The colour degradation of pear and apple juice concentrates

AP008

John Quill
Ardmona Fruit Products Cooperative
This report is published by the Horticultural Research and Development Corporation to pass on information concerning horticultural research and development undertaken for the Apple & Pear Industry.

The research contained in this report was funded by the Horticultural Research and Development Corporation with the financial support of the Ardmona Fruit Products Cooperative.

All expressions of opinion are not to be regarded as expressing the opinion of the Horticultural Research and Development Corporation or any authority of the Australian Government.

The Corporation and the Australian Government accept no responsibility for any of the opinions or the accuracy of the information contained in this Report and readers should rely upon their own inquiries in making decisions concerning their own interests.

Cover Price $20.00

HRDC ISBN 1 86423 139 4

Published and Distributed by:

Horticultural Research and Development Corporation
Level 6
7 Merriwa Street
Gordon NSW 2072

Telephone: (02) 418 2200
Fax: (02) 418 1352

© Copyright 1996
INTRODUCTION

One of the major problems confronting the producers of apple and pear juice concentrate is the darkening of juice colour during manufacture, storage and distribution. The colour degradation is due in part to polyphenol oxidation. This oxidation is due to the action of polyphenol oxidase that occurs naturally in the fruit, and can occur at any stage in the process. Traditional processes have gone to great lengths to reduce the oxidation by various methods, such as chemical inhibition, using agents like ascorbic acid or sulphites. Other processors use inert gas blanketing of the mash tanks and fruit press to reduce the oxidation.

Such methods are successful in producing a light coloured single strength juice for bottling or canning, etc., but not all polyphenols are protected. (Spanos & Wrolstrad 1990). Problems occur if this type of juice is concentrated and subsequently stored. During storage the colour development continues due to the polymerisation of phenolic compounds and the Maillard reaction, and the concentrate subsequently darkens to unacceptable levels. The rate of darkening is related to storage temperature and degree of concentration. (Toribo & Lozano 1986) (Beveridge & Harrison 1984) This darkening poses particular problems for processors exporting concentrate to distant destinations especially if in such transport the product is exposed to high temperatures. Product leaving Australia in a state quite acceptable to the customer rapidly deteriorates to an unacceptably dark colour and poor flavour.

The object of this project was to attempt to find a method of juice production that produces a juice that has good initial colour as well as long term colour stability as a concentrate. Several variations to the current commercial process were tried. The first method used was to pasteurise the fruit at the mashing stage, thus denaturing the polyphenol oxidase. The second method attempted to remove all the precursors to browning of the juice at the initial stages of processing, thus reducing colour degradation in the juice concentrate. The way this was attempted was to fully oxidise the mash at this stage. By fully oxidising the mash it was hoped to polymerise all the phenols to larger molecules. These larger molecules could then be removed by ultra filtration. The juice produced by this method should be more colour
stable as the precursors to oxidation have all been reacted and then removed. Not all colour degradation will be prevented as the process will have very little effect on Maillard browning.

**PASTEURISATION**

The first method of preventing polyphenol oxidase generated browning in juices attempted was to destroy the enzyme's activity by pasteurisation. Current commercial processes pasteurise the juice after pressing. In this case the fruit mash was pasteurised (90°C for 10 Min.) immediately after milling. The aim of this exercise was to attempt to denature the enzymes early in the process before any oxidation had occurred, and thus eliminate the use of anti-oxidants. After the pasteurisation step the mash was treated with the same enzyme combination as previous methods for one hour. The mash was then pressed using the Bucher Guyer press. The juice was then filtered using the ultra filtration procedure outlined above. The filtered juice was evaporated to 70.5° brix and stored at -12°C.

**OXIDISED PEAR JUICE TRIALS**

The second method was to fully oxidise the mash. Laboratory trials were conducted on pear mash to ascertain what effect the oxidation had on the juice colour. To be complementary with the commercial requirements of juice processors, the proposed process needed to allow for sufficient time at the mashing stage, for the enzymatic liquefaction of the juice. This process uses enzymes to break down the structure of the fruit to allow free and easy release of juice.

The mash was held at 50°C for 120 Min. Air was bubbled through the mash at 300 ml. per Min per litre of mash. This combination produced sufficient oxidation of the mash. Also added to the mash at this stage was an enzyme mixture at a concentration of 0.004%. The enzyme used has a combination of pectinase and cellulase activities, which improves the juice yields and the ease of pressing.

The mash produced by the above conditions was very dark coloured, was almost totally liquefied, and produced a black precipitate.

To produce this material in larger quantities, sufficient for ultra filtration runs, a similar treatment was trialled commercially in the
juice plant at Ardmona Fruit Products in Mooroopna Vic. Instead of bubbling air through the mash, the mash was held in tanks for the first hour, then transferred to a Rotary press (Bucher-Guyer HP 5000), and rotated inside the press for the second hour. The design of these units allows for intimate mixing of the mash and air.

The mash was then pressed in the usual manner, then pasteurised (93° for 15 sec.), screened using a Kason vibrating screen (500 micron mesh), then transferred to the ultra filtration feed tanks. At this stage the juice was further treated with pectinase enzymes as well as an amylase enzyme. This was done to facilitate the ultra-filtration process. The juice was held at 50°C for a further hour to allow the enzymes to function. It was then filtered. The plant is equipped with 13 mm. diameter tubes using a membrane having a nominal molecular weight cut off of 18,000. Trans membrane pressure was 350 Kpa. Juice velocity was 2.3 m. sec⁻¹.

Juice from this process was darker in colour than juice from the standard process (absorbance @ 425 nm. of 0.350 compared with the standard of approx. 0.270) This indicated that although most of the coloured material was being retained by the ultra filtration modules some was passing through with the clear juice.

Juice from this process was then concentrated to 70.5° brix, using a Unipectin triple effect evaporator, then stored @ -12°C.

**COLOUR STABILITY TESTING**

To rapidly estimate the colour stability of the juice concentrate, the colour deterioration was measured in the juice at 80°C. The concentrate was placed in 70 ml. sterile bottles then heated to 80°C using a Sharp R.7370 microwave oven. The 70 ml. jars were then immediately transferred to a Watson Victor model 71 incubator set at 80°C. At approximately 30 Min intervals a sample of the concentrate was removed from the bottles and diluted 50% by weight with distilled water. The absorbance of the concentrate was then measured at 425 nm. using a 10 mm. cell in a Phillips PU 8625 UV/Vis spectrophotometer. The absorbance readings were then plotted against time. Regression analysis was carried out on the results.

**RESULTS**

Graph one shows the results of the 80° colour degradation trials performed on concentrate from the standard Ardmona
procedure, the oxidised mash juice and the pasteurised mash juice. Regression analysis on the results gives the following relationships:

For Oxidised Mash \( \text{Abs.} = 0.961 + 0.0025t \quad r^2 = .988 \)

For Standard Mash \( \text{Abs.} = 0.728 + 0.0037t \quad r^2 = .988 \)

For Pasteurised Mash \( \text{Abs.} = 0.670 + 0.0034t \quad r^2 = .994 \)

where \( \text{Abs.} = \) absorbance @ 425 nm. through @ 10 mm cell and \( t = \) time in Min.

If the "b" value is used to describe the rate of colour degradation, it can be seen the results from the standard process and the pasteurised mash juices were very similar. This means pasteurised mash juice would be of some advantage to producers of single strength juices because the product would be free from any trace of anti-oxidant, but, as it shows no sign of improved stability as a concentrate, it is of limited value to concentrate producers.

The results of the oxidised mash juice show a high initial colour but it showed a lower rate of degradation. Thus the oxidised juice was shown to be significantly more stable.

**Graph 1**

![Graph showing absorbance over time for different juices](attachment:graph.png)

**ABSORBANCE RESINS**

Because the initial colour of the concentrate produced using the oxidation process was relatively poor, even though the colour degradation was less, the concentrate is of limited commercial value to juice producers. To improve the initial colour a number of adsorbent resins were tested to evaluate the removal of colour from the oxidised juice. If some of the colour precursors have been removed by oxidising
the mash, and if further colour is removed by an adsorbent resin, then the initial colour of the juice should be good and the colour stability of the concentrate should remain high as well. To test this, juice was treated as outlined above, for the oxidised mash process. The juice was oxidised; ultra filtered, then passed through adsorbent resins. These resins were arranged in columns of 40 mm. I.D. with a resin volume of 325 ml. Several different resins were trialled, all with different properties. The resin required needed to remove colour without altering the chemical or nutritional composition of the juice. Of all the resins tried the final type selected was XAD-16 from Rhom and Haas. This resin has proved to be very good at removing juice colour, shows a reasonable resistance to irreversible fouling, and is relatively easy to regenerate or clean. When juice is first passed through these resins the resulting juice is practically colourless. The longer the run proceeds the darker the juice becomes. By varying the amount of juice passed through the resins between regeneration cycles, it is possible to produce a juice of practically any desired colour. The shorter the juice runs are before regeneration, then the lighter the colour of the resultant juice becomes. It was found that the amount of colour removed by the resins is related to the anti log of the volume of juice passed through the resin. Graph 2 shows the relationship between the volume of juice run through the resin and the amount of colour removed from the original juice.
The regression line in graph 2 is drawn using the expression:
\[ \log_{10} C_r = 0.258 - 0.026V, \]
where:
- \( C_r \) = colour removed from the original juice in absorbance units
- \( V \) = Volume of juice passed through the bed in bed volumes.

(\( r^2 \) for this relationship = 0.956.)

This process was then applied on a commercial scale using juice produced at Ardmona using the oxidised mash process. The juice was then decolourised using XAD-16 in a 500 litre column. The juice was then evaporated and stored as with the other trials. The concentrate was then tested for colour stability at 80°C. The results are compared with results obtained from the non decolourised oxidised juice and shown on graph 3. It can be seen from these results that the decolourised juice has an almost identical rate of colour development as the non decolourised juice. Both of these results are significantly better than results gained from non oxidised mash juice.
For the decolourised juice  
Abs. = 0.217 + 0.0028t \( (r^2 = 0.971) \)

For the non decolourised juice  
Abs. = 0.644 + 0.0027t \( (r^2 = 0.973) \)

where:  
Abs. = Absorbance @ 425 nm. using a 10 mm. cell  
t = time in minutes at 80°C

In the above equations it can be seen that the slope of the two curves is almost identical.

APPLE JUICE CONCENTRATE

Similar trials were conducted with apple concentrate production. As with the pear juice the mash was held in tanks for the first hour, then transferred to a Rotary press (Bucher-Guyer HP 5000), and rotated inside the press for the second hour. As with the pears also added to the mash at this stage was an enzyme mixture at a concentration of 0.004%. The mash was then pressed in the usual manner, then pasteurised \( (93^\circ \text{C} \text{ for } 15 \text{ sec.}) \), screened using a Kason vibrating screen (500 micron mesh), then transferred to the ultra filtration feed tanks. At this stage the juice was further treated with pectinase enzymes as well as an amylase enzyme. The juice was held at 50°C for a further hour to allow the enzymes to function. Ultra-filtration was carried out as in previous trials.
Juice from this process was then concentrated to 70.5° brix, using a Unipectin triple effect evaporator, then stored @ -12°C.

DISCUSSION

The results show that there is a significant reduction in the rate of colour development in both apple and pear juice concentrates that have been made from mash fully oxidised at the mashing stage. A typical "b" value for standard juice is 0.004; for pasteurised juice it is 0.0037; whereas for the oxidised juice it is 0.0027. Thus the stability of the concentrate has been increased by about one third to one half.

The juice produced by the oxidised mash process is initially too dark and is unacceptable for some markets. Work with absorbance resins has shown that the initial juice colour can be reduced to the desired level. By using a combination of these two processes a juice is produced that has both good initial colour and enhanced storage stability. Also this process eliminates the use of undesirable anti oxidants such as SO₂. The procedure is very compatible with existing juice process equipment. The time taken for oxidation at the fruit mashing stage of production corresponds to the time required for enzyming of the mash, so that no extra hold time is required. Thus this process should enable Australian apple and pear juice concentrate producers to be more competitive in export markets.
References

Beveridge T. and Harrison J.E. 1986 Pear Juice Production from Heated Pear Mashes J. Canadian Inst. Food Science and Technology vol. 19 No.1


Toribo J.L. & Lozano J.E. 1986 Heat Induced Browning of Clarified Apple Juice at High Temperatures Journal of Food Science vol. 51, no., 1