 0.73

F(Tabulated) and LSD were calculated using the Tables presented by O'Mahony (1986)

APPENDIX IX

Analysis of Variance (ANOVA) for the appearance of
of the apple slices blanched in simulated and PAC-treated
solutions

Source of Variation	df	Sum of Squares	Mean Square	F	F(tabulated)	
					5%	1%
Total	119	806.20				
Treatments	4	126.28	31.58	19.85**	2.58	3.78
Judges	11	147.00	13.36	8.40**	2.01	2.68
Replicates	1	0.13	0.13	0.08	4.06	7.24
Interaction						
TxJ	44	459.92	10.45	6.57**	1.64	2.03
TxR	4	0.79	0.20	0.13	2.58	3.78
JxR	11	2.07	0.19	0.12	2.01	2.68
Error	44	69.99	1.59			

Tuckey's test (5% level)

The Standard Error (SE) = $\sqrt{1.59/24}$ = 0.26

The Least Significant Difference (LSD) = 2.43×0.26 = 0.63

F(Tabulated) and LSD were calculated using the Tables
presented by O'Mahony (1986)