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**THESIS
MASTERS IN TECHNOLOGY
(BIOTECHNOLOGY & BIOPROCESS ENGINEERING)**

**OPTIMISATION
OF
TOMATO PASTE PRODUCTION, STORAGE AND USE**

BY CLAIRE FRANCES CAMPBELL

**SUPERVISORS: Dr J E Bronlund
& Dr L V Chong**

ABSTRACT

The manufacture of tomato products is one of the key activities of Heinz-Watties. The optimisation of tomato paste in terms of its production, storage and use is important to understand as it is the base ingredient to many of the 21 major food brands Heinz-Watties supply in New Zealand. This thesis describes the work carried out to characterise tomato paste products in terms of the quality and quantity, correlations that exist between variables, the process variability at Heinz-Watties Hastings and formulation using tomato paste.

This thesis has identified that tomato paste needs to be accurately characterised in terms of both quality and quantity. Characteristics which influence the quality of tomato paste are factors such as the flavour, sweetness and viscosity to which the °Brix, total solids and insoluble or soluble solids must be known. °Brix measurement is affected by insoluble solids (which scatter light) resulting in an inaccurate reading when employing the refractometer °Brix method. To solve this, the tomato paste must be centrifuged in order to separate the insoluble from soluble portion within the tomato paste.

Colour, acidity and microbial stability are also important quality characteristics of tomato paste. These are measured by specific tomato paste colorimetric methods, pH and Howard mould count methodologies respectively. The quantity of tomato paste produced or the amount to use within recipes has been identified in this thesis to be accurately measured by measuring the tomato solids, insoluble and soluble solids and °Brix. This is due to the tomato paste being made up of total tomato solids and water which can be further broken down into solids which are insoluble (fibrous) & solids which are soluble.

Several different methods were identified within the thesis for measuring total solids. The best method in terms of repeatability was identified to be the vacuum oven method, however due to the twelve hour wait prior to obtaining results coupled with the large amount of equipment needed this would be restricted to a lab environment. Within the factory processing environment the best total solids method to employ would be that of the microwave oven method. Further testing beyond the scope of this thesis would need to be completed to perfect the methodology.

Correlations between variables were also explored within this thesis, to save time and equipment usage within the processing environment or to give an indication of variables during production. For example specific gravity can be measured instead of total solids (as long as the insoluble solids portion is known) and with the use of correlations the other parameters can be predicted. Further experimental validation beyond this thesis, using Heinz-Watties tomato paste does need to occur prior to use.

Other correlations investigations were that of the variables during dilution. The °Brix levels and viscosity were found to not change linearly during dilution. Therefore, by constructing simple mechanistic models on the interactions of the °Brix levels and viscosity on the proportions of insoluble and soluble solids simple equations have been devised within this thesis to allow the prediction of these parameters after dilution.

The current process of producing tomato paste at Heinz-Watties was characterised to identify the extent and cause of process variability. This work showed that although total solids levels are well controlled, the ratio of insoluble solids to total solids is not. The cause of this was most likely due to poor control over the break process and the extent of enzymatic pectin hydrolysis that occurs. Some suggestions on online measurement options to enable better control of this were explored within this thesis, such as, measuring specific gravity using an online densitometer (Coriolis mass flow meter) and to use previously mentioned correlations to determine total solids. Or alternatively online viscosity by the use of a tubular viscometer or refractive index meter.

Further work should be carried out beyond this thesis to investigate how tomato ripeness and break processing conditions could be controlled to ensure reduced variability in the ratio of insoluble solids to total solids. This is the key to good control of tomato paste and diluted tomato paste viscosity.

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1.0 PROJECT OVERVIEW

Tomato paste is used as a base ingredient to many of the 21 major food brands Heinz-Watties supply and it is estimated at having an input value of \$4.8 million per annum in factories around New Zealand. At the Hastings site of Heinz-Watties, tomato paste is produced during the months of November to March (depending on harvesting of the tomatoes) and used all year round for products such as spaghetti, baked beans, soups, meat and pasta sauces. During the time tomato paste is not being used, it is stored aseptically in 200L drums outside, within the factory premises.

The optimal utilisation of the tomato paste is reliant on the following issues:

- i) The adequate control of the paste quality during paste manufacture.
- ii) The accurate recording of stock levels in terms of quantity and quality of the stored product
- iii) The appropriate calculation of the amount of paste used during the formulation of the final products.

Each of the aspects listed above are dependent on the accurate characterisation of the tomato paste that is produced. This requires appropriate measurement methods which are being used that are repeatable, have the accuracy needed and are also suitable for use in an industrial environment. If such methods are available then the stock levels would accurately reflect the amount of tomato paste ingredient is in storage and the manufacturing process could be better controlled to produce more consistent paste quality. In addition to this the most appropriate measure of the paste composition could be used to calculate the amount of paste needed to achieve the required formulated product functionality (in terms of such aspects as flavour and colour).

The specific aims of this project were to firstly determine the most appropriate measurement methods for complete tomato paste characterisation. These methods were then used to assess the degree of variability of tomato paste production during the 2000 season at Heinz-Watties Australasia, King Street, Hastings. The project also investigated how physical and compositional properties of tomato paste are correlated and how they can be related to the functionality of formulated products.

2.0 REVIEW OF LITERATURE

In order to complete this project, an understanding of the tomato and tomato paste compositional, chemical and physical properties is needed. Factors which affect these properties include enzymatic activity occurring during ripening and processing and the physical changes in the tomato paste during production. An understanding of the concept of quality of both of tomatoes and tomato paste is also needed. The relevant information available in the literature is summarised below for each of these aspects.

2.1 INTRODUCTION

The tomato has a common place in the home, whether it be in the whole fresh form or in a processed form as in soups and sauces. On the world scale, it was the second largest vegetable crop in 1998 (Hayes *et al.*, 1998). Hayes *et al.* (1998) states that world production exceeded 70 million tonnes in 1993. The tomato is often referred to as a vegetable but botanically it is classified as a fruit of the Solanaceae or potato family, which originates from the Central and South America (Davies & Hobson, 1981). Within the Solanaceae family, the tomato takes the line of the genus *Lycopersicon* which is then subdivided into two groups (*Eulycopersicon* and *Eriopersicon*) which bear fruit of the red-yellow and purple-green colours respectively. The tomato *Lycopersicon esculentum* cultivated and used today was developed from *L. eulycopersicon*. The natural descendant of the subgenus *Eulycopersicon* is quite hard to follow; however, through native names it has been predicted that the 'original domestication' of the humble tomato took place in Mexico (Davies & Hobson, 1981).

Tomatoes were introduced into Italy around 1544 (Goose & Binsted, 1973). These were early varieties of tomatoes which were a golden-yellow colour and hence the use of the name 'Pomi d'oro', meaning the golden apple (Goose & Binsted, 1964; Goose & Binsted, 1973; Davies & Hobson, 1981).

From Italy the tomato made quick succession into other European countries such as England, Spain and France, then slowly around the world (Goose & Binsted, 1973). Initially around the time of the 16th century, the tomato was not used as a food product but was considered a decorative object and having medicinal purposes. In certain regions of the world, even up to the beginning of this century the tomato was considered poisonous (Goose & Binsted, 1964, 1973; Davies & Hobson, 1981). It was only around the middle of the 18th century before the tomato fruit was made a part of the human diet (Davies & Hobson, 1981).

During cultivation of the tomato along the lands in Italy bordering the Mediterranean Sea, the colour changed from yellow to red. It was also found that the unusual composition of 'seeds surrounded by gummy material, pulpy flesh and acidic juice' made it ideal for stirring and mashing into a puree. This puree went on to make up the basis of the many pasta dishes, which now make up the bulk of the Italian diet. From this concept it was found that if ripe tomatoes were crushed and spread out on stone slabs in the hot sunshine – they concentrated to a paste (Goose & Binsted, 1964). This paste then had salt added to it as a preserving agent so the paste could then be reconstituted in the winter months when no fresh fruit were present. Goose & Binsted (1973) state that this basic method is still in use in some areas of Southern Italy and Southern Europe by peasant families who have passed on the knowledge from generation to generation. Goose & Binsted (1973) attribute this practise as being the beginnings of the present day tomato paste industry. Commercial tomato paste production did not really begin until after the last world war (1947) due to the need of providing preserved foods for those in the field that needed it (Goose & Binsted, 1973).

Following the basic concept used by Italian peasant families, tomato paste today is now produced by the evaporation of water and hence concentration of tomato pulp from which the skins and seeds have been removed. Today tomato paste is not preserved by the addition of salt but specially designed packaging prevents spoilage and allows the storage and later use of tomato paste for formulation into other products at the factory or as an ingredient in kitchens at home.

2.2 DEFINITIONS

There are several terms used in the tomato paste industry that can cause confusion, especially in terms of concentrated products. Hayes *et al.* (1998) suggest that definitions cited in Goose & Binsted (1973) and Gould (1992) provide the clarity.

- *Tomato pulp* refers to the crushed tomatoes either before, or after the removal of skins and seeds.
- *Tomato juice* refers to the juice from whole crushed tomatoes from which the skins and seeds have been removed and which has been subject to fine screening, and is intended for consumption without dilution or concentration.
- *Tomato paste* is the product resulting from the concentration of tomato pulp, after the removal of skins and seeds, and contains 24% or more natural tomato soluble solids (NTSS). Tomato paste, which is marketed to the consumer in small packs and sold as a condiment, may also be described as tomato puree.
- *Tomato puree* is the term applied to lower concentrations of tomato paste (containing 8% to less than 24% NTSS). Unfortunately, tomato puree in the US can also be called 'tomato pulp'. A further complication in the US is that if the tomato puree satisfies certain legislative criteria it can also be called 'concentrated tomato juice'.
- *Tomato serum* is tomato juice that has been filtered or centrifuged to completely remove suspended solid material.
- *Pulp* refers to the suspended solid material in tomato juice, puree or paste which can be separated by centrifugation.
- *Tomato syrup* is tomato serum, which has been concentrated.

2.3 COMPOSITION

2.3.1 *COMPOSITION OF TOMATOES*

2.3.1.1 *Structure and Major Constituents of the Tomato Fruit*

Tomatoes have a unique structure. Davies and Hobson (1981) showed a simple model of the tomato with all its major components, which can be seen below as Figure 2.1.

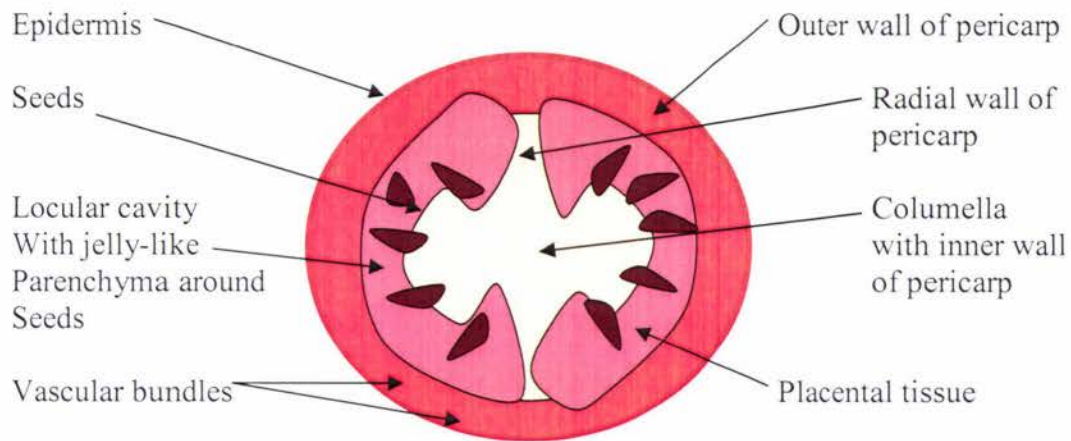


Figure 2.1 Cross section of a tomato fruit

The tomato is classified botanically as a fruit. It is known as a berry 'since the seeds are formed within a fleshy mesocarp' (Villari *et al.*, 1994). Tomatoes have three main parts; the skin, the pericarp (layer inside the skin) and the locular cavity (middle section). Within the skin lie four to five layers of cells under a thin cuticle (Villari *et al.*, 1994). The pericarp is made up of cells, which during maturation grow larger in size and thinner-walled, making the tomato feel soft. Within the locular cavity the seeds are encased in soft tissue known as parenchyma. The increase in the parenchyma or jelly-like material and the change to a pinkish colour in this locular region is also an indication of the tomato ripening. The cell walls within the tomato are made up of α -cellulose, pectins, hemicellulose and some protein.

The total solids content (TS) of a tomato is approximately 5-7% by weight, excluding seeds and skin (Barrett *et al.*, 1998). Of the solids, 80-90% is made up of water soluble solids (WSS) which are low molecular weight compounds such as sugars, organic acids, amino acids, soluble pectins and mineral salts. Water insoluble solids (WIS) make up the remaining fraction of total solids and are higher molecular weight compounds found in the cell wall and middle lamella regions. The WIS are the components which determine paste consistency (Barrett *et al.*, 1998). Alcohol-insoluble solids (AIS) are considered a measure of ripeness and textural properties in tomatoes and other horticultural crops (Barrett *et al.*, 1998). For the average tomato, AIS consists of 6% protein, 7% pectic substances, 4% hemicellulose and 6% cellulose. The general composition of an average tomato is shown in Table 2.1 below.

Table 2.1 Composition of a Tomato
(Basis: clean, ripe sound tomatoes) (Chambers, 1994).

Property	% (w/w)
Water	93.4
Carbohydrate	4.7
Glucose	1.29%
Fructose	1.55%
Sucrose	0.02%
Pectic	0.32%
Cellulose	0.25%
d-xylose	0.26%
Arabangalactan	0.31%
Protein	1
Nutrients	0.4
Ash	0.2
Fat	0.03
Vitamins & Minerals & other	0.27

Note: included in **other** are organic acids and carotenoid fractions along with other chemical substances found in tomatoes. These make up a small but important fraction of the chemical constituents and characteristics of the tomato fruit.

2.3.1.2 *Water*

Water makes up a substantial proportion of the tomato fruit (93.4%). The high water content and thus high water activity, provides an ideal environment for any micro-organisms that may spoil the fruit, especially if ideal temperature conditions are also reached, as is often the case during the summer months of processing. Therefore care must be taken when handling the tomato fruit, this is usually carried out by processing very soon after the tomatoes are harvested (ideally within the same day) (Goose & Binsted, 1973; Gould, 1974; Gould, 1992; Chambers, 1994).

2.3.1.3 *Carbohydrates*

This portion consists of reducing sugars and polysaccharides. The main reducing sugars present are fructose, glucose and sucrose (Goose & Binsted, 1973; National Food Processors Association, 1992; Chambers, 1994). The ratio of the isomers of d-fructose to d-glucose (1.0 to 1.2%) can also vary between fruit (National Food Processors Association, 1992).

During the ripening of tomatoes, metabolic reactions are responsible for the increase in amounts of sugar (pectin converting to sugar), thus enhancing the flavour and increasing the soluble solids content of tomatoes. The soluble solids content is made up of nearly all sugar and hence the sugar concentration in the tomato is used as a measure of the quality of the tomato paste produced. The sugar however is prone to fermentation, initiated by the presence of an agent (bacterial in the case of tomatoes). This fermentation is undesirable as it leads to the production of gases and off-flavours that can be identified as 'rotten, going-off tastes and smells'. As a consequence the identification and prevention of bacterial growth and fruit spoilage is paramount to ensure a good tomato paste end product (Goose & Binsted, 1973; Gould, 1974; Gould, 1992; Chambers, 1994; Morgan, 1996).

Prevention is carried out by an inspection of each truckload of harvested raw tomato fruit entering the Heinz-Watties plant. If the core sample of fruit examined has a high proportion of bacterial or fruit rot damage, the whole truckload is discarded (Quality Inspectors, Heinz-Watties, 1999).

The polysaccharides within the tomato provide the structure of the cell wall. The main polysaccharides are cellulose, hemicellulose and pectic substances. Cellulose is the most abundant polysaccharide and is responsible for the firmness of the cell wall. It is made up of glucose units connected by stable β -glycosidic bonds in a long molecule structure, making it insoluble in water and dilute acids or bases, yet soluble in Schweitzer's reagent (McGinnis, 1971). Hemicellulose is a carbohydrate polymer with no chemical similarity to cellulose. Hemicellulose and cellulose are however usually found together and are both responsible for maintaining the firmness within the structure of the cell wall (Meyer, 1961; National Food Processors Associations, 1992; Chambers, 1994).

The group of pectic substances which also resides in the cell wall are responsible for a number of functions rising from cementing cell wall layers, to ripening of the fruit. The group consists of pectin, pectic acid, pectinic acid and protopectin. Pectin is made up of mixture of D-galacturonic acid units and methyl esters of galacturonic acid and is responsible for the bonding of the layers between the cell walls. Pectic acid is mostly made up of α -D-galacturonic acid units while pectinic acid is similar with a few of the carboxyl groups esterified. The form of the pectic substance is dependent on the stage of maturity of the tomato fruit. In immature fruit, protopectin exists, which during the stages of ripening changes to colloidal pectin via the enzyme protopectinase then to pectic acid via pectin methyl esterase. Throughout this conversion, the tomato fruit becomes increasingly riper as indicated by the degradation of the cell wall, hence increasing softness of the tomato (Meyer, 1961; Chambers, 1994; Morgan, 1996).

Pectic substances can continue to degrade in the cell wall if microbial infection (such as bacterial rot) or damage such as bruising, occurs in the raw material. If this occurs the raw material becomes too soft and undesirable for processing. Alternatively the degradation of the pectic substances can continue if the enzymes are not controlled during processing. This leads to a decrease in the final viscosity of the tomato paste produced (Goose & Binsted, 1973; Gould, 1992; Chambers, 1994).

2.3.1.4 Protein and Fat

The protein and fat content within tomatoes do not play any major functional roles within the tomato fruit and exist in small proportions in comparison to the carbohydrates and water present. The predominant amino acids that have been found to be present in tomatoes (in descending order of content) are as follows; glutamic acid, aspartic acid, lysine, leucine, serine, alanine, threonine, valine, arginine and isoleucine. Others include glycine, phenylalanine, proline, histidine, tyrosine, tryptophan, methionine, cystine. The fat content consists mainly of triglycerides and fatty acids with no cholesterol present (Gould, 1992; National Food Processors Association, 1992; Chambers, 1994).

2.3.1.5 Nutrients, Vitamins and Acids

The nutrient content of tomatoes, even though it is a small proportion, includes all the essential trace elements required for cell growth and maintenance within a biological material. Nutrients present in tomatoes, (in descending order of concentration) are as follows; potassium, chloride, phosphorus, magnesium, calcium, sulphur, sodium, iron, zinc, copper, manganese and selenium (Gould, 1992; National Food Processors Association, 1992; Chambers, 1994).

The vitamin content of tomatoes is also very low, but tomatoes are a significant source of Vitamin B and C. From the transportation from the field and processing, the vitamin content may decrease if the fruit undergoes rough treatment, as vitamins are usually in a form that can be readily oxidised if in contact with oxygen and heat (Goose & Binsted, 1973; Gould, 1992; National Food Processors Association, 1992; Chambers, 1994).

Organic acids are present in the tomato in small quantities, but are important to the flavour of the tomato fruit. Citric acid is the main organic acid, making up 60-80% of the total acid

content of tomatoes with malic acid (10-20%) and very small quantities of acetic, lactic and fumaric acids (1-2%) making up the remainder of the total acid content. (Meyer, 1961; National Food Processors Association, 1992; Gould, 1992; Chambers, 1994). The tomato provides the following source of nutrients compared with the United States and the New Zealand recommended dietary allowances (see Table 2.2).

Table 2.2. Daily dietary allowances of nutrients for USA and NZ

Nutrient/ Vitamin (mg per 100g)	Quantity within the Tomato per 100g	US Recommended Dietary Allowance	NZ Recommended Dietary Allowance	
			MEN	WOMEN
Protein	0.91%	65.0 g	35	45
Vitamin A	1500 (i.u.)*	5000.0 (i.u.)	750 µg retinol equivalent	750 µg retinol equivalent
Vitamin C	14.5 mg	60.0 mg	40 mg	30 mg
Thiamine	0.049 mg	1.5 mg	1.1mg	0.8mg
Riboflavin	0.025 mg	1.7 mg	1.9 mg	1.2 mg
Niacin	0.75 mg	20.0 mg	19 mg	13 mg
Calcium	32 mg	1.0 g	800 mg	800 mg
Iron	0.5 mg	18.0 mg	150 mg	120 mg
Vitamin D	-	400.0 (i.u.)	-	-
Vitamin E	-	30.0 (i.u.)	-	-
Vitamin B ₆	-	2.0 mg	1.3-1.9 mg	0.9-1.4 mg
Folic Acid	5.4 mg	0.4mg	200 µg	200µg
Vitamin B ₁₂	-	6.0µg	2.0 µg	2.0 µg
Phosphorus	18 mg	1.0 g	1.0 g	1.0 g
Iodine	-	150.0 µg	150 µg	120 µg
Magnesium	12 mg	400.0 mg	320 mg	270 mg
Zinc	-	15.0 mg	12 mg	12 mg
Copper	-	2.0mg	-	-
Biotin	1.8 mg	0.3 mg	-	-
Pantothenic Acid	0.23 mg	10.0 mg	-	-

(The 1998 New Zealand Dietetic Association Inc. Clinical Handbook, 1988; National Food Processors Association, 1992)

i.u. represents international units

* represents content is % US RDA

2.3.1.6

Carotenoids and Chlorophylls

Tomatoes are characterised by a vibrant red colour when ripe, which is due to the carotenoid content located within the chromoplasts of the tomato cells. Colour development occurs because the carotenoid content is accompanied by a quantity of chlorophyll, approximately by the ratio of 3-4 parts chlorophyll to one part carotenoid. As the tomato ripens the ratio of chlorophyll to carotene decreases, hence the development from a green colour to a red colour. Lycopene is the specialised carotenoid that is responsible for the red-colour within the ripe tomato fruit (Refer to the 5.4 Colour - Lycopene section) (National Food Processors Association, 1992; Gould, 1992; Chambers, 1994; Tikellis, 1998; Heinz-Watties Australasia, 1999).

2.3.2 COMPOSITION OF TOMATO PASTE

Tomato paste consists of crushed and disintegrated pericarp tissue that is suspended in a clear serum (Hayes *et al.*, 1998). Hayes *et al.* (1998) states that of the 5-10% dry matter in the whole ripe fruit about 75% is soluble. However this is dependent on the tomato variety and conditions and region of cultivation and harvesting. At Heinz Watties, Hastings, the average tomato paste consists of 24-26% total solids (Heinz Watties Analytical Bench Manual, 1999). The composition of tomato paste is shown in Table 2.3.

Table 2.3: Composition of Tomato Paste

(Basis is on an average composition of tomato paste of 28-30% soluble solids (tomato pulp concentrated approximately 5.6 times)) (Chambers, 1994)

Property	% (w/w)
Water	69.0
Carbohydrate	22.5
glucose	7.24%
fructose	8.72%
sucrose	0.13%
pectic	1.81%
cellulose	1.39%
d-xylose	1.47%
arabangalactan	1.74%
Protein	4.1
Nutrients	1.0
Ash	2.9
Fat	0.5
Vitamins & Minerals & other	0.05

Note: included in **other** are the organic acid, carotenoid fractions along with other chemical substances found in tomato paste. These make up a small but nutritionally important fraction of the chemical constituent of tomato paste.

2.3.2.1 *Water*

Tomato pulp has been concentrated into tomato paste, hence reducing the water content from 93.4% to 69%. Most of this water is bound up within the tomato paste fibres hence the paste has a low water activity. The low water activity together with the aseptic packaging, (very low oxygen content and use of sterilised packaging equipment) of the tomato paste provide an environment unsuitable for the growth of micro-organisms that may spoil the paste (Chambers, 1994; Fennema, 1985).

2.3.2.2 *Carbohydrates*

This portion consists of the reducing sugars and polysaccharides of the tomato pulp, now in a more concentrated form (22.5%) within the tomato paste. The sugar present is still prone to fermentation, but this is unlikely after sterilisation of the tomato paste. Spoilage may still occur if contamination occurs before filling, or if holes exist in the storage bag. If this occurs the product is discarded as it cannot be used for inclusion in tomato products elsewhere in the plant (Goose & Binsted, 1973; Gould, 1974; National Food Processors Association, 1992; Gould, 1992; Chambers, 1994).

Caramelisation is another reaction that can occur with the concentrated fructose and glucose. Here the sugars undergo dehydration forming anhydrosugars, a chemical reaction which is a direct result from the heating of the sugars, during the evaporation or sterilisation stages of the process. Caramelisation is recognised as product spoilage and is noticeable in the final product. It is characterised as brown or burnt pieces with a burnt flavour due to the condensation reaction which polymerizes unsaturated ring systems. Correct control of the processing conditions can decrease the chance of this occurring. Evaporation at a lower temperature under vacuum and a shorter residence time in the sterilisation stage are some possible approaches taken by industry to avoid this problem (Fennema, 1985; Chambers, 1994).

The cellulose and hemicellulose content makes up only a little of the fibre in the tomato paste. This is because it exists mainly in the skin and seeds of the tomato fruit which are removed in the first stages of production. Pectin substances make up the majority of the fibre content and contribute to the overall viscosity of the final product (Goose & Binsted, 1974; National Food Processors Association, 1992). The enzymes which break down the pectin structures are inhibited by the heat treatment within the process (break process), hence the viscosity of the final product should not decrease unless contamination of the paste occurs. The activation of the enzymes occurs to different extents depending on the type of paste produced. Although the viscosity can be different between different types of pastes, the actual viscosity of one type of paste should still remain constant upon storage.

2.3.2.3 Protein

The level of protein in tomato paste is the same as in the tomato fruit, however in a more concentrated and sometimes, in a different conformational form due to the concentration process the tomato pulp undergoes. The conformational changes that take place are due to heat. This also results in a change in the protein's properties. Changes such as the hydrolysis of peptide bonds and modification of the amino acid chains are dependent on the intensity of heat treatment as well as the duration. As a result different properties can result depending on the type of tomato paste produced. The water activity, pH and concentration of other molecules also have an effect on how the properties of the proteins changes during processing (Fennema, 1985; Chambers.1994).

2.3.2.4 Nutrients

Overall the concentration of nutrients in tomato paste increases through the concentration process. However due to the structure and susceptibility of some of the nutrients to heat treatment, a fraction of the nutrients are destroyed, so that they are not concentrated to the same extent as the tomato pulp itself (approximately 5.6 times). However once the tomato paste is packed aseptically, it is expected that no nutrient losses occur, due to the lack of oxygen required for oxidative reactions (Fennema, 1985; Chambers, 1994).

2.3.2.5 Vitamins and acids

Due to the structure and form of some of the vitamins, not all are present in the fully concentrated amount. For example some of the vitamin C present in the tomato pulp is lost through oxidation reactions when in contact with oxygen and heat during the process, but the remainder is concentrated (National Food Processors Association, 1992; Chambers, 1994). Other water-soluble vitamins, such as thiamine, riboflavin, folic acid and vitamin B₁₂, behave similar to that of vitamin C. In each case the heating stage of the process step is the most destructive (Fennema, 1985; Chambers, 1994).

Organic acids such as citric acid are concentrated. Due to their low pH, spoilage of the tomato paste is prevented as the acid environment is undesirable for micro-organisms. This enables the long term aseptic storage of tomato paste (Fennema, 1985; Gould, 1992; National Food Processors Association, 1992; Chambers, 1994).

2.3.2.6 *Carotenoids and chlorophylls*

These compounds are very susceptible to oxidation when in the presence of heat and oxygen. Hence within the processing of the tomato pulp, some of carotenoid will cleave into two molecules of vitamin A and produce a loss in red colour (hence the darker red paste for Hot Break in comparison to Warm Break). Once aseptically packaged the compounds are stable. Studies into the changes in the carotenoid compound, lycopene during processing have not been carried out, but at the end of paste production the lycopene levels are more concentrated than that in the tomato fruit (Chambers, 1994; Tikellis, 1998).

2.3.2.6.1 Lycopene

Lycopene is the red pigment found in tomatoes and share some of the biochemical functions and physical properties of other carotenoids, such as the common synthesis precursor to cholesterol (isopentenyl pyrophosphate (IPP)). It has readily available antioxidising power as well as being required for the absorption of dietary lipids in the human digestion system.

The difference between lycopene and other carotenoids is in the structure, having two open β -ionone rings on the end of the acyclic carotenoid structure. As a result lycopene has no vitamin A activity in comparison to the structurally similar acyclic β -carotene, which is a

precursor to vitamin A synthesis. Antioxidants are thought to reduce the formation of oxygen derived species that may go on to change the structure of other biological systems such as DNA. Lycopene is said to have 'excellent anti-oxidative and free radical scavenging properties, which are superior to those of β -carotene' (Tikellis, 1998).

A few studies have been conducted on the relationship between a diet of high lycopene and low containing foods and the incidence of coronary heart disease and cancer (Tikellis, 1998; Shi *et al.*, 1999; Heinz Watties Australasia, 1999). Further studies must be completed before lycopene can be held as the primary reason for the decrease in such diseases. However these initial studies suggest that 'the antioxidant effect of lycopene, in combining with free radicals that would otherwise damage the DNA, that is thought to be the key to the protective effect' (cited from Tikellis, 1998, referral from Gerster, 1997).

Tomatoes have been reported to be one of the primary sources of lycopene. In processed tomato paste, the availability of the more readily available all-*trans* isomer is much greater and more highly concentrated than in raw tomatoes (Tikellis, 1998).

2.4 CHEMICAL CHANGES IN TOMATO SYSTEMS

It is important to understand the reactions that occur in the fruit and paste during ripening and processing the tomatoes as these changes have a direct impact on the final paste composition and functionality. These aspects are reviewed in the following section.

2.4.1 *CHANGES DURING RIPENING*

Many different reactions take place during the ripening and processing of tomatoes. These reactions affect the content and functionality of pectin, colour and the volatile components and nutritional components (such as the lycopene content) in the tomato. (Sieso & Crouzet, 1977; Buescher, 1979; Villari *et al.*, 1994; Chou & Kokini, 1987; Barreiro *et al.*, 1997; Hayes *et al.*, 1998; Barrett *et al.*, 1998; Hidalgo *et al.*, 1998; Tikellis, 1999). Most of these reactions go through many complex pathways.

The main steps causing the ripening process are as follows; (Brady *et al.*, 1987; Morgan, 1996)

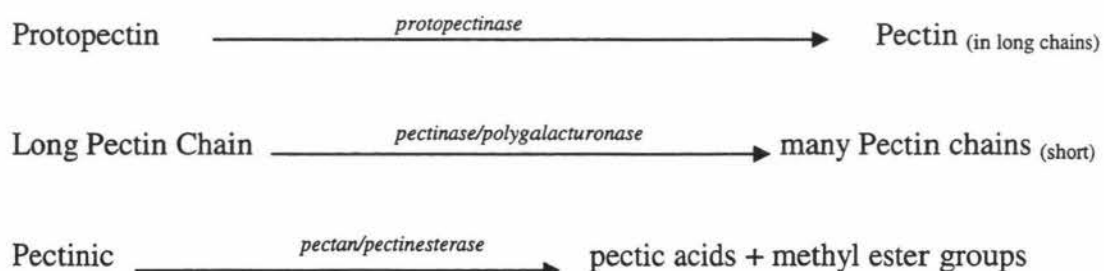
1. Chlorophyll degradation and the disappearance of the photosynthetic system (this results in the loss of the green colour within the tomato).
2. An increase in the β -carotene and lycopene levels (hence the development of red colour).
3. An increase in the rate of synthesis of ethylene.
4. The rate of respiration and the levels of associated compounds increase.
5. The depolymerisation of starch which increases the quantity of soluble pectins, resulting in the softening of the cell wall.
6. An increase in flavonoids and aromatic compounds, resulting in the development of the characteristic organoleptic properties of the ripened tomato.
7. An increase in the citrate levels and a decrease in malate levels occur (change in the citric acid : malic acid ratio).
8. A decrease in the levels of the toxic α -tomatine compound.
9. An increase in cellulase activity, therefore further softening of the cell walls and ripening of the tomato fruit.

2.4.2 *PECTIN AND ENZYME ACTIVITY*

The cell wall is the most significant part of the tomato with respect to the ripening mechanism. Furthermore, changes to the cell wall directly influence the characteristics of the tomato paste that is produced. For this reason changes to the cell wall will be covered in more detail.

The high molecular weight compounds that exist within the cell wall (such as, pectin, cellulose and fibre) determine the texture of tomato tissue and the rheological and flow properties of processed tomatoes (Luh *et al.*, 1984). Pectin is transformed into different forms as ripening occurs and the breakdown of pectin is directly correlated to the softening of the tomato fruit (Gould, 1992). Polygalacturonase (PG) and pectin methylesterase (PE) are the major enzymes responsible for the softening of the tomato. (McColluch *et al.*, 1950; Luh *et al.*, 1971; Luh *et al.*, 1984; Gould, 1992).

The mechanism of the breakdown of pectin is as follows:



where:

Protopectinase - cleaves the proto to pectin bonds leaving pectin

Pectin Methylesterase (pectinase) – causes the demethylation of pectin
(Food Nutrition Board, 1981)

Polygalacturonase – causes the hydrolysis of α -1,4-galacturonide bonds in pectin. (Food Nutrition Board, 1981)

2.4.3 CHANGES DURING PROCESSING

The processing of tomato material into tomato products such as tomato paste has an important effect on the length of the pectin chain of the tomato (Chou & Kokini, 1987). This was also observed by Luh *et al.*, (1971), Luh *et al.*, (1984), and Barrett *et al.* (1998) who all showed the influence of the break temperature on the consistency of concentrated tomato paste. Break temperature is the temperature at which the crushed tomato pulp is heated up prior to evaporation. Different break temperatures result in different types of tomato paste being produced. Hot break tomato paste has a break temperature of 95°C while warm and cold break paste have a break temperature of 75°C but different residence times within the evaporator. The break temperature affects the enzymatic pathway given in section 2.5.2. Previous studies (Luh *et al.*, 1984; Barrett *et al.*, 1998; Chou & Kokini, 1987; Stoforos & Reid, 1992) have showed that more pectin is retained as the break temperature is increased.

The ability to retain pectin and hence control the consistency of the tomato paste can be achieved by controlling the break temperature. A high break temperature results in a tomato paste with greater consistency and serum viscosity (Luh *et al.*, 1984). The high breaking temperature causes the inactivation of the enzyme polygalacturase, and therefore allows the retention of the long and high molecular weight pectin chains (Luh *et al.*, 1984).

Consistency is believed to be specifically controlled by the pectinic and pectic acid portions of the tomatoes. Hence a tomato paste with a high consistency may be explained by a larger quantity of pectin remaining after processing. Pectic fractions with large molecular masses, such as cellulose and fibre, may also remain. These have the ability of absorbing water within their structures, thus creating higher consistency within the product (Luh *et al.*, 1984; Barrett *et al.*, 1998).

Luh *et al.* (1984), also observed that varieties of tomatoes which contained high molecular weight pectin portions, had thicker consistency. It can therefore be concluded that both tomato variety and process conditions are vital for the production of the desired product. Many research studies have involved genetic manipulation, such as the altering of polygalacturonase and pectin esterase enzymes in order to improve paste properties (Barrett *et al.*, 1998). This particular manipulation resulted in the greater presence of high molecular weight pectic substances after processing. This in turn caused an increase in the paste viscosity without changing the quantity of concentration and other process steps. Therefore an understanding of the steps that are responsible for differing factors of tomato paste consistency and quality can lead to further improvement to the raw material or growing techniques before the tomatoes are even processed.

Another change that occurs during processing is to the volatile compound fraction. Processing destroys the most volatile components (hexanal, hexenal and hexanol). Nutrient and vitamin losses also occur as a result of the heating stage of processing, which also causes the production of aromatic compounds and furan byproducts which change the organoleptic properties of tomato paste. The degree of loss and change in organoleptic characteristics are dependent on the processing conditions (Sieso & Crouzet, 1977; Fennema, 1985; Chambers, 1994).

2.5 PHYSICAL PROPERTIES & MEASUREMENT OF TOMATO PRODUCTS

In order to characterise the functionality of tomatoes and tomato products, measurement methods are required. This section outlines the important measurements made in the tomato processing industry.

2.5.1 VARIETY

The choice of tomato variety used for processing is a factor that involves careful consideration. In normal practice varieties are developed over a long period of time, to create a tomato that is ideally suited to the area, growing conditions, process requirements and the desired products (Goose & Binsted, 1973; Gould, 1992; Kale, 1999). At Heinz-Watties Hastings, varieties are cultivated with feedback to the farmer, agricultural advisor and processor to ensure that the correct raw material is cultivated and processed into the product within the quality parameters required. In the Hastings operation, six varieties of tomatoes are grown (utilising only five main varieties). These tomatoes have varying pH, soluble solids content, viscosity and acidity all of which are parameters regarded important by the grower and cultivator (Kale, 1999). When developing a variety, some of the key variables considered are good initial plant growth; good yield for the field and nutrients provided in that area; as well as whether the fruit can withstand rain when ripe; or whether it is resistant to specific diseases and mould. In addition colour, acidity, soluble solids content and viscosity are considered. There is no one tomato that has all the right characteristics to be a 'paste' tomato. Therefore the tomato varieties utilised are a combination of features for a high-grade paste while ensuring a profit for the growers.

In the future there may be other important factors to consider in tomatoes, such as lycopene. Lycopene is an antioxidant that has been found to be linked to the reduction in the rate of prostate cancer by Harvard Medical School in the United States (Tikellis, 1998;

Smellie, 1999). To ensure that customers are getting high amounts of the powerful antioxidant, varieties of tomato that contain high portions of this component may be selected for in the future. Continual development and research into tomato varieties occur annually, ensuring the continual production of profitable high grade end product for both the grower and manufacturer.

2.5.2 SOLUBLE SOLIDS

The main tomato and tomato paste polysaccharides are that of the reducing sugars, (fructose, sucrose and glucose), pectic substances, cellulose, d-xylose and arabangalactan (glucuronic acid).

Table 2.4 Polysaccharide content within an average tomato and tomato paste (Chambers, 1994)

Carbohydrate	TOMATO PASTE <i>(Basis is on an average composition of tomato paste of 28-30% soluble solids (tomato pulp concentrated approximately 5.6 times))</i>	% w/w	TOMATOES <i>(Basis: clean, ripe sound tomatoes)</i>	% w/w
		22.5		4.7
glucose		7.24%		1.29%
fructose		8.72%		1.55%
sucrose		0.13%		0.02%
pectic		1.81%		0.32%
cellulose		1.39%		0.25%
d-xylose		1.47%		0.26%
arabangalactan		1.74%		0.31%

The sugar components make up the soluble solids fraction of the tomato paste. Because the soluble solids fraction makes up the majority of the solids in the past the level of concentration of the tomato-paste is based on measurement of the sugar concentration ($^{\circ}$ Brix). $^{\circ}$ Brix is measured at Heinz-Watties, Hastings and around the world using a refractometer (Goose & Binsted, 1973; Gould, 1992; National Food Processors Association, 1992; Analytical Bench Manual, 1999).

The refractometer measures the refractive index of the solution which is the ratio of the speed of light travelling through the substance to the speed of light travelling through the air.

The soluble solids fraction is usually separated from the insoluble solid fraction, (containing the pectinic and fibrous material) using a centrifuge (Goose & Binsted, 1973; National Food Processors Association, 1992; Gould, 1992; Analytical Bench Manual, 1999). The time required to separate the insoluble solids from the paste out is dependent on the type of paste produced, as higher break temperature (as with hot break paste) causes the tomato paste to retain the serum more strongly than a warm break paste. For this reason it is tempting to measure the °Brix of the whole paste without separation of the serum first. There are no reports in the literature on the effect of this or the effect of temperature and the time on the °Brix measurement. It therefore is important to quantify the accuracy of the °Brix measurements and their dependence on insoluble solid levels, time and temperature. These effects are reported in chapter 3.

2.5.3 TOTAL SOLIDS

Tomato paste, like any biological material, consists of solids and water. The solids component is made up of soluble solids and insoluble solids. The soluble solids fraction is that of the reducing sugars, fructose, glucose and sucrose together with other soluble components. The insoluble solids fraction contains the fibrous material such as the cellulose, hemicellulose and pectinic substances that are found in the cell wall of the processed tomatoes (Goose & Binsted, 1973; Gould, 1974; Fennema, 1985; Gould, 1992; National Food Processors Association, 1992; Chambers, 1994; Barrett *et al.*, 1998, Heinz-Watties Analytical Bench Manual, 1999).

The total solids content of tomato paste can be determined by drying. Several drying based moisture measurement methodologies exist based on the different type of evaporation or drying technique to be employed. Vacuum ovens, forced air ovens, microwave ovens and infra-red ovens are some of the devices employed (National Food Processors Association,

1992; Goose & Binsted, 1974; Gould, 1992). Each method employs different conditions and settings so as not to destroy the sample during the measurement process. According to the Official Methods of Analysis of the Analytical Chemists of America (AOAC), total solids are best determined using a vacuum oven at a temperature of $70^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and at a pressure of 28 inches of mercury. The tomato paste is mixed with a known amount of diatomaceous earth and distilled water, so as to prevent burning, before entering the oven for 12 hours (Gould, 1992; Analytical Bench Manual, 1999).

Within Heinz-Watties in Hastings, the total solids level is tested periodically, employing a forced air oven method (drying at 110°C for 2 hours). This is because Heinz-Watties uses the °Brix measurement as the basis of concentration of the tomato paste produced (Analytical Bench Manual, 1999). The total solids content of tomato paste, whether it be of cold, warm or hot break type is approximately 24-26% of the tomato paste (Heinz-Watties Analytical Bench Manual, 1999).

In order to optimise the use of tomato paste it is important to be able to accurately measure total solid levels in tomato paste. For this reason a comparison of the available methods was required to identify the most suitable method for use in this work an in the factory environment. These aspects are covered in Chapter 3.

2.5.4 COLOUR

The colour of tomatoes and tomato paste is due to the carotenoid fraction and it also is an important attribute of the paste produced. Within this carotenoid group, β -carotene and lycopene are the main constituents with lycopene being more predominant.

Colour is a very crucial factor to consider in the tomato paste produced and in tomato based formulated products. The ripening and processing of the original tomatoes are two factors which affect the final colour. For this reason strict guidelines are taken to sort and then correctly process the tomatoes. To quantify colour, a colorimeter is used. At Heinz-Watties a Hunterlab colorimeter is employed. This uses the a, b, a/b scale which determines colour according to an 3-D axis of blackness to whiteness (L), greenness to redness (a), blueness to yellowness (b) (Goose, 1964; Goose, 1973; Gould, 1992; Barrett *et al.*, 1998; Analytical Bench Manual, 1999). Colour is a very important measure of tomato paste quality as it has been directly related to 'maximum flavour' (Goose & Binsted, 1973). For this reason colour is an important factor tested for in formulated tomato products, such as spaghetti and baked beans.

Other instruments can be used to measure tomato colour. The Munsell system compares the sample colour by varying the proportion primary colours in a spinning disc system. The Lovibond system uses a series of graduated colour glasses to which the sample is compared against (Goose & Binsted, 1973). Other devices such as the Gardner Colour meter use the principle of measuring the primary colours in the sample with a photoelectric cell. Each of these colour determination methods are still used and a large number of methodologies exist, despite an international system (CIE) agreed upon in 1931. All the other systems can be converted to the international system if required. The international system or the CIE (Commission Internationale de l'Eclairage) is not an exact methodology, nor does it use a specific instrument. Instead the method used must have a standard observer which has a starting point from which coloured light can be mixed. The mixture must then be able to be broken down into co-ordinates within a triangular graph. In this way each colour can be given a mathematical value (Goose & Binsted, 1964).

At Heinz-Watties, the colour using the Hunterlab a, b, L scale of the tomato paste and subsequent products are compared to a colour tile which matches the colour required of the tomato paste or product. The colour tile for tomato products originates from the need to produce consistent products where precise standardisation of colour was required.

2.5.5 DENSITY PREDICTIONS

Tomato paste exists, as a homogenous mixture of soluble and insoluble solids and water. Numerous sources suggest a highly correlated relationship between the total solids fraction and the specific gravity of tomato paste exists (Goose & Binsted, 1973; Gould, 1974; Gould, 1992; National Food Processors Association, 1992; Analytical Bench Manual, 1999). Specific gravity is the ratio of the weight of a specific volume of tomato paste to the exact same volume of water, with both samples being at the same temperature (Goose & Binsted, 1964; Goose & Binsted, 1973; Barrett *et al.*, 1998, Analytical Bench Manual, 1999).

If it is assumed that the ratio of insoluble solids to soluble solids is constant then the soluble solids content is linearly affected by change in the total solids content during concentration. For this reason a direct correlation between specific gravity and total solids, and subsequently to °Brix, can be determined.

This is beneficial during processing as a tomato paste at a certain °Brix level can be said to have a certain total solids content. Therefore when calculating the quantity of tomato paste tomato solids to be added within a recipe or determining within a tomato paste, the °Brix measurement can be used. Alternatively, the °Brix of the tomato paste can be calculated from the measured density of the density of the paste. This is beneficial during reformulation when in-line mass flow meters are employed. Some mass-flow meters can be programmed to predict the density of a material flowing through them. From this, the total solids content and therefore the °Brix of the paste can be routinely measured online. The relationship between total solids and density (or specific gravity) relies on the assumption that the density of tomato solids is constant no matter what form those solids are in (soluble or insoluble) or what variety of tomato is used for production of the paste. The relationship between total solids and °Brix relies on the assumption that the level of insoluble and soluble solids is constant for a particular paste product (hot break/warm break). These assumptions require testing before methods to use one measurement to infer another property are developed.

2.5.6 RHEOLOGY

The functional properties of tomato paste and tomato paste based products are largely related to rheological properties. For this reason it is important to be able to relate composition to rheological properties. Tomato paste is a pseudoplastic liquid, as the shear rate is increased it will become less viscous and undergo shear thinning (Harper and El Sahrigi, 1965; Rao *et al.*, 1981; Barrett, 1998). There are a number of models that can predict flow behaviour of pseudoplastic materials. The three most common are the simple power law, the Casson model and the Herschel-Bulkley model. Several studies, have been conducted which have attempted to model tomato paste in order to reliably predict the flow behaviour of tomato paste at a range of shear rate conditions. This information is required because varying levels of shear rate are applied to the tomato paste during handling and processing. These changes alter the flow behaviour of the tomato paste. If a model can be used to predict the change in tomato paste flow behaviour under differing shear conditions, then optimal control of the production process can be achieved to avoid other deteriorative changes in the product during manufacture. In addition, this information would allow the prediction of the formulated tomato product consistency and the amount of tomato paste used could be adjusted in order to obtain the desired final product quality (Charm 1963; Harper & El Sahrigi, 1965; Rao & Bourne, 1977; Rao *et al.*, 1981; Tanglertpaibul & Rao, 1987; Salome *et al.*, 1990; Lorenzo *et al.*, 1997). The following section outlines the experimental data and rheological models that have been used to describe the flow behaviour of tomato paste and tomato products.

2.5.6.1 Experimental data and rheological model fitting

The power law model is shown below as equation 2.1 (Harper & El Sahrigi, 1965)

$$\tau = K \times \gamma^n$$

(Eqtn 2.1)

where:

- τ Shear stress (Pa)
- K consistency index (Pa.sⁿ)
- γ shear rate (s⁻¹)
- n flow behaviour index (dimensionless)

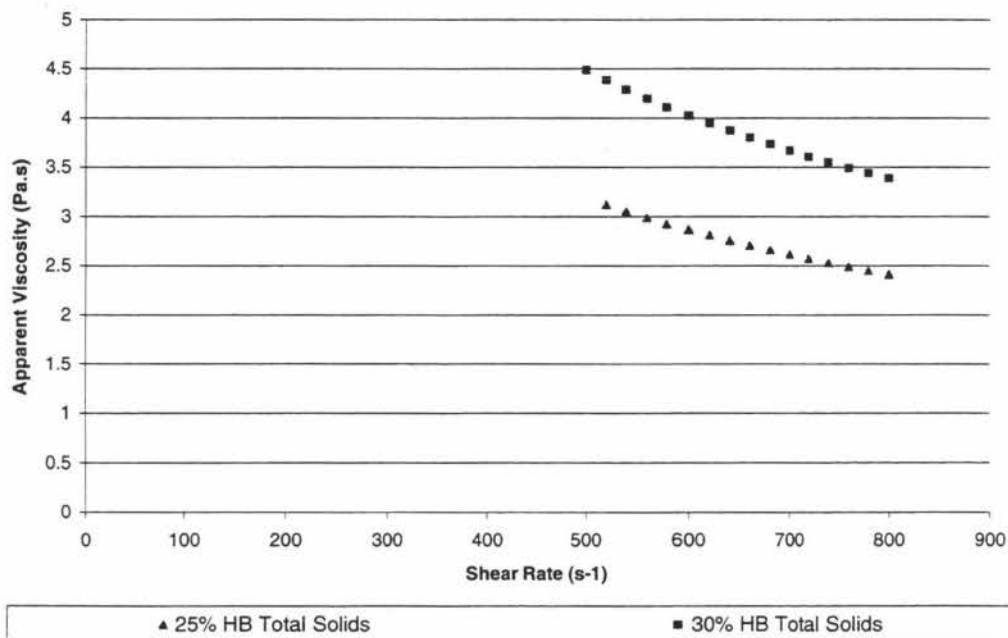


Figure 2.2 Shear rate verses apparent viscosity for 25% and 30% total solids hot break tomato paste at 32.2°C

The power law model is illustrated by Figure 2.2 above. The model was used to calculate the apparent viscosity using shear rates of between 500 and 800s⁻¹ (as in the experiment of Harper & Sahrigi (1965)) for hot break paste at total solids contents of 25% and 30%. The overall trend for both total solids contents of hot break paste, is a decreasing apparent viscosity with increasing shear rate.

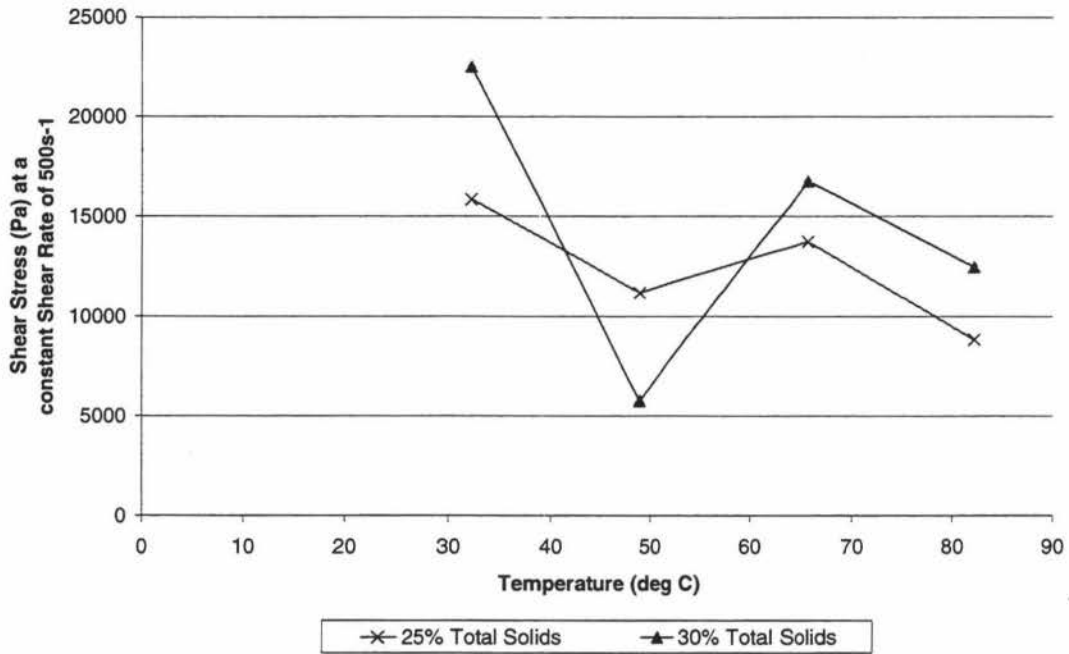


Figure 2.3 Graph of shear stress vs temperature for 25% and 30% total solids (% TS) for hot break tomato paste at a constant shear rate of 500s^{-1} (Temperature Range $32.3\text{-}82.2^\circ\text{C}$)

Both the 25% and 30% total solids hot break tomato paste experience a general decreasing trend in shear stress with increasing temperature, with a sudden decrease in shear stress around 50°C (Figure 2.3). This shows that the hot break tomato paste reaches a certain temperature where its shear stress is at its lowest point before increasing in shear stress. Figure 2.3 also shows that the higher total solids tomato paste (30%) undergoes a greater decrease in shear stress at 50°C . This phenomenon is not covered within the simple power law but is another reason why other models were developed and which will be discussed further on in this section.

The values used in Figure 2.2, Figure 2.3 and the study by Harper & El Sahrigi (1965) are shown in Table 2.5. Laminar flow of the tomato concentrates was assumed to occur.

Table 2.5 Simple power law experimental values used in Figure 2.2 (Harper & El Sahrigi, 1965).

TOTAL SOLIDS	Temperature (°C)	η_a (Pa.s) (@ $\dot{\gamma} = 500 \text{ s}^{-1}$)	n (@ $\dot{\gamma} = 500 - 800 \text{ s}^{-1}$)	K (Pa.s ⁿ) (@ $\dot{\gamma} = 500 - 800 \text{ s}^{-1}$)
25%	32.2	0.317	0.405	12.9
	48.9	0.224	0.415	10.5
	65.6	0.275	0.43	8.0
	82.2	0.117	0.43	6.1
30%	32.2	0.45	0.40	18.7
	48.9	0.115	0.42	15.1
	65.6	0.335	0.43	11.7
	82.2	0.25	0.445	7.9

A further study of the simple power law was carried out by Rao *et al.* (1981), where both warm break and hot break tomato paste were used. The consistency index, or K value, was found to increase with increasing concentration of total solids of the tomato paste (as shown by Figure 2.4). Due to this Rao *et al.* (1981) proposed a further relationship was needed to explain this behaviour. The change in the consistency index (K) could be described by using an exponential or power law as shown in equations 2.2 and 2.3 respectively.

$$K = a_1 \times e^{b_1 \times TS}$$

Exponential equation (Eqtn 2.2)

$$K = a_2 \times (TS)^{b_2}$$

Power equation (Eqtn 2.3)

where :

- a_1, b_1 exponential equation constants
 a_2, b_2 power equation constants (whose values are determined by the type of tomato paste dealt with)
 TS total solids content (%)

Both hot break and cold break tomato paste types have differing constant values as listed in Table 2.6.

Table 2.6 Constants for consistency index equations for hot break and cold break tomato paste at 25°C (Rao *et al.*, 1981)

Tomato Paste Type	n	Exponential			Power		
		a_1	b_1	r^2	a_2	b_2	r^2
Hot Break	0.223	0.022	2.35	0.979	1.37	0.13	0.964
Cold Break	0.175	0.019	2.5	0.986	1.94	0.13	0.912

These different variables allow the individual representation of the hot break and cold break tomato paste which as discussed earlier do have different properties such as viscosity and enzyme activity.

As can be seen from Figure 2.4 below, the K value increases at different rates with increasing total solids content for hot break and cold break tomato paste. For cold break paste the power equation yields a lower consistency index value than hot break paste. Figure 2.4 also shows if using the exponential equation the consistency index value is higher for cold break paste than for hot break. This may be due to the breaking process which causes a different final consistency of tomato paste

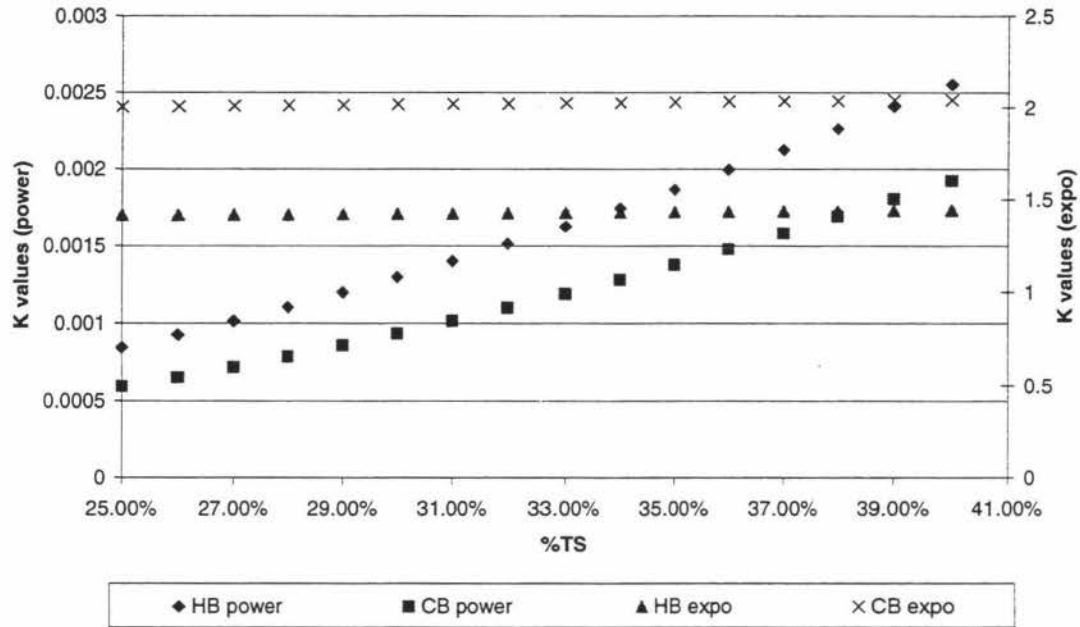


Figure 2.4 K values for hot break (HB) and cold break (CB) tomato paste vs total solids (%TS) using exponential and power equations to determine K (consistency index).

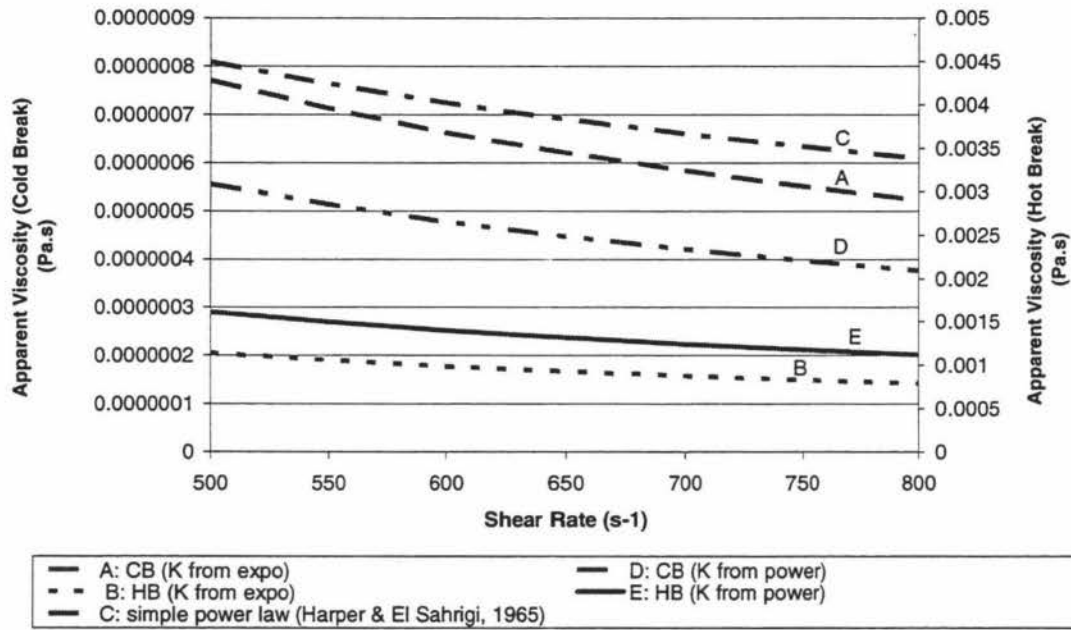


Figure 2.5 Apparent viscosity vs shear rate for hot break (HB) and cold break (CB) tomato paste using the simple power law data as per Rao *et al* (1981) and Harper & El Sahrigi (1965).

Figure 2.5 shows the apparent viscosity of hot break tomato paste decreases with increasing shear rate. The power equation used to calculate K gives a higher value of apparent viscosity than the exponential equation used to calculate K. The general trend of the cold break tomato paste is the same as that of the hot break, with a decrease in apparent viscosity with increasing shear rate but at much lower values of apparent viscosity than compared to the hot break. This difference in apparent viscosity can be related back to the different enzyme activity within the hot break and cold break paste. As noted earlier, the hot break process involves the breaking of the tomatoes at a much higher temperature than that of the cold break, hence inactivating many of the enzymes whose functionality is that of breaking up the fibres into smaller pieces thus destroying the structure of the tomato paste. So the hot break tomato paste retains many of the fibres within the paste creating the more viscous nature of hot break tomato paste. In contrast, the cold break tomato paste is broken at the lower temperature, resulting in the enzymes being not inactivated and hence continuing their function of breaking up the pectin fibres and thus destroying the structure of the tomato paste, in other words creating a less viscous tomato paste (Smit & Nortje', 1958; Goose & Binsted, 1964; Sieso & Crouzet, 1977; Barreiro *et al.*, 1997).

The use of the simple power law conducted by Harper & El Sahrighi (1965) included only one value of K over the whole range of % total solids, it does not take into account the changes in apparent viscosity caused by composition. The different representations of the simple power law as per Rao *et al.* (1981) and Harper & El Sahrighi (1965) can be seen in Figure 2.5. The apparent viscosity decreases with increasing shear rate for both representations of the simple power law. However the overall values of apparent viscosity are three times higher for the hot break Harper & El Sahrighi (1965) representation compared to that of the Rao *et al.* (1981), 0.0039 Pa.s and 0.001 Pa.s respectively at a shear rate of 650s^{-1} .

Harper & El Sahrighi (1965) also found a difference in the rheological behaviour when different methods of concentrating were used. Direct evaporation concentration was compared to reconstituted paste (where centrifuging the insoluble solid component, then concentrating the serum before recombination occurs). Apparent viscosity was 3:1 higher in the evaporated concentrates compared with the reconstituted concentrates (Harper & El Sahrighi, 1965). The higher apparent viscosity in the evaporated product was also noted in the study carried out by Mannheim & Kopelman (1964). Flow-behaviour charts of the concentrates tested all followed the curve dictating the behaviour of a pseudoplastic material (Harper & El Sahrighi, 1965). This difference in apparent viscosity between the evaporated product and reconstituted could be due to the difference in the ratio of insoluble solids to total solids. The concentration of the reconstituted samples were adjusted to be the same according to Harper & El Sahrighi (1965) using a refractometer, however it is the actual fibrous component that will dictate the viscosity of the tomato paste, as previously seen and mentioned with the difference of hot and cold break tomato paste.

A similar study by Rao *et al.* (1981) confirmed the pseudoplastic flow behaviour stated above. Tomato pastes from four different tomato cultivars with total solids contents from between 18% to 30% were tested. These were then mixed with puree or juice from the same cultivar in order to produce the larger range of total solids contents of 5.6% to 36%. Thirteen to sixteen different concentrates were studied over the 5.6% to 36% total solids range. Rao *et al.* (1981) found that the flow characteristics of each cultivar followed pseudoplastic behaviour.

This study also showed that for the Nova cultivar the apparent viscosity (100s^{-1} , 25°C) followed the Arrhenius temperature relationship, where the activation energy equalled 9.56 kJ/mol.

Another model used to describe the flow behaviour of tomato paste is the Casson model (Eqtn 2.4)

$$\tau^{0.5} = K_o + K_c \times \gamma^{0.5} \quad (\text{Eqtn 2.4})$$

where:

τ Shear stress (N/m^2)

[where the yield stress is the point at which the material gives way when the Force (stress) applied on the material (per unit area) is greater than the opposing force that holds the material at a stable form.]

τ_o Yield stress (N/m^2)

τ_o intercept of a graphical plot of $\gamma^{0.5}$ verses $\tau^{0.5}$

K_c slope of a graphical plot of $\gamma^{0.5}$ verses $\tau^{0.5}$

This model is more complex than the power law as it shows that there is a minimum shear stress that must be applied to the paste before the flow will occur, rather than forcing the intercept of the flow curve through zero.

The yield stress (τ_o) must be determined experimentally. The following relationship (Eqtn 2.5) relates the yield stress to the total solids concentration for tomato paste, valid for the range of 5.6% to 36% total solids (Rao *et al.*, 1981 and Rao *et al.*, 1998).

$$\tau_o = a_o + a_1 \times TS + a_2 \times TS^2 \quad (\text{Eqtn 2.5})$$

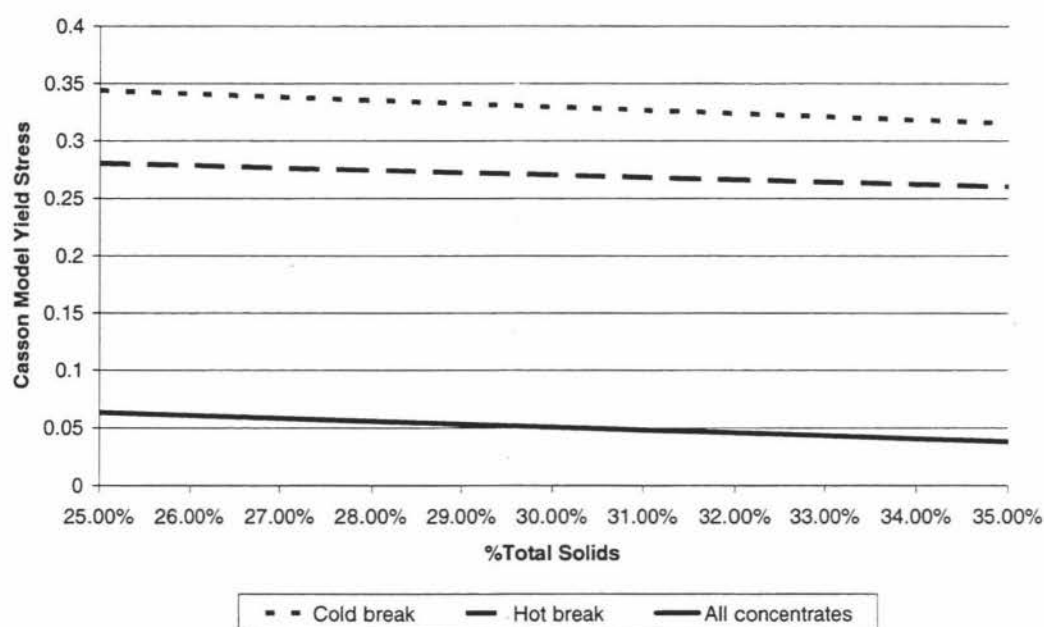
where :

C Concentration (expressed as % total solids)

a_o, a_1, a_2 Coefficients dependent on the type of tomato paste

Table 2.7 Coefficient values for determining yield stress for the Casson model (Eqtn 2.5)

Type of Tomato Paste	a_0	a_1	a_2	r^2
Cold Break	-0.415	0.2854	-0.0039	0.990
Hot Break	-0.332	0.2065	-0.0018	0.880
All Concentrates	-0.126	0.2517	-0.0033	0.845

**Figure 2.6** Yield stress vs total solids (% TS) for hot break (HB), cold break (CB) and all concentrates of tomato paste.

This relationship determining the yield stress of the Casson model shown above, displays that yield stress increases almost linearly with increasing concentration of total solids of tomato paste. Hot break paste has a greater yield stress value than cold break tomato paste over the range of concentration examined. This is probably due to the higher break temperature hot break paste undergoes which affects the fibres of the tomato paste allowing them to withstand a higher stress than the warm break tomato paste before flow will occur.

From this data the Casson model could be graphed (as seen in Figure 2.7). Data used is as in Table 2.8.

Table 2.8 Variables for Casson Model as used in Figure 2.7

Casson Model Variable	Cold Break	Hot Break
K_0	7.8	7.0
K_c	1.85	1.1513
$\tau^{0.5}$	6-15	6-15
$\gamma^{0.5}$	0-24	0-24

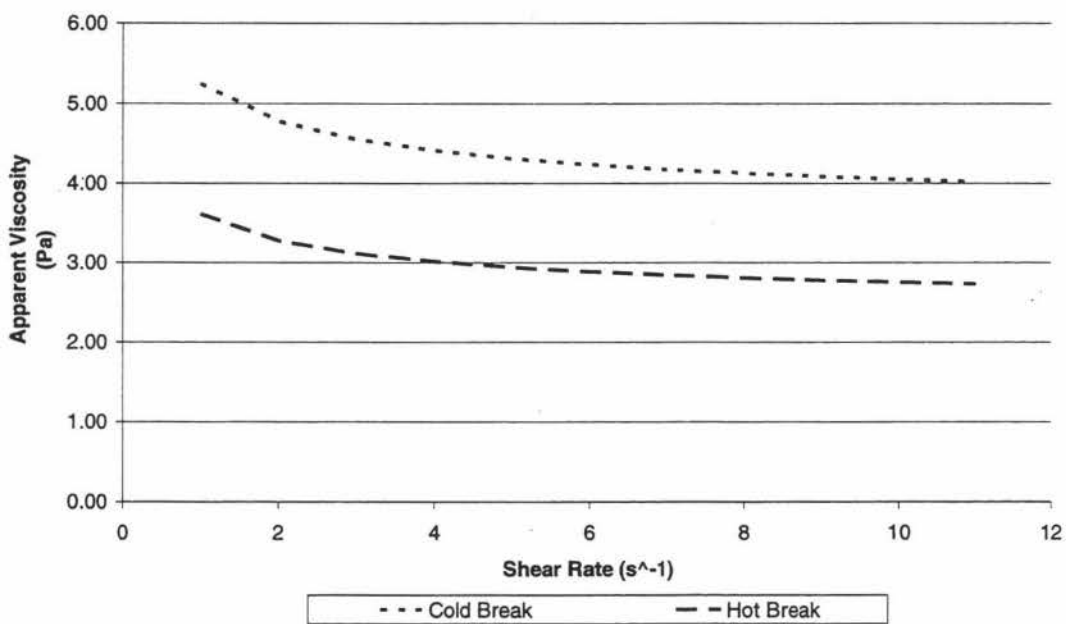
**Figure 2.7** Apparent viscosity vs shear rate for hot break (HB) and cold break (CB) tomato paste using the Casson model

Figure 2.7 shows the apparent viscosity is proportional to shear rate for shear rates above 3s^{-1} only. Rao *et al.* (1981) confirms this trend and concludes that while the Casson model represents the data well it should not be used for predicting apparent viscosity at low shear rates.

The Herschel-Bulkley model is yet another model used to describe the flow behaviour of tomato paste. (Rao et al., 1981)

$$\tau = \tau_o + K_1 \times \gamma^{n_1}$$

(Eqtn 2.7)

where:

τ	Shear stress (Pa)
K_1	Consistency index (Pa.s ⁿ) *
γ	Shear rate (s ⁻¹)
n_1	Flow behaviour index (dimensionless) *

* where K_1 and n_1 are determined from a linear regression of $\log(\tau - \tau_o)$ vs $\log \gamma$

The Herschel-Bulkley model (Eqtn 2.7) depicts the flow behaviour of tomato concentrates at differing levels dependent on the concentration of the mixture. The model is similar to that of the Casson model, in that it has a yield stress and to the power law in that the effect of increasing shear rate is non linear with respect to the resulting shear on the fluid. The yield stress used in the Herschel-Bulkley model is the same as discussed above for the Casson model. The consistency index (K_1) is different for the differing types of paste, as is the flow behaviour index (n_1). The resulting consistency index k_1 is shown to follow the relationship given in Eqtn 2.8 where the specific values and the flow index are summarised in Table 2.9.

$$K_1 = a \times e^{(b \times TS)}$$

(Eqtn 2.8)

Table 2.9 Variables for Herschel-Bulkley Model used in Figure 2.8

Factor	n_1 min to max	a	b
Cold Break	0.27 – 0.63	0.052	0.18
Hot Break	0.43 – 0.59	0.217	0.14

The Herschel-Bulkley model was calculated using both the minimum and maximum flow behaviour index values (n_1) at 30% total solids for both cold break and hot break tomato paste. The resulting model is as follows:

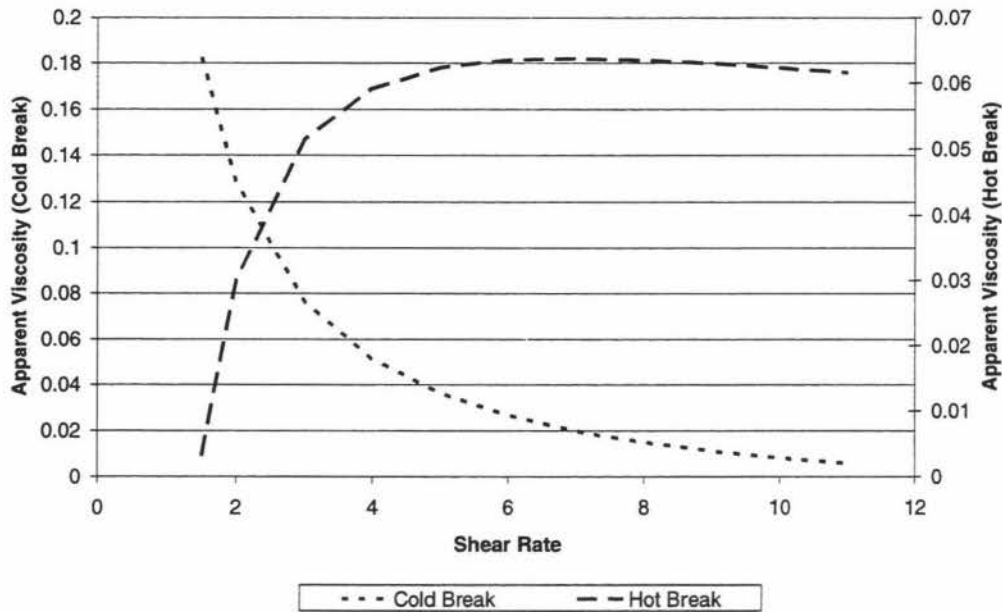


Figure 2.8 Shear stress vs shear rate for cold break tomato paste using the Herschel-Bulkley model (TS=30%)

In conclusion, literature shows that tomato paste flow behaviour can be best described by the Herschel-Bulkley model. The yield stress is only important when the total solids is increasing and above 1%. As we are mainly interested in diluted tomato paste, the power law model is best. We then have Eqtn 2.7 where k is dependent on the total solids as given by Eqtn 2.8. From this the sensitivity of the tomato paste to concentration and temperature can be estimated and the apparent viscosity for a paste at a given shear rate can be predicted.

2.5.6.2 Viscosity

The viscosity of a tomato paste is dependent on the processing conditions and the structure of the tomato paste (Luh *et al.*, 1984; Xu *et al.*, 1986). The differing types of tomato paste that are produced, cold break, warm break and hot break, each have increasing break temperatures (low heating, 75°C and 95°C) and hence increasing viscosity (Chambers, 1994; Xu *et al.*, 1986). The differing cultivars of tomatoes have different viscosity values depending on the process as well. This is why certain tomato cultivars are especially used for the production of the differing types of paste (Xu *et al.*, 1986; Kale, 1999).

Chou & Kokini (1987) studied whether the rheological properties are affected by the biochemical components of the tomato paste processed. The amount and length of the pectin chains (dependent on the processing technique) were found to increase as the break temperature increases. Furthermore, the viscosity increased as holding time increased. Cold break tomato paste had an intrinsic viscosity value three times lower and a chain length with a molecular weight of thirty eight times lower compared to that of hot break tomato paste. (Note: the intrinsic viscosity is a measure of the hydrodynamic volume taken up by a molecule within a polymer.) Other carbohydrate polymers (other than pectin) such as cellulose and fibres are also said to be directly related to the quality factors of raw tomatoes via texture and processed tomatoes (Xu *et al.*, 1986) by absorbing water and hence increasing the consistency of the concentrated form (Smit & Nortje', 1958; Luh *et al.*, 1984). The mechanism behind this increase in pectin content is due to the high breaking temperature with which the tomatoes are subjected to, which inactivates the enzymes responsible for normally cleaving the long molecular pectin chain.

For these reasons, the particle size and distribution as well as the insoluble solids to total solids ratio within the tomato concentrate have a bearing on the rheological behaviour of the paste (Marsh *et al.*, 1980; Xu *et al.*, 1986; Chou & Kokini, 1987; Rao *et al.*, 1998).

The acidity level also has an effect on the rheological properties of the tomato concentrate. The specific viscosity decreases as pH decreased, with the optimal viscosity occurring at pH 4.6. The degree of esterification of the pectin chain of approximately 57% for hot break paste causes the optimum viscosity at pH 4.6, whereby the lower pH values where de-esterification occurs causes a lower viscosity. For cold break paste however, the degree of esterification is lower than that of the hot break at 28.5% (Chou & Kokini, 1987). This is due to the fact that in cold break tomato paste the pectin methyl esterase is not inactivated whereas in hot break it is. The activity of the pectin methyl esterase is also seen in the pH drop. All of these changes are because of the enzyme activity and the degree of inactivation by the heat within the breaking process.

These factors also explain the different parameters between hot and cold break paste as discussed in the rheological modelling above. To produce the flow behaviour correctly, it would be better to relate the model parameters to the insoluble solid content of the paste.

2.6 PRODUCTION PROCESS

Tomato paste is produced at the Heinz-Watties King Street, Hastings site generally between the months of January and April.

The process involved with producing tomato paste can be broken into four sections.

- i. Tomatoes received from the field.
- ii. Tomato preparation before going through either a:
 - hot break
 - or warm break process.
- iii. Packaging of the tomato paste for later use or:
- iv. Direct feed of tomato paste into the production line.

These sections are based on what happens at Heinz-Watties, Hastings, Heinz-Watties, 1999) and also illustrate the basic sequence of operations in almost all factories manufacturing tomato paste (Cruess, 1938; Goose & Binsted, 1973; Flynn & Crowth, 1980; Hayes *et al.*, 1998).

2.6.1 *TOMATOES RECEIVED FROM THE FIELD*

The tomato field is monitored and when the correct quantity of tomatoes in the field are at the right condition the tomatoes are mechanically harvested. The tomatoes are then transported by trucks to the factory and weighed on a weigh-bridge as soon as they arrive. While on the weigh-bridge a core sample is taken out (approximately 25 kg). This is then spread out onto a conveyor and undergoes a quality inspection by one of the trained quality inspectors. Firstly the dirt is removed and weighed. This proportion is deducted from the total trailer weight. The tomatoes on the conveyor are then washed and the green ones are removed and weighed. The proportion of green tomatoes are calculated but not deducted off the truck weight.

The breakers are then removed, weighed and the proportion worked out. The breakers are the green tomatoes that are just getting red (therefore breaking red). A large proportion of these may indicate that the field needed a little longer before picking. This information will be fed back to the grower to keep up the communication between the company and the grower on conditions and desired product. Any rotten, broken and over-ripe fruit are also removed, weighed and recorded.

The proportions of each of the different fractions determine whether the fruit is to be processed or whether it is rejected and taken back to the field. Information about the proportion of dirt, greens, breakers and overripe fruit provide invaluable information to the field staff, who help growers to produce high quality fruit while also giving process staff information on the grade of paste to be produced. It must also be noted that the quality inspection staff follow strict procedures and guidelines to ensure no bias occurs towards either Heinz-Watties Ltd. or the growers.

2.6.2 PREPARATION OF TOMATOES FOR PROCESSING

The tomatoes are emptied from the truck and are washed, manually inspected and sticks etc are removed from the tomato lot before skin removal occurs. This is a very important step as it is paramount that only high-grade tomatoes continue to be processed. Traces of debris and any mould growth are removed to minimise contamination of the final product.

Washing and sorting can occur by many different methods such as using simple static tanks or to high-pressure jet devices with in-built compressed air agitation (Goose & Binsted, 1973).

Skin removal occurs by a shot of steam onto the tomatoes which causes the skin to split and shrivel up and then removed. The tomatoes are then processed. At Heinz-Watties Hastings this is by either a hot break, warm break or a cold break process. These three different processing conditions dictate which type of tomato paste is being produced and hence which products it will be used as an ingredient. For the purpose of this study only warm break and hot break processes will be reviewed.

Firstly the tomatoes are crushed or 'broken' (hence the 'break' of the hot or warm break process). This is to form a pulp with reduced particle size, making it easier to concentrate during further processing.

2.6.3 HOT BREAK PROCESS

Undergoing a hot break process means that immediately (i.e.: within three seconds) (Goose & Binsted, 1973) after the tomatoes are crushed they are put into a three-stage evaporator system where the tomato product undergoes a heat treatment of up to 90-94°C. Hot breaking destroys the pectic enzymes and hence yielding a more viscous product that does not separate on standing (Gould, 1992).

2.6.4 WARM BREAK PROCESS

Undergoing a warm break process means that after the tomatoes are crushed they are heated to only 70°C. This gives a less viscous tomato paste, in comparison to that of the hot break paste and hence it is used in different products than hot break paste. The lower processing temperature yields less enzyme denaturation; hence the pectin enzymes continue to degrade the pectin chains. This is why the tomato paste has a less viscous nature (Smit & Nortje', 1958; Goose & Binsted, 1964; Sieso & Crouzet, 1977; Gould, 1992; Barreiro *et al.*, 1997).

2.6.5 PACKAGING OF THE TOMATO PASTE FOR LATER USE

The tomato paste once produced can take two routes. It can be packed away for later use or directly feed into another part of the plant and immediately used in the production of Heinz-Watties Ltd. products. Paste to be stored for later use is packed through an aseptic line into an aseptic 200L Scholle bag which is placed inside a 200L stainless steel drum. The 200L bags are primarily made of HF and PE and have a tap/valve fitting where the tomato paste is aseptically filled into the bags. Aseptic filling occurs by an operator thrusting the bag's valve fitting up into the aseptic head that grabs the valve head. The valve is then subjected to a shot of steam for a specified time before the cover part of the valve is removed.

Another shot of steam is directed onto the top that sterilises it as well as opening the bag slightly so entry of the tomato paste is easier. Tomato paste is then filled into the bag slowly before another shot of steam, the cover part of the valve being replaced and then the bag removed from the aseptic unit. It must be noted that the whole aseptic head unit is kept at saturated steam temperature of 112°C ensuring all components are sterile and to minimise the possibility of contamination (Packaging Specifications Sheets for Heinz-Watties, 1999; Eagleton, 1999)

Once the aseptic bag is filled, it is pushed into the drum, the inner plastic liner bag of the drum is gathered and tied, and the lid of the drum is attached. Information concerning all four drums in a pallet is sealed into the top of one of the drums. For example drum A916828 would have information at the top of the drums about the grade of tomato paste, the colour level, the °Brix level, pH reading and whether it is HB or WB for that drum and the three prior to it, that is, A916827, A916826, A916825. Labelling of each drum also occurs with specially coloured sticker labels adorning each drum telling of the grade and type of tomato paste inside and it's characteristic drum number for future reference when needed in product production. For example: A920637 WB4 means this drum is labelled as number A920637 which also corresponds to an exact time and date of production and the product contained within is that of warm break tomato paste of grade four, which is the highest made at the Hastings plant of Heinz-Watties Ltd.

Four drums are packed onto one pallet and this configuration is then covered with a black polyethylene liner, which is tied around all four drums. The finished pallet is then transported out to the back of the Hastings, King Street site next to the railway line where they are stored alongside each other before being used in the production of products. This storage outside is also a common occurrence elsewhere around the world such as in Italy and other Mediterranean countries (Villari *et al.*, 1994). Another important note that must be made is that the first tomato paste produced at Heinz-Watties may not be the first to be used in the factory. This is because the tomato paste to be used is dependent on the grade and mix of tomato paste to be used to produce the certain products required by the market. For example, Japanese meat sauce may be required therefore production involves HB1 tomato paste to be recalled into the factory.

2.6.6 FLOW CHART

(Refer to Appendix Two for full process flow chart as per Heinz Watties Hastings)

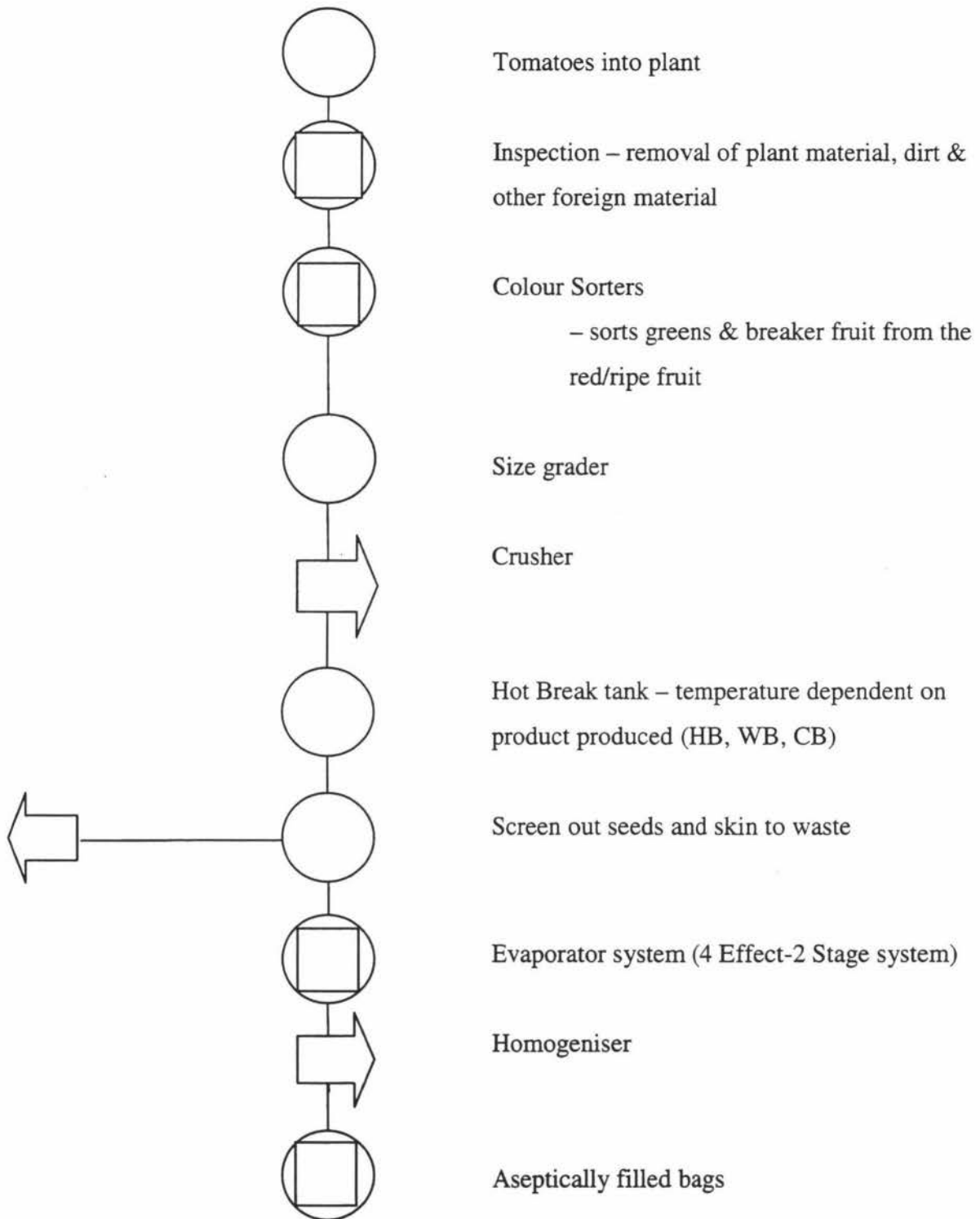


Figure 2.9 Flow chart of tomato paste processing

2.7 QUALITY

The final stage of ensuring a high quality of the final product is within the processing stage. Throughout the production of tomato paste, the production variables are monitored in order to establish a consistent level of tomato paste for each of the grades produced. Such variables include the evaporation temperature, pressure and holding times in each evaporator. At the end of the production line samples are taken every half an hour for routine quality control and to hold a sample as indication of the production line.

The quality of the final product is dependent on three main areas to maintain a high quality and consistency. They involve having a high quality of the soil in which the tomato plants are grown then the raw material or tomato fruit. Finally the quality at all stages of the process must be upheld. These factors combined will ensure the quality of the final product to be high enough for the consumer market.

There are two main sources of contamination of tomato paste. The first is soil-borne and is the source of the majority of contamination (quality infield). The second is known as field diseases, which attack the vines and actual tomato fruit (quality in-fruit). Both of these can exist within the manufacturing and processing of tomato paste and contributing to an overall lower quality product.

2.7.1 QUALITY WITHIN THE FIELD

The main factor when dealing with the quality within the field is the soil in which the tomato plant grows to bear the tomato fruit.

2.7.1.1 Soil-Borne Micro-Organisms

The soil borne micro-organisms provide the majority of the contamination in the raw material due to the ability of the tomatoes having organism-filled dust and dirt attached to the soil surface when harvested. Some of this dirt and the micro-organisms may carry over into the processing even after washing hence influencing factors such as taste and stability of the tomato paste, as well as faecal contamination. The Genus *Bacillus*, *Corynebacterium*, *Escherichia*, *Lactobacillus*, *Micrococcus* and *Pseudomonas* can be present and all contribute different factors in changing the flavour of the tomato paste, while Genus *Enterobacter* can be an indicator of faecal contamination which is not tolerated within a food product. Most of these organisms are destroyed during the heating and concentration processes where the heat, limiting oxygen and lowering of the water activity of the product inhibits growth (Gould, 1974; Fennema, 1985; Gould, 1992; Chambers, 1994).

Through present crop management procedures, the fungal diseases should be at a low level due to the fungicides applied. Moulds and yeasts will still be present and although processing will destroy most of them, a low level is acceptable. Soil-borne organisms should be adequately dealt with by the washing and sterilisation procedures. It must be noted that the presence and numbers of all these organisms are dependent on the weather conditions, which directly reflect the ideal or non-ideal growth conditions for the specific micro-organisms. For example moulds will be more prevalent in warm, wet weather when the tomatoes are harvested, hence a higher level of mould may be encountered (Goose & Binsted, 1973; Gould, 1974; Gould, 1992; Chambers, 1994).

2.7.2 *QUALITY OF THE FIELD*

When dealing with the quality of the fruit harvested the main factor to consider and prevent is that of diseases in the field.

2.7.2.1 *Field Diseases*

There are three categories of field diseases that attack the tomato plant and the fruit itself; they are either bacterial, fungal or viral diseases. The impact of some of these diseases may disrupt tomato production but sprays can control most of these.

Bacterial diseases include Bacterial Canker, which infects the fruit initially with small white spots developing into brown scabby lesions. This is very contagious within tomatoes and destructive, thus crop rotation to a non-tomato relative for at least three years is important, or soil sterilisation before planting could also occur. Bacterial Speck is another disease, which initially begins with raised black specks that develop a dark green halo. Copper sprays are used and crop rotation again is important. Bacterial Spot has a larger lesion than Bacterial Speck and usually is within wounds or natural openings of the tomato fruit. Bacterial Spot is controlled just as with Bacterial Speck with copper sprays and crop rotation.

Fungal diseases include moulds such as Anthracnose, Black and Gray Mould and Rots such as Fruit Rot and Sclerotinia Stem Rot (or Timber Rot). Late Blight is also a fungal disease of interest when dealing with tomatoes. To deal with these diseases, resistant tomato varieties can be selected for, specific fungicides used as well as the rotation of crop varieties between years and ensuring good drainage (Goose & Binsted, 1973; Gould, 1974; Gould, 1992; Chambers, 1994).

2.7.3 *QUALITY IN PROCESSING*

When tomato paste is being produced, a number of tests are completed to ensure the product is being processed to a specific standard for the company and hence will produce a high quality product. While processing, the degrees Brix or the soluble solids of the tomato pulp to be concentrated is important to know, along with the actual physical condition of the pulp such as the colour, acidity, traces of mould and black specks. These factors give an indication of the product and its quality. However different factors are applicable to different users. The quality standards that consumers may look for such as colour and acidity, whereas buyers of the paste for use in other products may look towards the ratio of sugar and acidity which is important in soup manufacture (Goose & Binsted, 1973).

At Heinz-Watties, the degrees Brix level is monitored in-line during processing in order to ensure the correct process conditions are used to concentrate the pulp to the desired °Brix level or soluble solids level. Samples are taken from the aseptic filler in-line which are then subjected to testing in order to determine the tomato paste is up to specifications. The tests that are carried out at Heinz-Watties involve firstly the °Brix, the colour (via the Hunterlab colorimeter), the specific gravity and the pH (via a simple pH meter). The percentage mould the sample contains is also monitored along with the consistency via the Bostwick consistency test and the blotter test (Analytical Bench Manual, 1999).

The amount of mould is determined in accordance with the Howard Mould Count procedure which has been acknowledged as the official AOAC (9th Edition) method of evaluating mould in tomato products (Goose & Binsted, 1973). At Heinz-Watties the samples must have less than 50% positive tests with mould (Cooley, 1999). This data then indicates the amount of percentage rot within the tomato paste concentrate. A graphical representation of the relationship of Mould Count to the % Minimum Rot can be seen via data obtained by studies conducted by Goose & Binsted (1973), as shown in Figure 2.10. The logarithmic regression fits reasonably well to the data graphed as can be seen from the regression coefficient ($R^2=0.987$) that is near one, where one represents the exact fitting of the model to the data.

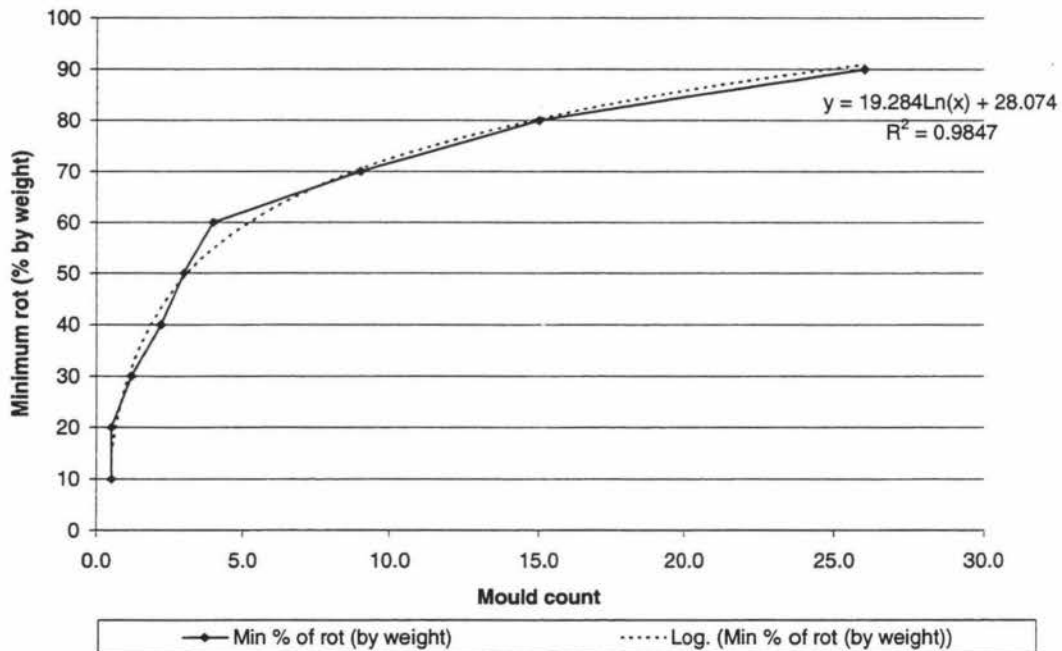


Figure 2.10 Mould count vs % minimum rot (by weight) in tomato paste samples (Goose & Binsted, 1973).

It must be noted that this procedure must be done with great care due to the fact that distinguishing between tomato fibres and mould filaments is difficult (Goose & Binsted, 1973; Cooley, 1999; Analytical Bench Manual, 1999).

The consistency of the tomato paste is firstly evaluated by the Bostwick consistency method. This uses a slide in which the tomato paste is let down over time and hence yielding an indication of the consistency of the product (Goose, 1964; Goose, 1973; Barrett *et al.*, 1998; Analytical Bench Manual, 1999). However as previously mentioned, it is capable of testing a limited range of tomato paste concentrates. Hence data cannot be determined when the concentrations are greater than 15% total solids (Tanglertpaibul & Rao, 1987). An alternative method has been developed by Takada & Nelson (1983). They found the weight ratio of the precipitate part of a sample (obtained after centrifugation) to the initial sample correlates well with tomato product results from the Bostwick consistency and Efflux viscosity (determined by a tube viscometer) (Tanglertpaibul & Rao, 1987).

The other measure of consistency involves what is called the Blotter test. This procedure involves a small amount of tomato paste being dropped onto a piece of filter paper and allowed to stand for a specific amount of time. The result is a colourless liquid ring penetrating out from around the red tomato centre. The distance that this ring has penetrated out from the centre then corresponded to previously obtained values for low consistency and high consistency tomato products, hence the consistency of the sample can be rapidly ascertained (Analytical Bench Manual, 1999; Barrett *et al.*, 1998). This simple method was tested against other measurements of consistency, such as the Bostwick consistometer and Adams consistometer. The Blotter test was found by Davies *et al.* (1981) to correlate reasonably well with the Bostwick consistency and the Adams consistometers, having R^2 values of 0.75 and 0.73 respectively. The Bostwick consistency and Adams consistometers are thought to measure similar rheological factors which is confirmed by the similar R^2 values against the Blotter test (Davies *et al.*, 1981). The tube viscometers did not correlate with the Blotter test because these devices measure different rheological factors than the other consistency instruments (Barrett *et al.*, 1998).

The acidity measurement, via a pH meter, is important for determining the use of the tomato paste. For example, a paste with an acidity level of pH 3.3 could be used for sauce production more readily than for the production of soup in which the acidity must be around pH 4.6 (Goose & Binsted, 1973; Heinz-Watties Recipe Sheets, 1999).

CHAPTER 3 CHARACTERISATION OF TOMATO PRODUCTS

3.1 INTRODUCTION

The important functional and quality parameters of tomato paste for use in paste derived formulations are:

- Flavour
- Sweetness
- Viscosity
- Colour
- Acidity
- Microbial stability

As such, it is important that the measurements made during paste manufacture, are appropriate to completely characterise the product with respect to these factors. In addition, the measurements made, must be suitable for the calculation of the amount of paste to add to formulations. Ideally, each measurement method should be accurate, precise (little deviation) and be applicable to the industrial environment (rapid, easy to carry out and operator independent).

At present there are a variety of measurements carried out to attempt to characterise tomato paste, and many alternative methods are also available. This chapter outlines work done to identify which compositional or physical properties best characterise tomato paste quality during manufacture and in tomato product formulation and how they are best measured.

3.2 IDENTIFICATION OF KEY PROPERTIES FOR MEASUREMENT

The functions and parameters discussed above (flavour, sweetness, viscosity, colour, acidity and microbial stability) are difficult to measure directly or are dependent on other factors as well as paste composition (for example, viscosity is shear dependent). As such, it is important to define a set of measurement techniques that directly measure compositional or physical properties that can be then linked to paste functionality. The identification of these properties is discussed below.

➤ Tomato Flavour

This is linked to a large number of tomato volatiles which are omitted during the enzymic and chemical reactions of the tomato solids such as through the ripening process, imparting a greenness or fresh taste to the pulp (Kazeniak & Hall, 1970). While after processing these reactions impart a cooked flavour (Sieso & Crouzet, 1977).

➤ Sweetness/sugars

Sweetness is directly linked to the soluble solids concentration, not the °Brix value. About 50% of the dry matter in cultivated tomatoes is made up of sugars, mostly fructose and glucose but with minute quantities of other sugars including rabinose, xylose and galactose. Over the process of ripening the ratio of glucose to fructose changes from 1.8 in green tomatoes to around 1 in ripened fruit (Petro'-Turza 1986-1987). This change is important with regard to sweetness, as it is known that fructose has twice the sweetening power than glucose (Stevens *et. al.*1977). Despite this fact, it is relatively difficult to link sweetness to just one or two components as there is a significant interaction with minor constituents and between sugar content and pH. As a result total reducing sugar, °Brix or soluble solids are the most useful indicators of sweetness.

➤ Viscosity

As previously mentioned in 2.3.2.2 pectin substances contribute to the majority of the fibre content and to the overall viscosity of the final product. Changes occur in the pectin content through ripening and processing of tomatoes and tomato paste. These changes have a direct impact on the composition and functionality of final paste and that of paste derived products.

Within the ripening process, pectin is broken down by two major enzymes, PG (polygalacturonase) and PE (pectin methylesterase). The shorter pectin chains that remain result in a softer tomato. (Chou & Kokini, 1987; Smit & Nortje, 1958)

The length of the pectin chain is also affected by the temperature at which the tomato pulp is heated up prior to evaporation to become tomato paste. The higher the temperature, the faster the inactivation of the enzymes which break up the pectin chains, hence lowering the viscosity.

These pectin chains make up the insoluble solids portion of the tomato paste, so the ratio of insoluble solids to total solids is an important parameter to measure throughout processing. Unlike °Brix, the insoluble solids to total solids ratio contributes to the final viscosity and the final consistency of the tomato paste and its formulations. (McColloch *et. al.*, 1950; Xu *et. al.*, 1986)

➤ Colour

Colour is an important attribute of tomato paste and paste derived products. Lycopene is the predominant carotenoid and contributes to the red pigment of tomato paste (Barreiro *et. al.* 1997). These components are present in the insoluble solids fraction of the paste as evidenced by the relatively translucent colour of the serum fraction of centrifuged paste. In the method of Khachik *et. al.* (1992) you can see that the carotenoids are extracted from tomato paste using organic solvents and are not water soluble. The thermal degradation of lycopene is one of the principle causes of colour loss during processing. Isomerisation of the *trans* lycopene isomer to the *cis* form during heating causes this change in colour.

There are however many other reactions that contribute to the final colour of tomato paste. The presence of chlorophyll in the juice from pulping non-rip fruit is converted to pheophytin which is an olive green colour (Barreiro *et. al.* 1997). Also important are the Maillard browning reactions of sugar and oxidation of ascorbic acid. As a consequence the final paste colour is a result of an array of complex reactions, initial fruit composition and ripeness, whose combined mechanisms are not fully understood.

As a result, colour is best characterised by measurement of colour co-ordinates directly rather than by quantifying the concentrations of the principle pigments (Lycopene)

Colour cannot be described by a single reading. Throughout the years several systems have been established; the two major ones are described here.

The Munsell system involves three properties, hue (a), value (b) and chroma (L). The Hunterlab colorimeter measures these properties using three photo cells.

- 'a' measures the blue to yellowness
- 'b' measures the green to redness
- 'L' measures the Luminance or the white to black

Any change in one of these variables will affect the other two in terms of visual appearance, which closely represents the human sensitivity to colour. (Goose and Binsted, 1973, 1964)

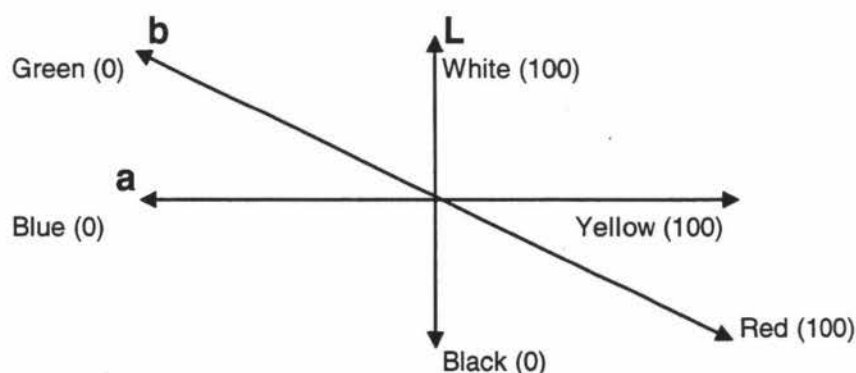


Figure 3.1 Munsell colour system

For a sample. In terms of tomato paste, a good season (first grade paste) is reported by the National Food

Processors (1992) to have an a/b ratio of over 1.9. Below 1.8 does not prove acceptable for products where a bright red colour is desired.

The second system is the CIE system which involves the measurement of a different three factors, Y, x and y. Y is a measure of the Lightness (expressed as a % of perfect reflectance) where x and y are both chromacity co-ordinates.

These two systems have been found to be interchangeable by derivation. Firstly the CIE system (x, y, Y) must be converted into Tristimulus values (X, Y and Z respectively).

$$X = Y \left(\frac{x}{y} \right)$$

$$Y = Y$$

$$Z = Y \left(\frac{1-x-y}{y} \right)$$

(Eqtn 3.1, 3.2 and 3.3 respectively)

From here a,b and L equation can be rearranged where a, b and L are replaced by a*, b*, L* which correspond to the tristimulus values of the illuminant used in the x, y and Y equation (Gould, 1992).

$$L^* = 116 \left(\frac{Y}{Y_0} \right)^{\frac{1}{3}} - 16$$

$$a^* = 500 \left[\left(\frac{X}{X_0} \right)^{\frac{1}{3}} - \left(\frac{Y}{Y_0} \right)^{\frac{1}{3}} \right]$$

$$b^* = 200 \left[\left(\frac{Y}{Y_0} \right)^{\frac{1}{3}} - \left(\frac{Z}{Z_0} \right)^{\frac{1}{3}} \right]$$

(Eqtn 3.4, 3.5, 3.6 respectively)

Where Y_0 , X_0 and Z_0 are the tristimulus values of the illuminant used.

Next step is the rearranging of these equations for Y, X and Z

$$Y = Y_o \left(\frac{L^* + 16}{116} \right)$$

$$X = X_o \left(a^* - 500 + \left(\frac{Y}{Y_o} \right)^{\frac{1}{3}} \right)$$

$$Z = \left[\left(\frac{Y}{Y_o} \right)^{\frac{1}{3}} - b^* + 200 \right]^3$$

(Eqtn 3.7, 3.8 and 3.9 respectively)

Y, X and Z can then be rearranged using equations 3.7, 3.8 and 3.9 to achieve Y, x and y (CIE system) variables.

➤ Acidity/Flavour

The acidity or flavour of tomato paste is caused by concentrations of organic acids in the soluble solids fraction and is affected by the degree of pectin hydrolysis in the breaking stage of the production process. The most direct measure of this is pH (Gould, 1992; Goose and Binsted, 1974).

The characteristic sweet-sour taste of tomatoes and its overall flavour intensity are due to:

- Reducing sugars (fructose and glucose)
- Free acids (mainly citric acid)
- Volatile substances
- Ratio of sugar/acids
- Interplay of the above
- Minerals (potassium and phosphate especially as they buffer or affect free acid levels so they affect taste indirectly)
- Free amino acids affect taste is debatable

The tomato like flavour is determined by volatile substances. These develop

- during ripening partly
- during pulping/grinding
- because of enzyme activity
- derived from fatty acids and amino acids

No key one compound is identified but there are a group of compounds that are thought to contribute to the green or fresh flavour of raw tomatoes, these include *cis*-3-hexenal, *trans*-2-hexenal, 2-isobutylthiazole, hexanal, *cis*-3-hexen-1-ol, 2E,4E-decandienal and 6-methyl-5-hepten-2-one etc (Sieso & Crouzet, 1977).

During processing these compounds can evaporate (they have been found in evaporator condensates) and new components form. These include components which impart the cooked smell of thermally treated tomato products, for example, dimethyl sulphide and acetaldehyde and turfarol (Sieso & Crouzet, 1977). Several processing steps such as grinding/maceration, oxygen amount, heat and ripeness of the original tomatoes also contribute to the final flavour of tomato paste. The flavour release can be explained by what is formed or destroyed during tomato paste production. Several studies have identified components after stages in the tomato paste process. (Sieso & Crouzet, 1977). Tomato paste can undergo different heat pre-treatments such as cold break, warm break and hot break as previously mentioned in Chapter 2. This causes a different ratio of the most volatile (hexanal, hexenal, hexenols) and heat induced products such as aromatic compounds (6-methyl-5-heptn-2-one) and furan (furfural) by-products. Some volatile compounds of fresh fruit like linalyl acetate are present.

The increase of hexenals when tomato paste is heated can also be explained by how the hexenal products are formed.

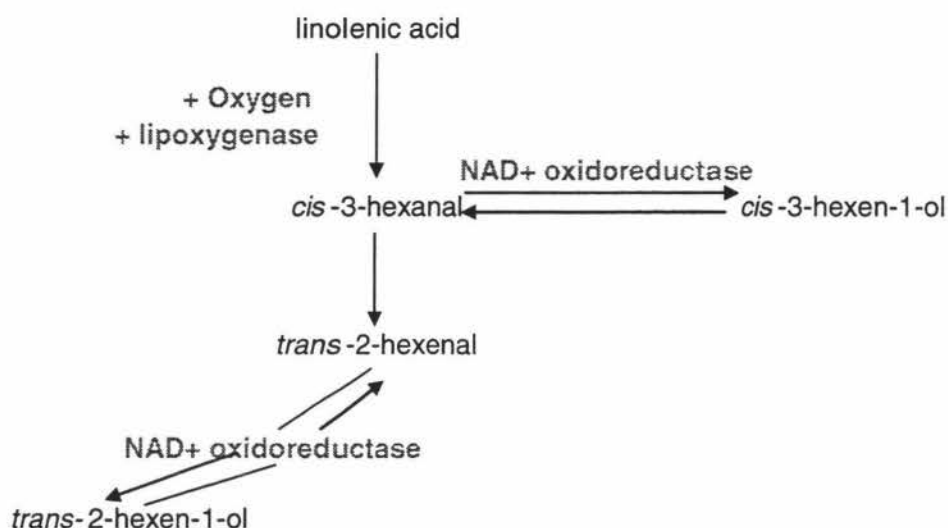


Figure 3.2 Production of hexenal products

cis-3-hexanol is formed during the crushing of the fruit, while the reduction reactions (involving NAD⁺ oxidoreductase) occur during the stripping of the volatile compounds and during the first stages of heating. As the heating increases the enzyme (NAD⁺ oxidoreductase) denatures. Due to the enzyme denaturation there is a relative amount of both *trans*-2-hexenal and *trans*-2-hexen-1-ol in the heated product (Sieso and Crouzet, 1977).

Concentration strips compounds that are involved in the aroma of fresh tomatoes such as 3-methyl butanol, *trans*-2-hexenal, *cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol and 2-isobutylthiazol. While increasing benzene derivatives such as styrene (also found in wine making proceeding from the decarboxylation of cinnamic acid), toluene, o-m m- and p-xylene, enxaldehyde, phenylacetaldehyde and 2-phenylethanol.

The heat pre-treatments and concentration also has an effect on the viscosity and final consistency of tomato paste which involves the degradation of carbohydrates yielding thermal products such as ethyl benzene & trimethyl benzene that contributes to the final flavour and acidity of tomato paste and tomato paste derived products. (Xu *et. al.* 1986; McColloch *et. al.* 1950)

➤ Microbial stability

Due to low pH and high temperature and aseptic processing, there is only likely to be a long term problem with fungal contamination. Microbial stability is also reflected by the tomato quality entering the process. Mould counts and pH are the important properties to measure.

Mould counts using the Howard Mould count technique have been the official method of determining the mould contained in tomato products. It is a direct measure of the quality of the raw materials used to create tomato paste. Original work by BJ Howard established standards by the Food & Drug Administration in 1916 (Goose & Binsted, 1973). Since then stricter limits have been enforced so then all tomato products (except tomato juice) packed, sold and shipped in the USA have to have a 40% positive fields. Other countries followed and most follow a 50% or 60% positive field test limit as the maximum acceptability of imports and products within the country.

The Howard Mould test has established itself as a quality measure in a court of law in London. In 1963 a case was brought before a Magistrates Court concerning an import of tomato paste with a high mould count. On investigation it was found that the tomato paste was made from a significant number of rotten fruit. Since then sterilisation has been a key processing step when manufacturing tomato paste.

As with many of the key factors of tomato paste, the quality of the original raw materials is an important factor to ensure the quality of the final product. This is indeed the case with tomato paste. The amount of mould in the mould count is a good indication of rotten fruit being used in the production or not. As during the development of mould the tomato tissue is broken down into rot. However there is always the possibility that contamination of good fruit can occur during manufacturing if dirty equipment is used.

The repeatability or precision of the Howard Mould count is also an issue. The identification and differentiation of mould fragments from that of tomato tissues is very difficult and requires the tuition from an experienced analyst before proceeding to complete the test. There is also an issue of distribution of the mould through the tomato paste sample which may or may not affect the repeatability. This repeatability is a factor to investigate during this project as, not only, does it give an indication of the quality of the tomato paste produced, but also a useful evaluation of the factory hygiene (Goose & Binsted, 1973; Gould, 1992; National Food Processors, 1992).

It is clear from the above discussion that there is no one measurement that will characterise tomato paste with respect to the functional properties of interest (flavour, sweetness, colour, acidity, viscosity and microbial stability). Instead a number of measurements must be carried out simultaneously. Because viscosity is a key property of tomato paste and paste derived products, the content of pectic compounds which impart high viscosity should be assessed. This is best done by quantifying the amount of insoluble solids (either directly or by difference) in the paste. Differences are likely to result from variation in fruit ripeness and inadequate control over the break process which destroys pectic enzymes in the fruit. With some reliable measurement of insoluble solids control of the break process will be possible.

The sweetness of tomato paste is imparted by a range of sugar compounds (primarily glucose and fructose) and interactions with the acidity of the pulp. The level of sugar in pulp or paste must therefore rely on the measurement of total reducing sugars, °Brix or soluble solids content of the sample.

The tomato flavour is due to a large number of volatile compounds which include compounds that impart a fresh or greenness to the pulp and compounds produced during processing that impart a cooked flavour. As such it is difficult to quantify the level of these compounds without advanced analytical techniques that would not be suitable to the factory floor

Colour is an important and complex attribute of tomato paste and paste derivatives. The predominant red pigment is lycopene within tomato paste and paste derivatives. Along with Lycopene many other complex reactions occur which contribute to the colour such as the presence of chlorophyll and pheophytin as well as the Maillard browning reaction.

Acidity is important with respect to flavour and can be assessed by measurement of titratable acidity or pH. pH is also important with respect to microbial stability as levels lower than pH4 effectively inhibit bacterial growth. Fungal spoilage must be characterised by direct measurement using microscopical techniques.

In summary the following compositional and physical properties must be quantified; soluble solids, insoluble solids (or total solids), pH, colour and fungal levels.

3.3 SEPARATION OF THE PULP AND SERUM FRACTIONS OF TOMATO PASTE

The separation of the fibrous pulp and serum fractions from warm break tomato paste involved the centrifugation at 8,000rpm for one hour at 15-20°C. From here the serum fraction (supernatant) was poured off and the pulp fraction (decantant) was scraped out of the centrifuge containers.

3.4 SOLUBLE SOLIDS MEASUREMENT

There are several methods available for the measurement of soluble solids including the use of refractometers (°Brix), separating out the insoluble solids by centrifuge and drying (oven, freeze-drying etc). Of these, °Brix determination is the most widely used method and is standard practice in the tomato processing industry (ISO 2173, 1978; Schiweck & Clarke, 2001; Analytical Bench Manual, 1999; National Food Processors Association, 1992). This section investigates how to carry out accurate measurement of °Brix in concentrated tomato paste samples and compares the reliability of this process with the other methods of soluble solids measurement.

3.4.1 BRIX MEASUREMENT PRINCIPLES

°Brix measurements represent the concentration of soluble solids in liquids by direct measurement of the refractive index. The refractive index of a liquid changes linearly with increasing solute concentration and therefore solute concentration can be estimated from refractive index with a calibration curve. At Heinz Watties, King Street a Bellingham and Stanley RFM300 digital refractometer is used to measure °Brix in tomato paste (Analytical Bench Manual, 1999).

3.4.1.1 Operation

The concentration of tomato paste is measured by smearing a small layer (1-2mm thick) of tomato paste across the glass piece of a refractometer at constant temperature (25°C). The refractometer is held at constant temperature by setting up a water bath from which the water circulates through the refractometer and around the glass section the tomato paste is applied to. A lid is then placed over the sample smearing any excess tomato paste away and ensuring the light refracted through the sample is not interfered with. The soluble solids and insoluble solids fractions, once separated, are measured in exactly the same way as the tomato paste.

3.4.1.2 *Calibration*

The standard practice of calibration used for both the analogue and digital refractometer involves the use of distilled water (as a zero reading) and a sucrose solution corresponding to the average concentration of the sample you are to measure. For example if a sample of tomato paste (manufactured at Heinz Watties to be 28°Brix) was to be measured, the sucrose solution would be made to around 30°Brix. However if the concentration of the sample is going to range, a two point calibration using a sucrose solution at a high and low concentration should be used to calibrate the refractometer. Constant temperature of the refractometer is important.

3.4.1.3 *Mechanism*

The °Brix measurement represents the concentration of the sugar content within the tomato paste. It is measured by either a digital refractometer such as the Bellingham-Stanley refractometer (as used in this project) or a non-digital refractometer such as the Abbe refractometer model. A refractometer uses the principle of light refraction to determine the concentration of the tomato paste. The refractometer is based on the critical angle effect which defines the borderline between refraction and total internal reflection of light at the prism/tomato paste interface. Digital automatic refractometers determine the exact position of the borderline by use of a light sensitive integrated circuit. Bellingham-Stanley goes a little further by incorporating special software for the interpreting 'fuzzy' borderlines. This technology automatically takes a reading removing the subjective reading which often occurs with optical mechanical refractometer such as the Abbe refractometer.

The quality measurement is an indication of how defined the borderline is, thus how precise the measurement can be (<http://www.bs-ltd.com/ltd/frameset.html>, Bellingham Stanley August 2000).

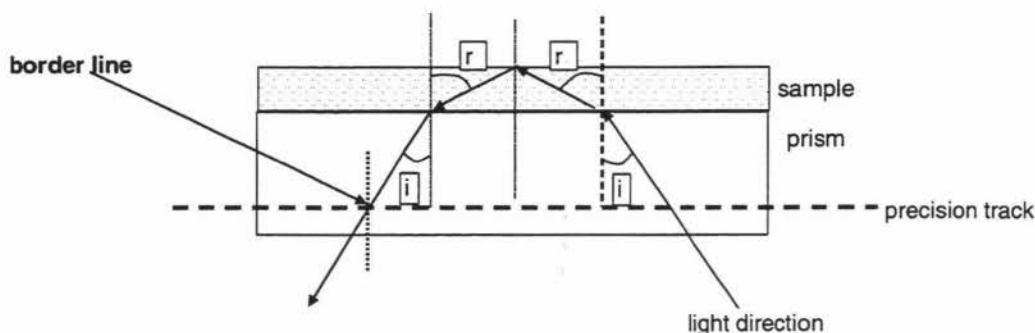


Figure 3.3 Refractometer working principle (where: r : angle of refraction; i : angle of incidence)

A quality parameter also was calculated using the digital refractometer. This indicates the quality of the reading or the clarity of the light at the sample-prism interface. The presence of solids in the sample will scatter the light and make the measurement interface broader and less clear. This results in a loss in precision. The quality parameter is a measure of this phenomena. The presence of pectic compounds (insoluble solids) in paste are likely to cause this to occur although there are no reports on how significant factor this is. The higher the quality parameter the more precise (less spread) the value has (<http://www.bs-ltd.com/ltd/frameaset.html>, Bellingham Stanley August 2000)

3.4.1.4 Time & Temperature

Bellingham Stanley and Abbe refractometer manufacturers, suggest that when operating the refractometer, the time that the sample is on the refractometer and the temperature the refractometer is at should be held constant. As the increase in temperature gives a decrease in density and since the measurement is based on refraction, light travels more rapidly through a lower density medium, therefore refraction decrease with increasing temperature. It is not known how significant these factors are when measuring tomato paste. (<http://www.bs-ltd.com/ltd/frameaset.html>, Bellingham Stanley August 2000)

To identify just how important, time, temperature and insoluble solids are, a series of experiments were conducted. From these investigations the best practice of determining the soluble solids content could be identified.

3.4.2 INITIAL INVESTIGATIONS

A preliminary investigation was carried out to assess the repeatability of °Brix measurements on Warm Break tomato paste. Ten repeat measurements using the Bellingham and Stanley RFM300 Refractometer were carried out on the following samples after calibration of the instrument.

- Whole tomato paste at 25°C
- Serum fraction (after centrifugation at 8,000 rpm and 15-20°C for 60 minutes)
- Bottoms fraction (after centrifugation of whole paste at 8,000 rpm, 15-20°C and for 60 minutes and then washed and re-centrifuged four times. This fraction is very high in insoluble solids.)
- Paste diluted to 12°Brix with distilled water at 25°C

The results of each sample were averaged and the sample standard deviation was determined. The 95% confidence limits were used to quantify the level of precision (spread) achieved for each sample using Eqtn 3.10 (Hitzmann 2000).

$$\bar{x} \pm \Delta x = \bar{x} \pm t_{n-1}^{0.95} \times \frac{s}{\sqrt{n}}$$

Eqtn 3.10 (Hitzmann, 2000)

Table 3.1. Repeatability of °Brix measurements

Sample	\bar{x}	n	S	Δx
Whole tomato paste	28.51	66	0.217594	0.053491
Serum fraction	26.81	66	0.024043	0.005911
Bottoms fraction	29.23	66	0.478832	0.117711
Diluted paste (12°Brix)	12.23	66	0.057553	0.014148

The table above shows two issues arising from the increase in insoluble solids content. Firstly the spread or variation in °Brix value increases with increasing insoluble solids. Secondly the mean (\bar{x}) value of °Brix increases as the insoluble solids content increases, (outside the confidence limits) which shows an inaccuracy with the reading of the °Brix values if using whole tomato paste.

Because the serum, whole paste and bottoms fractions originated from the same paste sample the results should be the same. These results indicate that insoluble solids do significantly affect both the accuracy and precision of °Brix measurements. The effect of insoluble solids on °Brix measurements were further investigated in this project.

3.4.3 EFFECT OF TIME ON °BRIX READINGS

The time taken for the sample to come to equilibrium in the refractometer could result in potential errors if significant. A series of simple experiments were therefore carried out to quantify the change in °Brix readings as a function of time.

The Bellingham and Stanley RFM300 was connected to a laptop PC via the RS232 serial connection and continuously logged every 20 seconds using the logging software supplied with the instrument. A sample was placed on the refractometer and the data recorded until a stable reading was recorded. This experiment was repeated several times with different whole warm break tomato paste samples.

Typical results are shown below in Figure 3.4.

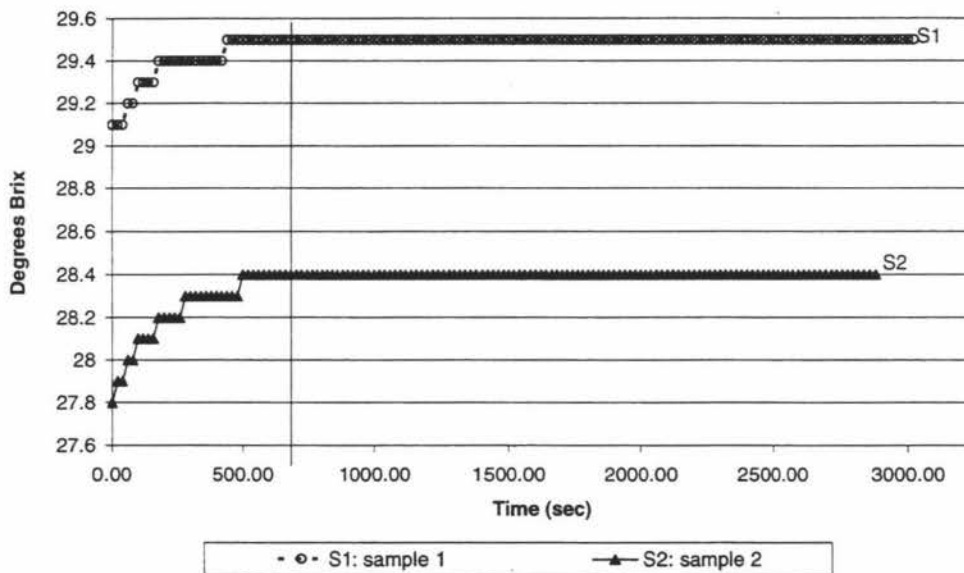


Figure 3.4 °Brix vs time for whole warm break tomato paste

These show that the samples reached a stable reading after approximately 10mins. The largest error observed if this time period is not observed was 0.6 °Brix which is significant. For this reason it is important that at least 10 minutes is left before the sample reading is taken.

3.4.4 EFFECT OF TEMPERATURE ON °BRIX READINGS

Temperature could also affect readings and for that reason it is possible to control the temperature of the refractometer prism and sample by pumping water through the instrument from a controlled temperature water bath. The affect of temperature was investigated to test if it had significant changes to measurement accuracy and precision.

3.4.4.1 Methodology

The water-bath temperature was adjusted over the range of 25°C to 40°C and the °Brix readings were measured via the logging mechanism previously described in section 3.4.3. The °Brix readings were measured over a 2 to 3 minute period to allow thermal equilibrium of the sample and prism to occur. Whole warm break tomato paste, the serum fraction, 12°Brix diluted paste and a 30°Brix sucrose solution was measured over the differing temperatures to investigate the effect.

3.4.4.2 Results

Table 3.2 Summary of °Brix measurements over a range of temperatures

SAMPLE	25°C		30°C		40°C	
	MEAN	QUALITY	MEAN	QUALITY	MEAN	QUALITY
Paste 1	28.72	55.0	28.77	50.3	28.88	50.8
Paste 2	28.78	46.0	29.42	50.5	28.84	50.9
Paste 3	30.03	47.8	29.06	51.6	28.76	52.7
Serum 1	27.40	97.0	27.32	97.8	27.23	85.8
Serum 2	27.32	97.6	27.31	98.0	27.22	98.0
Serum 3	27.40	97.0	27.33	98.0	27.18	98.0
12°Brix 1	11.60	72.0	11.67	71.29	11.49	68.4
12°Brix 2	11.62	73.0	11.60	70.9	11.52	69.4
12°Brix 3	11.63	70.6	11.68	72.2	11.57	70.0
Sugar Solution	30.90	93.4	30.90	99.0	30.9	98.0

The samples quickly equilibrated to that of the prism temperature, as the prism temperature did not drop significantly when the sample was added.

The results show that the sugar solution is independent of temperature in the 25-40°C range as the same value was seen. In comparison, it is very hard to see if temperature influences the °Brix readings in the whole paste and the diluted 12°Brix tomato paste as there were significant variances between the replicates anyway. The serum sample shows very small variation over the temperature range 25-40°C as well as much less variation between the replicates in comparison to that of the whole paste and diluted tomato paste.

In conclusion there are very small, if any, temperature effects in the range 25°C-40°C for whole tomato paste, 12 °Brix diluted tomato paste and tomato paste serum samples. It is probably worthwhile continuing to control the prism temperature during measurements but the affect of temperatures is obviously of much less importance than insoluble solids.

3.4.5 EFFECT OF INSOLUBLE SOLIDS ON °BRIX MEASUREMENTS

It was clear from the preliminary experiments, that the errors are likely to be caused by the presence of insoluble solids in paste samples during refractometry measurements. These errors were significant with respect to both the accuracy and precision of the experiment and appeared to be correlated with the quality parameter given by the Bellingham and Stanley refractometer.

To investigate this effect further a series of experiments were carried out using a warm break tomato paste with varying amounts of insoluble solids. A sample of warm break paste was centrifuged for 60 minutes at 8000 rpm. The serum phase was then separated from the bottoms by decanting and each fraction was mixed well. Each fraction then was analysed for total solids using the vacuum oven drying method given in section 3.5 of this work. The serum fraction was then measured for °Brix levels using the refractometer at 25°C and the reading and quality parameter was recorded. A small amount of the bottoms fraction (containing large amounts of insoluble solids) was then mixed back into the serum and the °Brix reading taken. This process was continued until all the bottoms had been mixed back into the serum (to give whole paste).

A second experiment was made in a similar way but starting with the bottoms fraction and gradually adding back serum into the sample. In this way the effect of insoluble solids on °Brix measurements could be made at even higher insoluble solids concentrations than for whole paste.

The results of these two experiments are illustrated in Figure 3.5

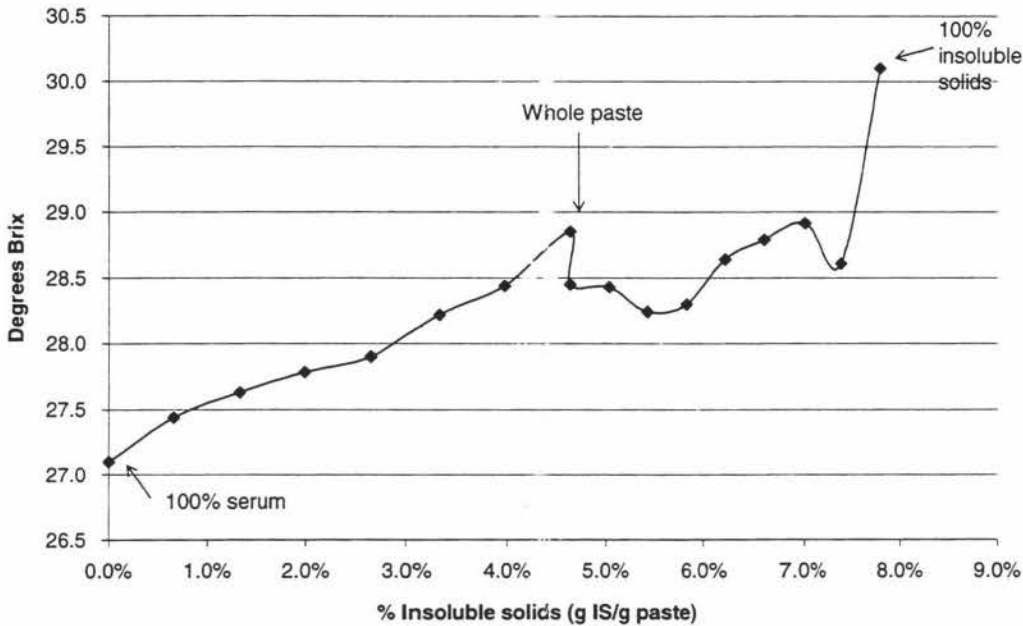


Figure 3.5 °Brix vs g of insoluble solids/g of tomato paste

An obvious trend is illustrated by Figure 3.5. As the fraction of insoluble solids increase the °Brix value increases. Therefore the insoluble solids content has an effect on °Brix. °Brix has previously been seen to be influenced by the insoluble solids content in section 3.4.2 (Table 3.1)

A °Brix value between the 100% soluble solids and 100% insoluble solid can be seen. Where as, a 1.6°Brix value can be seen between that of whole tomato paste and whole serum (soluble solids). Equating this in terms of stock levels, a 1.6 °Brix difference using an average whole warm break tomato paste of 27.1 °Brix equates to a 5.9% difference in °Brix value between that of whole paste to that of a serum reading. Or alternatively this is a 5.9% overestimation in °Brix reading which equates to a 283,200 kg overestimation in tomato paste stock levels per annum (where basis is 4.8 million kg of tomato paste /annum).

Figure 3.6 illustrates the quality as the insoluble solids fraction increases. As can be seen a polynomial trend-line fits the data reasonably well ($R^2=0.9199$).

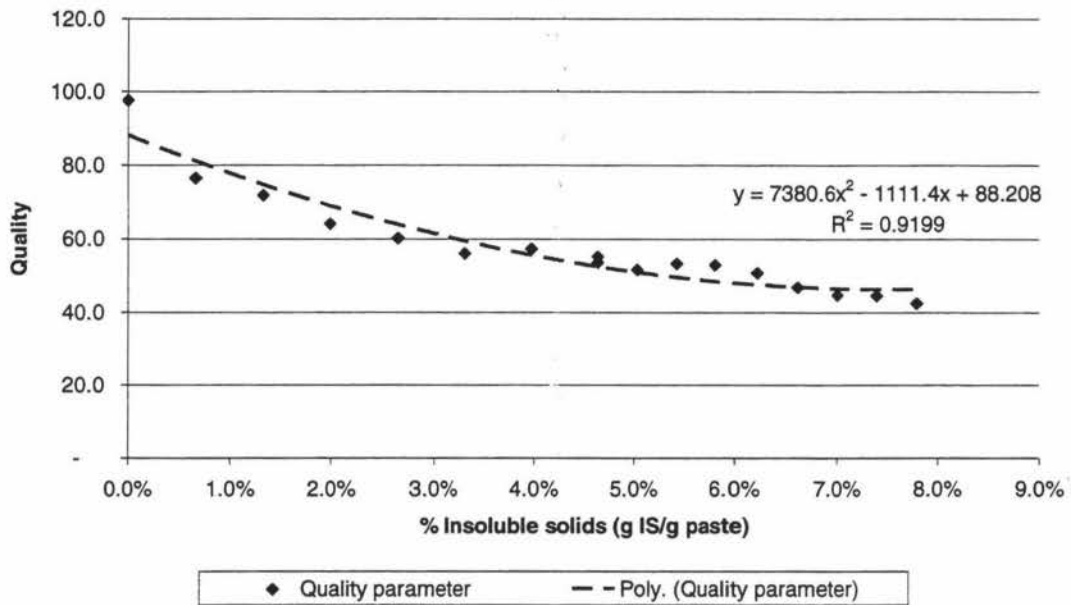


Figure 3.6 Quality parameter vs g of insoluble solids /g of tomato paste

As the grams of insoluble solids to grams of tomato paste increased the quality measurement (obtained from the Bellingham Stanley refractometer) decreases. This enforces the issue that the insoluble solids fraction should be at 0% in order for the quality of the measurements to be at 100%. Figure 3.6 also reiterates this concept.

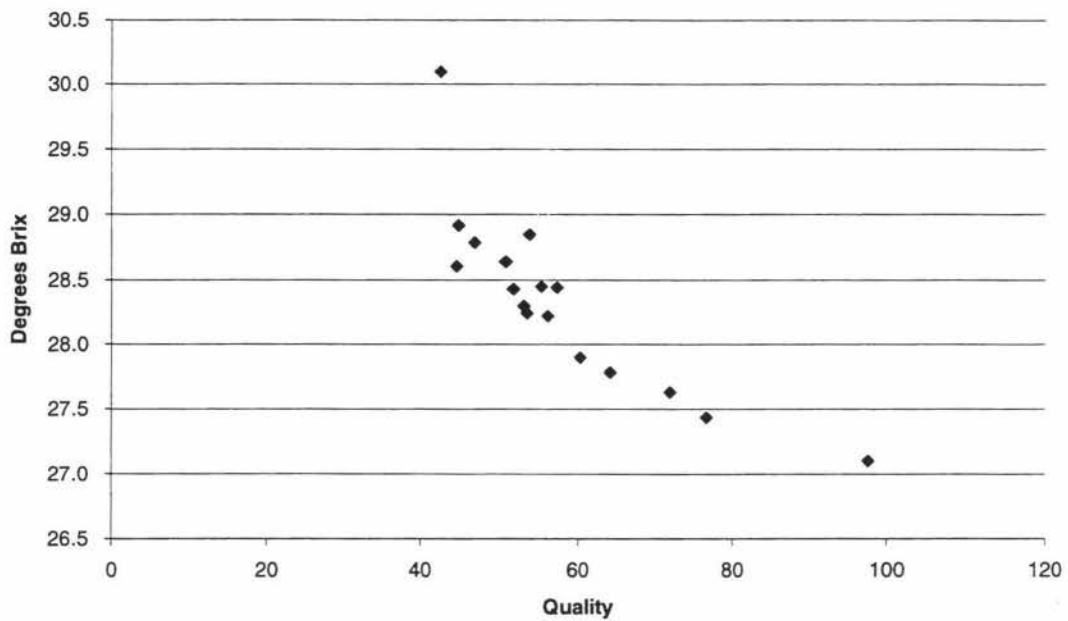


Figure 3.7 °Brix vs quality

As shown by Figure 3.7, as the °Brix increases the quality decreases.

Therefore in order for precise and accurate measurements of the concentration of tomato paste to be established the insoluble solid material must be separated before a measurement is to be made using the serum or soluble solids fraction.

3.5 TOTAL SOLIDS

Total solids represents the tomato solids remaining after water is expelled. There are a variety of methods to determine the total solids of tomato paste, using different pieces of apparatus. The following four methods were found to be the main ones in use for total solids determination of tomato paste.

1. AOAC Vacuum Oven Method (VOS)
2. AOAC Forced Air Oven Method (FAO)
3. Microwave Method (MOS)
4. Freeze Drying (FREEZE)

(National Food Processors, 1992; Goose & Binsted, 1964, 1973; Gould, 1974, 1992; Heinz Watties Analytical Manual, 1999)

A review of these methods and the experimental determination of the precision and repeatability of each of the four methods listed above was conducted. The conditions involved in the methodology of each total solids method can be seen in Table 3.3.

Table 3.3 Total solid method comparison

DRYING METHOD	FEATURES			COOLING TIME (in dessicator)
	time	temp (°C)	other features	
1. VOS	12 hrs	70°C	Vacuum Pressure : 23" Hg or 590 mm Hg Combine with diatomaceous earth to prevent burning	20 minutes
2. FAO	12 hrs	100°C	Dry heat Combine with diatomaceous earth to prevent burning	20 minutes
3. MOS	6 minutes	-	Power = Low	10 minutes
4. FREEZE	3 hrs freezing & 24-36 hrs drying under vacuum	-70 °C freezer	Dried under vacuum until constant weight achieved. Dependent on the shared or sole use of apparatus	20 minutes

3.5.1 METHODS

3.5.1.1 *FAO*

1. Diatomaceous Earth and dishes were put into the 100°C oven for 24hours prior to use
2. Diatomaceous earth and dishes were put into dessicator to cool
3. Pan and lid was weighed
4. 0.6g approx of diatomaceous earth was added
5. 1-2g of tomato paste was added and the final weight was recorded
6. Little distilled water was added and the tomato paste and diatomaceous earth were mixed together into a thin paste with spatula, spatula was then cleaned off using extra distilled water to allow any excess tomato paste and diatomaceous earth to remain in pan.
7. Tin and lid and sample were placed in the forced air oven for 12hours.
8. Cooled for 20mins in the dessicator
9. Dry weight weighed and the % of the dry to the wet weight was calculated

3.5.1.2 *MOS*

Method did not include tomato paste and diatomaceous earth being mixed together to prevent burning. The 1-2g of tomato paste was weighed straight out onto a tared glass filter paper and put into the microwave oven at LOW for six minutes.

3.5.1.3 *VOS*

This employed exactly the same method as the FAO except the samples were placed into a vacuum oven under 23" Hg (590mm Hg) pressure for 12hours.

3.5.1.4 Freeze

A known quantity of tomato paste was measured into a sealed flask and frozen at -70°C for 3 hours before being removed and dried in the vacuum oven under 23" Hg (590mm Hg) pressure for 24-36 hours until constant weight was achieved.

These four drying procedures were tested using the same warm break tomato paste ($^{\circ}\text{Brix} = 29.52$). Eight replicates were made for the vacuum oven and forced air oven methods while six were done for the microwave method and 5 for the freeze drying methodology due to the limited number of flasks available.

Experimental comparison of the four total solids methods involved the use of the same tomato paste and the use of standard procedures if available, as in the case of the vacuum and forced air ovens. The microwave method was developed due to the use of a different oven to the one stated in HW Canada procedures. Both the vacuum oven and forced air oven method involved the tomato paste to be mixed with diatomaceous earth in order to eliminate burning.

The results of each sample were averaged and the sample standard deviation was determined. The 95% confidence limits were used to quantify the level of precision (spread) achieved for each sample.

$$\bar{x} \pm \Delta x = \bar{x} \pm t_{n-1}^{0.95} \times \frac{s}{\sqrt{n}}$$

Eqtn 3.10 (Hitzmann, 2000)

Table 3.4 Summary of total solids measurement results

Total Solids Method	x	n	S	Δx
VOS	29.97	8	0.0016	0.0013
FAO	27.03	8	0.0247	0.0207
MOS	32.35	6	0.0046	0.0048
FREEZE	31.72	6	0.0020	0.0025

The four total solids methods give a 5.3% variation in the mean total solids, with the Forced Air Oven (FAO) method having the lowest mean value and the Microwave Oven Method (MOS) having the highest. In terms of the spread of the results the Forced Air Oven had the highest spread followed by the Microwave oven and Freeze drying methods. The Vacuum Oven method (VOS) indicates the lowest spread or variation hence the increased repeatability of results. Other factors to consider are summarized in table 3.5 below.

Table 3.5 Advantages and disadvantages of the four total solids methods

Method	ADVANTAGES	DISADVANTAGES
1. VOS	- Oven easy to obtain - Consistent results	12 hour wait
2. FAO	- Oven easy to obtain	12 hour wait Burn on also occurs if tomato paste is not evenly mixed with the diatomaceous earth
3. MOS	- Quick results achieved - Conventional oven used and easy to obtain	Must make sure the sample is even in distribution otherwise burn on occurs
5. FREEZE		Must ensure sample is frozen first then also long time delay when under vacuum (24-36 hrs)

The best method out of the four reference methods trialled in this study is the vacuum oven method. The VOS method gave the lowest variation between results, hence the best repeatability. The disadvantage of this method is the 12 hour wait before the sample results are obtained. Coupled with this is the large amount of equipment needed; drying containers, diatomaceous earth (both of which need to be dried for 12 hours before use), dessicator and vacuum oven.

Within the factory processing environment, a quick method needs to be employed. This dismisses the use of the VOS which has been previously reported as being a very repeatable method of determining solids. The microwave oven method would therefore be the most direct way of achieving a quick and accurate result of total solids. This project involved the use of a conventional microwave oven and identified that care must be taken with the even distribution of the sample before drying. A conventional oven is also easily obtainable. During this study a specific microwave oven has been found to exist specifically for determining the moisture contents of foods. This device is said to achieve repeatable results in a quick fashion and without the tendency of burning. The scope of this project does not cover tests of this device which would have to be completed before it's use as a possible measure of tomato paste total solids.

3.6 INSOLUBLE SOLIDS MEASUREMENT

The insoluble solids fraction was removed from the soluble solids fraction by centrifuging at 8,000 rpm for one hour at 15-20 mins. To improve the purity of the pulp solids the pallet was washed with distilled water and re-centrifuged to separate the fractions. This washing and re-centrifugation was repeated. A third washing was then carried out with the use of a vacuum filter to remove the excess moisture.

The number of washes that the insoluble solids fraction required was determined on the basis of the °Brix of the wash water. As can be seen from Figure 3.7 the third wash results in a wash water of 0 °Brix. This indicated that the pallet was free of soluble solids in the pulp.

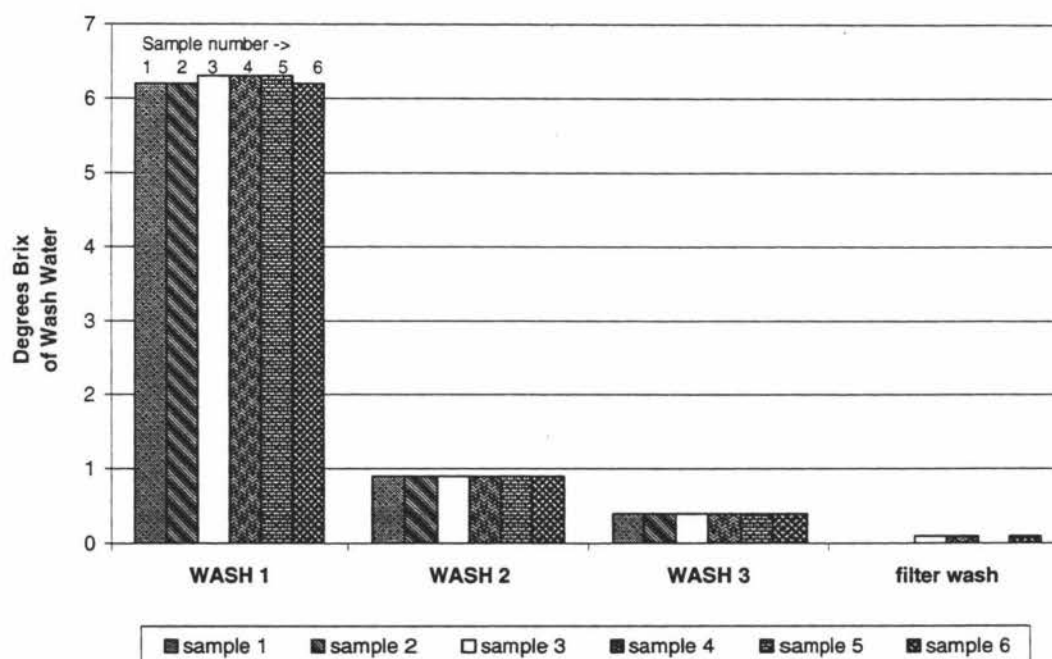


Figure 3.8 Progressive decrease in °Brix of the wash waters as the insoluble solids fraction is washed and re-centrifuged in order to isolate the insoluble solid (IS) fraction

The insoluble solids component was measured by drying under the same methodology as the whole tomato paste under the Forced Air Oven method.

1. The insoluble solids and diatomaceous earth
2. Mixed with little distilled water
3. Dried in the forced air oven at 100°C for 12 hours
4. Cooled for 20mins in the dessicator
5. Dry weight weighed and the % of the dry to the wet weight was calculated

3.7 pH MEASUREMENT

The pH of the tomato paste is a very important feature again as, already mentioned, goes towards the characterising the final use of the tomato paste. The pH is a scale commonly used and the method that was used for the project and Heinz-Watties is the same. This method involves using an electronic pH meter that works on the principle of conductivity. The conductivity of the solution to which the probe is sunk into is compared to that of a range of reference solutions (standardised buffer solutions) to which the pH meter is calibrated against.

When measuring the acidity (pH level) of the tomato paste the pH meter is specific to the range in which the pH's are likely to fall. For example if the tomato paste is highly acidic pH=2-4, then the pH meter and probe would be especially designed to handle these conditions.

For the case of tomato paste the acidity is 4-5. A specific pH probe and meter to that of the tomato paste is used. The pH probe is calibrated using a 2 point calibration process using buffers pH 4 and pH 7 as they pertain to the region of testing. pH is dependent on temperature so the temperature of the buffers (when calibrating) and the samples to be tested, must be maintained at the same temperature. For the purpose of this study both the pH buffers and the tomato paste samples were kept at 25°C before the pH was measured. This involved immersing the pH probe into a volume bag where the temperature may be different and cause an inaccurate measurement.

Variation between measuring one sample 20 times at 25°C is shown in Table 3.7. These results indicate a low amount of spread of values and a high level of repeatability from the low standard deviation and low Δx .

Table 3.6 Repeatability of the pH measurement

	x	n	S	Δx
pH	4.330	20	0.0470	0.0220

3.8 COLOUR MEASUREMENT

At Heinz-Watties the colour is measured using a Hunterlab colorimeter. The colour of the 12°Brix diluted tomato paste is compared to that of colour tiles which are the reference point to which the tomato paste is compared to. During the project a Minolta colorimeter was used which also gave the Y, x and z coordinates on the standard colour scale and the reference point used was a white colour tile. The tomato paste sample here needed not to be diluted, which would involve an inherent error from the Bellingham Stanley from which the diluted °Brix measurement would be measured from. Colour is a very important feature of tomato paste quality and final use in different products due to the consumer perception of tomato products being of the rich red colour. Also as mentioned previously the tomato paste colour is also of great importance in the increased knowledge of the beneficial antioxidant lycopene, which is the red colour pigment within the tomatoes.

During this project the colour of the tomato paste was measured using a Minolta digital colorimeter. Using the CIE colour system and was calibrated against a white tile (Y=93.8; x=0.3164, y=0.3339).

The precision of the Minolta digital colorimeter was tested using one warm break sample tested 20 separate times. The results are shown in Table 3.8. All the variables measured (Y, x, y) show a good repeatability and a low level of variance which is indicated by the small values of low Δx and low (S) standard deviation.

Table 3.7 Precision of colour measurements using the Minolta digital colorimeter

	x	n	S	Δx
Y	7.757	20	0.009787	0.004581
x	0.4168	20	0.0001399	0.000065487
y	0.32694	20	0.0001142	0.000053470

3.9 MOULD COUNT MEASUREMENT

The amount of mould is determined in accordance with the Howard Mould Count procedure, which has been acknowledged as the official AOAC (9th Edition) method of evaluating mould in tomato products (Goose & Binsted, 1973). At Heinz-Watties the samples must have less than 50% positive tests with mould (Cooley, 1999).

Howard mould count method used in this project involved the following steps:

1. Dilute tomato paste down to 7°Brix
2. Add 5 drops of blue indicator(1% Methylene blue solution, stored at 4°C)
3. Mix well
4. Add a dab to the specialised Howard mould plate
5. Push the top down
6. Plate has 25 squares
7. Under a microscope count each square that has mould in it
8. Work out the % of total squares which is the % mould for that sample.

(Goose & Binsted, 1973; Cooley, 1999; Analytical Bench Manual, 1999).

The precision of the Howard Mould count was also tested and as can be seen from Table 3.9, the variance of data and the repeatability are not very good as indicated by the high values of standard deviation and Δx .

Table 3.8 Precision of Howard mould count

	x	n	S	Δx
No. positive squares	3.25	16	2.113	1.126
% positive	13%	16	8.454%	4.505%

3.10 CONCLUSIONS

In conclusion, this chapter has showed that soluble solids, insoluble solids (or total solids), colour, pH and mould counts are all important factors to measure in order to properly characterise the important functional and quality parameters of tomato paste (such as, flavour, sweetness, viscosity, colour, acidity and microbial stability).

In order to measure soluble solids, centrifugation of the tomato paste is needed to separate the soluble solids from the insoluble solids. The soluble solids (serum) content can be established by drying via a vacuum oven with diatomaceous earth for 12 hours at 70°C. The concentration (°of sweetness) of the soluble solids can be measured with the °Brix scale using a digital refractometer under constant temperature and time.

Insoluble solids content can be established by the drying of the washed insoluble solids component (remaining from the centrifugation of the tomato paste after decanting the serum). The insoluble solids can be dried under the same conditions as the soluble solids, vacuum oven at 70°C for 12 hours.

Total solids can be measured directly by drying. The Vacuum oven method at 70°C for 12hours has been found to give the most repeatable and the lowest variation in results in this investigation.

The pH value (acidity level) can be directly read via a pH meter that is designed and calibrated for pH values around pH 4-5 (the usual acidity of tomato paste). Samples of tomato paste must be kept at the same temperature at which the pH meter is calibrated (usually 25°C).

When measuring colour, a good colorimeter should be used which has standard colour systems being measured (L, a and b or Y, x, y) and calibrated against a white tile. The colour variance must be tracked and should be compared to that of standard values specified for the production of tomato paste (a/b (yellowness to redness scale) =1.9 or above for first grade tomato paste).

Controlling the microbial activity is a vital part of any food processing and therefore frequent measurements should be conducted during processing to ensure that the tomato paste is within standards. However the current test method, the Howard Mould count does not have a high level of repeatability. Due to this other methods beyond this thesis should be explored. In addition to this ensuring that the raw material is graded properly and the process lines are kept clean from material build-up will contribute to a low microbial activity.

Therefore in order to properly characterise tomato paste in terms of its flavour, sweetness, viscosity, colour, acidity and microbial stability, soluble solids, insoluble solids, total solids, pH, colour and the Howard mould counts should be measured.

CHAPTER 4 CORRELATIONS BETWEEN VARIABLES

Chapter 3 has introduced that certain variables/characteristics are important when determining the characteristics of tomato paste. It has also been identified that only one measurement is not enough to characterise tomato paste with respect to the functional properties such as viscosity, flavour, sweetness, colour, acidity and microbial stability.

Preceding studies have also suggested that some variables are difficult to measure, in terms of time, equipment or precision. For example, total solids take a long time to measure and soluble solids are not easy to measure directly. Another thing that is suggested is that correlations may exist between the relationships of the variables. If so, this would be advantageous as then specific variables could be determined indirectly and less overall measurements may be required. Errors associated from these measurements and other variables could be included when using these correlations and these could then be used to identify the best ways of characterising tomato paste. The exploration of existing correlations is investigated in this chapter, followed by experimental study into whether these correlations are practical.

Modelling was carried out from knowledge of the components that exist within tomato paste. Tomato paste is made up of total solids and water. Within the total solids are soluble solids and insoluble solids, which can be classified as the sugar (serum) fraction and fibrous fraction respectively. The variables examined by mathematical modelling then experimental research were that of specific gravity and total solids (SG and TS); total solids, soluble solids, insoluble solids and °Brix (TS, SS, IS and °Brix) and Viscosity.

4.1 SG AND TS

The objective of this section of this chapter was to determine the relationship between the specific gravity (SG) and total solids (TS). Within this main objective several other issues were investigated. The first was whether the differing proportions of insoluble solids and soluble solids (which make up the fraction of total solids) have an effect on the specific gravity and total solids relationship. The second issue explored was whether the differing type of tomato paste (that is, hot break or warm break) has an impact on the specific gravity and total solids correlation. Lastly, was the connection temperature may or may not have on this specific gravity verses total solids relationship.

4.1.1 LITERATURE

Several reports in the literature, (Goose & Binsted, 1973; Gould, 1974; Gould, 1992; National Food Processors Association, 1992; Analytical Bench Manual, 1999) suggest that there is a direct correlation between specific gravity and total solids.

4.1.1.1 *Dr Andy Crawford's correlation (Heinz North America Technical Services, 1998)*

Dr Andy Crawford, USA developed a correlation for internal use at Heinz (USA) based on hot break tomato paste using HUSA tomato varieties (RHB 29-31 Natural Tomato Soluble Solids [NTSS]). Tomato paste samples used were from four Heinz Watties North American tomato paste factories with total solids being measured using vacuum oven and microwave oven methods. True density was measured using an Anton Paa DMA 58 density meter. (Heinz North America Technical Services, 1998)

4.1.1.2 *Tomato Bulletin data (National Food Processors Association, 1992)*

The tomato bulletin data, developed refractive index verses specific gravity of pure hot break tomato paste (with an average total solids of 26%) by the National Food Processors Association (1992) (varieties not specified). Total solids were measured using the AOAC vacuum oven method. While specific gravity was measured using tomato paste diluted by a ratio of 1:1 and with both water and product at 25°C. The tomato paste used for this specific gravity vs total solids correlation comes from five Californian canners from 1973-1974 seasons. (National Food Processors Association, 1992)

4.1.1.3 *Heinz Watties Analytical Bench Manual (Analytical Bench Manual, 1999)*

Heinz Watties Hastings Analytical Bench Manual shows a correlation table with specific gravity values corresponding to a total solids value. The specific gravity was measured using a diluted tomato paste sample diluted 1:3 with water at 25°C and the total solids value was read off at this corresponding specific gravity. No details on the tomato variety or type of tomato paste were specified. (Analytical Bench Manual, 1999)

The correlation between specific gravity and total solids using data from literature (Dr Crawford's data, tomato bulletin and Heinz Watties data) is shown by the following graph by Fig 4.1.

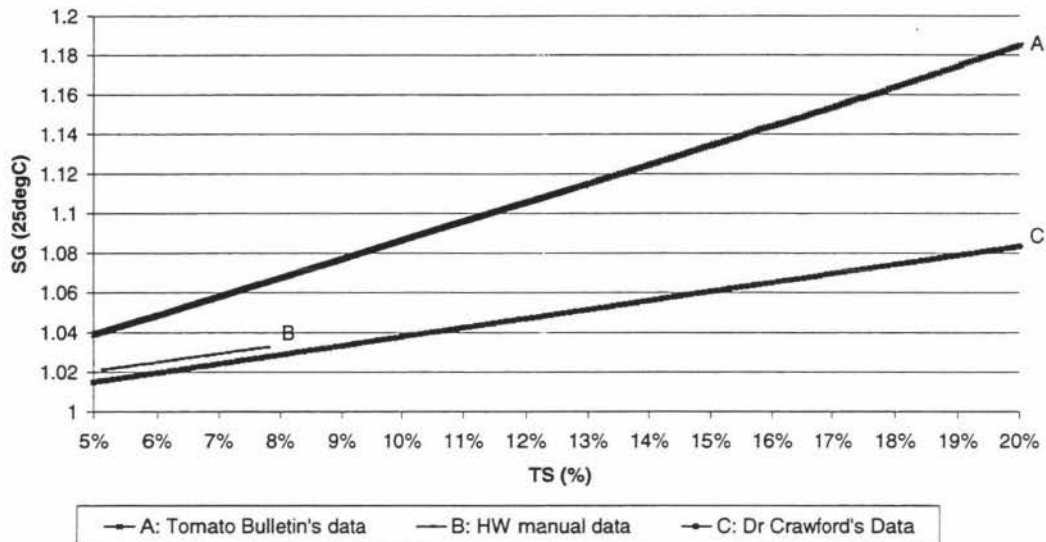


Figure 4.1 Specific gravity (SG) vs % total solids (% TS) using Dr Crawford, Tomato Bulletin and Heinz Watties analytical manual data correlations at 25°C

As can be seen by Fig 4.1 all of these studies show a direct correlation of specific gravity to that of %total solids. The Heinz Watties analytical manual data shows a similar gradient, but slightly higher values of specific gravity verses of total solids to that of Dr Crawford's data. Whereas the Tomato Bulletin data, shows both a higher specific gravity with a different gradient to that of the other literature data. One of the reasons could be due to the different varieties of tomato used and experimental methods. Temperature differences, at which specific gravity was measured at, may also cause the total solids to vary. Constant temperature was stated in all the models with tomato bulletin data and Heinz Watties data obtained at 25°C but the temperature was not given in Dr Crawford's data.

4.1.2 MODELLING

Choi & Okos (1986) suggest that the following simple model can be used to relate density to composition

$$\frac{1}{\rho} = \sum_{i=1}^I \frac{x_i}{\rho_i} \quad (\text{Eqtn 4.1})$$

Density for the individual food components (as a function of temperature (°C)) can be given as empirical values by Eqtns 4.2, 4.3, 4.4.

$$\rho_{sugar} = 1.599.1 - 0.31046T \quad (\text{Eqtn 4.2})$$

$$\rho_{fibre} = 1311.5 - 0.36589T \quad (\text{Eqtn 4.3})$$

$$\rho_{water} = 997.18 + 0.0031439T - 0.0037574T^2 \quad (\text{Eqtn 4.4})$$

Note that these equations are based on the assumption that the insoluble solids component is different per sample.

As previously mentioned tomato paste can be thought of as a simple mixture of water and total solids, which are made up of sugar and fibre. Using this simple context allows the Choi & Okos model (Eqtn 4.1) to be expanded to that of the following shown in Eqtn 4.5 or 4.6.

$$\frac{1}{\rho_{TP}} = \frac{x_{sugar}}{\rho_{sugar}} + \frac{x_{fibre}}{\rho_{fibre}} + \frac{x_{water}}{\rho_{water}} \quad (\text{Eqtn 4.5})$$

or

$$\frac{1}{\rho_{TP}} = \frac{x_{SS}}{\rho_{sugar}} + \frac{x_{IS}}{\rho_{fibre}} + \frac{(1 - x_{SS} - x_{IS})}{\rho_{water}} \quad (\text{Eqtn 4.6})$$

where

$$1 = x_{water} + x_{SS} + x_{IS} \quad (\text{Eqtn 4.7})$$

Specific gravity is the density of a substance divided by the density of water at 25°C ($\rho_{\text{water (STD)}} = 994.86 \text{ kg/m}^3$ (Choi & Okos, 1986)) and therefore from Eqtn 4.6 and 4.7 we get

$$SG = \frac{\rho_{TP}}{\rho_{\text{water (STD)}}} = \frac{1}{\frac{x_{SS}}{\rho_{\text{sugar}}} + \frac{x_{IS}}{\rho_{\text{fibre}}} + \frac{(1-x_{SS}-x_{IS})}{\rho_{\text{water}}}} \quad (\text{Eqtn 4.8})$$

The relationship illustrated by Eqtn 4.8 shows that the correlation between SG and TS is dependent on what fraction of the tomato paste (TP) is soluble (X_{SS}) and insoluble (X_{IS}). As previously mentioned in chapter 2, the insoluble solids to total solids ratio (IS/TS) changes with the tomato variety, throughout the production season and is also dependent on the ripeness of the fruit. The variability of the IS to SS ratio develops from the change in composition during the ripening process. The unripe green tomato has a high proportion of insoluble solids (the fibrous fraction) in comparison to the soluble solids (sugar) fraction. As the tomato ripens the enzyme which breaks down the fibrous chains is activated. Within these fibrous chains are sugar components, which are discharged as the fibrous chains are broken up. This increases the soluble solids component and hence the sweeter ripe tomato flavour.

The effect of what fraction of the total solids is soluble can be explored by considering what happens to the Choi & Okos (1986) correlation for different ratios of IS/TS in the expected range of processing tomato paste

That is:

$$SG = \frac{1}{\frac{(1-\frac{IS}{TS}) \times TS}{\rho_{\text{sugar}}} + \frac{\frac{IS}{TS} \times TS}{\rho_{\text{fibre}}} + \frac{1-TS}{\rho_{\text{water}}}} \quad (\text{Eqtn 4.9})$$

$$\rho_{\text{water (STD)}}$$

The impact of varying IS/TS ratios from 2% to 3% (typical insoluble solids content of warm break tomato paste) is illustrated by Fig 4.2.

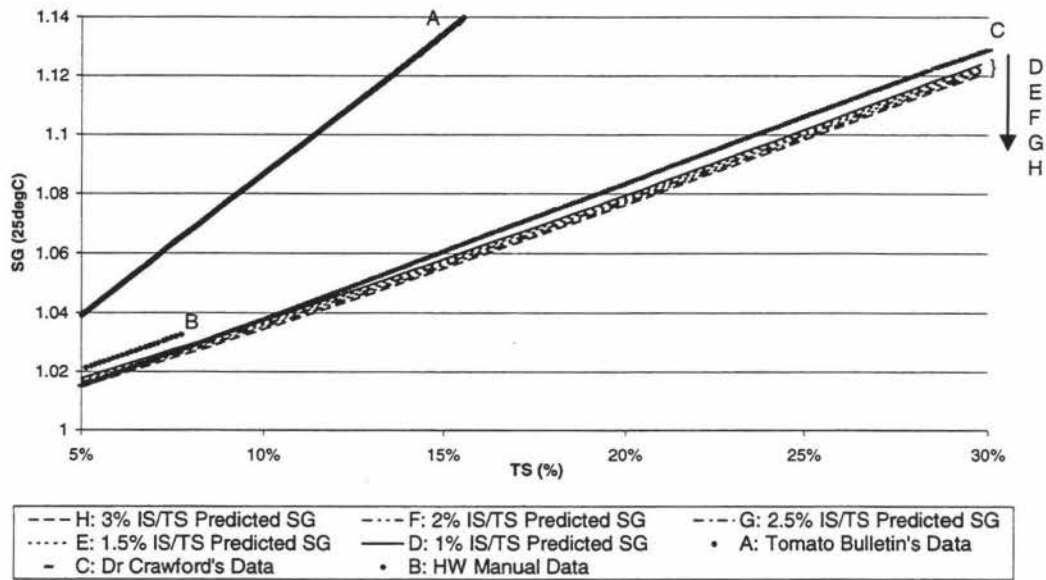


Figure 4.2 Specific gravity (SG) vs % total solids (% TS) at differing insoluble solids to total solids ratios (IS/TS) at 25°C using Choi & Okos (1986) model with Literature data overlaid.

Figure 4.2 illustrates the model of Choi & Okos (1986) with differing IS/TS ratios (lines D-H) with the addition of trends (lines A-C) indicated by the literature data within Fig 4.1. As can be seen from the overall Fig 4.2, there is a difference in the Choi & Okos specific gravity value over the differing insoluble solids level at constant temperature of 25°C. The model also shows a similar trend to that of both the Heinz Watties analytical manual data and that of Dr Andy Crawford's data. The tomato Bulletin data still shows a unique trend. The Choi & Okos model is very close to Dr Andy Crawford's data at the lower end of the % total solids scale and even though it shows a similar trend it does deviate further away as the % total solids increases. The differences between the correlations could be that of different varieties of tomatoes used and the different component ratios to that of the model.

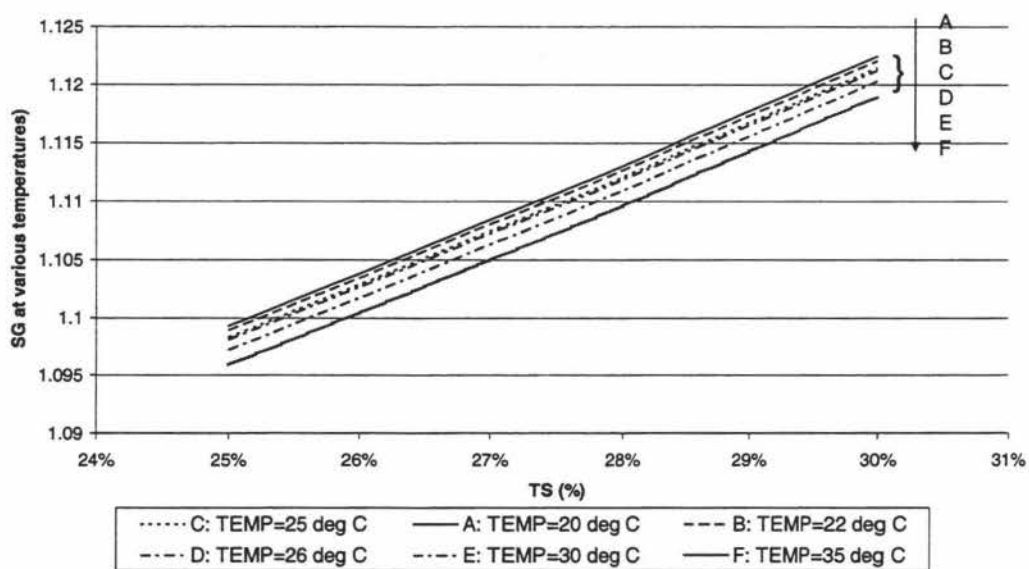
If this model (Choi & Okos model) relationship as shown by Fig 4.2 between specific gravity and total solids at differing IS/TS fractions is true, then at a specific gravity value of 1.100, total solids could vary from 25.0 to 25.4%. Secondly if the uncertainty in the specific gravity measurement is investigated (± 0.005) the specific gravity at 1.100 would vary from 1.095 to 1.105 which in turn causes the total solids to vary from 23.9% to 26.5% (across the range of IS/TS of 0.02-0.03%). Or at a constant IS/TS content of 0.03, specific gravity at 1.100 would vary from 1.095 to 1.105, which leads to a total solids varying from 23.9% to 26.1%. Therefore total solids vary by 2.2 to 2.6% if the insoluble solids to total solids ratio varies, thus in order to help obtain a more accurate total solids measurement the insoluble solids fraction must be known. However the uncertainty in the specific gravity reading still exists which would still contribute to an overall uncertainty in the total solids measurement.

From Chapter 3 it was stated the variation in experimental methods or the precision of total solids is $\pm 2.5\%$. If a comparison is made to that of the variation of total solids in the specific gravity correlation the total error is less than the experimental error in measuring total solids. In addition the time it takes to determine specific is much less than for measuring specific gravity as well as there is less equipment involved.

4.1.3 TEMPERATURE

The Choi & Okos (1986) density functions for the food components (Eqtns, 4.2, 4.3 and 4.4) can be seen to have a direct link with temperature. Figure 4.3 illustrates the specific gravity versus total solids relationship at constant IS/TS content with varying temperature (20°C-35°C).

Figure 4.3 Specific gravity (SG) vs %total solids (TS), using Choi & Okos (1986) density functions at differing temperatures.



As

can be seen from Fig 4.3 there is a considerable difference in specific gravity over a 10°C

temperature change over the typical total solids range used. This illustrates the influence that temperature has on the density value and as stated in literature, should be regarded as an important factor when determining density or specific gravity, and ideally all measurements should be at constant temperature. If this temperature model is true, then if there was a temperature effect of 10°C (25°C-35°C) specific gravity would vary over 10°C at TS=27% by 0.0024 (at specific gravity =1.100 would range from 1.1101 to 1.1125). At a constant specific gravity (for example 1.100) total solids would range by 1.2%. Therefore temperature does have a large affect on the specific gravity reading that creates a difference in total solids (IS/TS constant).

4.1.4 COMPARISONS

When comparing the literature data to the relationship modelled by Choi & Okos, it must be noted that all the data sets are based on values measured at a constant temperature therefore removing the variation of density with temperature. In the case of the variability of the insoluble solids component, none of the literature data take into account the insoluble solids/total solids ratio of the tomato paste the specific gravity/total solids relationship is based on. In doing so, they (Dr Crawford's data, tomato bulletin and Heinz Watties analytical manual data) do not take into account IS/TS variations in the different varieties of tomatoes entering the processing line or within processing which lead onto contrasts in characteristic properties (such as viscosity and flavour) even if the total solids are the same.

4.1.5 EXPERIMENTAL DATA

An experiment was carried out to show whether the insoluble solids component affected specific gravity in the way outlined by the literature data. Warm break tomato paste was centrifuged to give the serum and insoluble solids fractions. Six different pastes were made up with differing ratios of insoluble solids to total solids in the range of 0 to 0.25 (IS/TS). The specific gravity/total solids model suggested by Choi & Okos (1986) was used with a water density value from the CRC Handbook of Chemistry and Physics (1988) to predict the specific gravity against the experimental total solids values. Figure 4.4 shows the experimental data for specific gravity versus total solids.

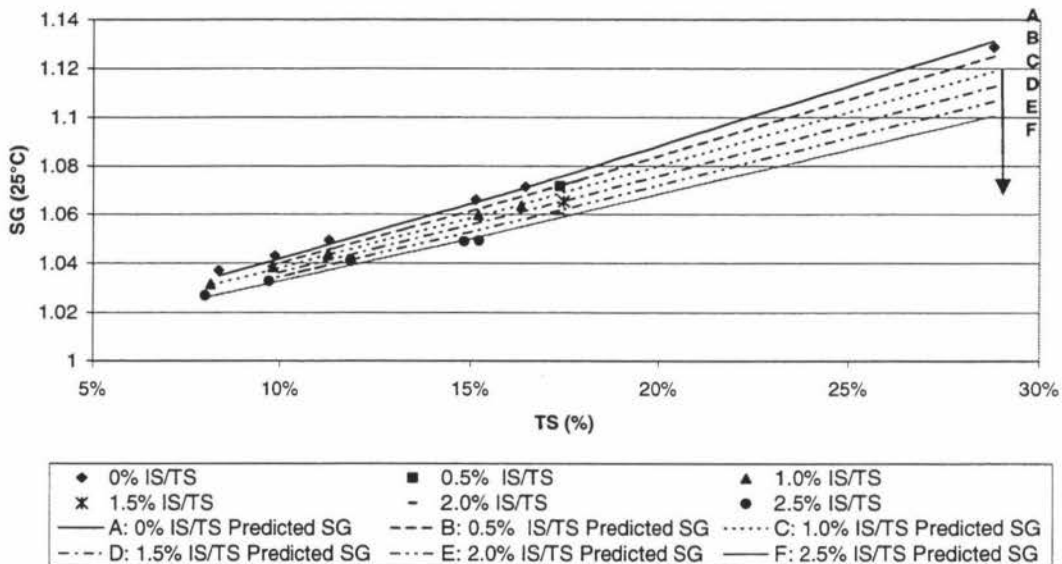


Figure 4.4 Specific gravity (SG) vs %total solids (TS) at different ratios of insoluble solids to total solids for warm break tomato paste.

The experimental data illustrated by Figure 4.4 clearly shows that specific gravity increases with the increase in the amount of insoluble solids are present in the warm break tomato paste.

The data on Figure 4.4 was then overlaid with the Literature data of Dr Andy Crawford, Bulletin and Heinz Watties manual data giving Figure 4.5.

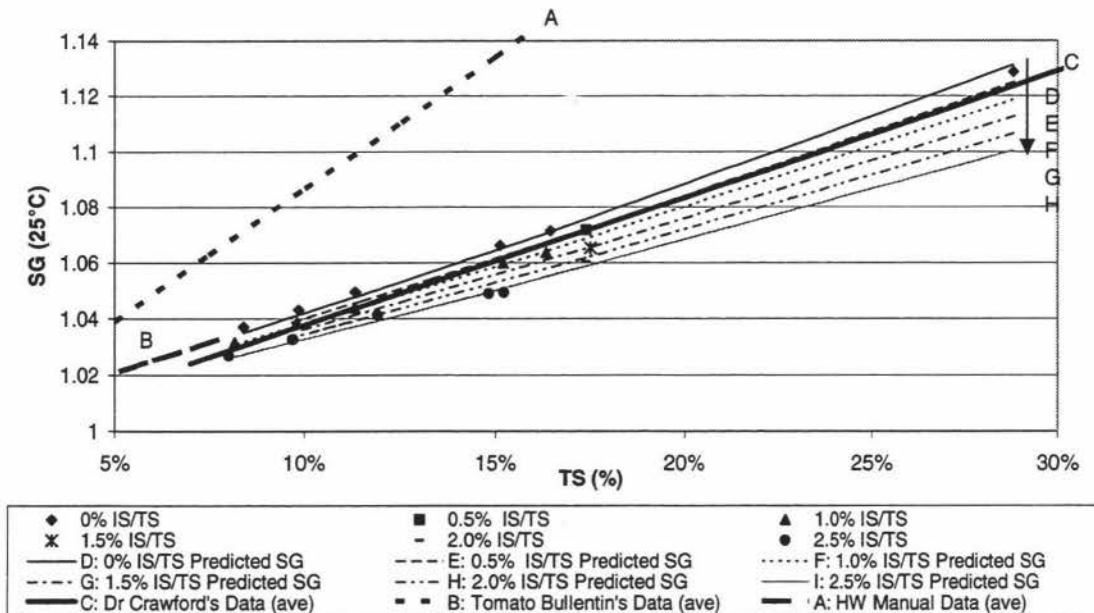


Figure 4.5 Specific gravity (SG) vs %total solids (TS) of experimental values with Choi & Okos model (using CRC Handbook density values) and literature data at differing IS/TS ratios overlaid

Figure 4.5 shows the experimental data to be closely related to that of Literature data from Dr Andy Crawford and the Heinz Watties manual. The difference of specific gravity verses the different insoluble solids to total solids ratio, covers above and below that of Dr Crawford's data line and may account for the variance between the literature data of Dr Crawford's and bulletin data. Some of this variation can also be explained by the variability of temperature as this has been previously explained as being important in measuring specific gravity and total solids and when using this correlation of Choi & Okos (1986).

However these factors do not explain all the variation of the experimental and literature data. Some of the variation can be explained by experimental precision of the various methods used in testing tomato paste and the different varieties and ripeness of tomatoes entering the production line, which in turn leads to inherent variability of the tomato paste, produced.

4.1.6 INLINE MASS FLOW METER

Within many processing environments inline mass flow meters are being established in order to establish continuous systems with built-in control and measurement of online data. The mass flow meter determines the mass of product moved per area of the in-line pipe it is attached to. In the case of reformulation of tomato paste the mass of product moved per area can be recalculated to give the density of the tomato paste moving through the pipe as density represents kg/m^3 or kilogram of product per volume of the pipe. For tomato paste a mass flow meter which has a single straight measuring tube is ideal so as the meter does not become blocked.

When installing a mass flow meter the density measurement must be calibrated. Some models come pre-calibrated from the factory, which is carried out using a standard sucrose solution, or silicon oils using temperature controlled-speed regulated pipe arrangements (Osorno, 2000). However with a tomato paste system it is advised that calibrations should occur with using a tomato paste of a known density and temperature (Osorno, 2000, EMC Industrial Group, 1999). Whilst calibrating mass flow meters in USA, the typical process deviations of temperature over the range of typical solids used were investigated and compensated for within the calibration.

From the previous sections of this chapter, the measurement of density has an additional factor which strongly influences it, that of insoluble solids. Also the tomato paste when being manufactured or reformulated will not be fully characterised if only one measurement is made. Therefore if the insoluble solids content of the tomato variety used is measured (as this is a function of the tomato ripeness and variety) and the processing conditions (namely temperature and time) are known, then the densities as per Choi & Okos (1986) equations 4.2, 4.3, 4.4 can be calculated and the previous correlation illustrated by Figure 4.4 or 4.5 could be used to establish the total solids of the tomato paste or reformulation. This would prove to be highly advantageous as manufacture may be improved to produce a more consistent tomato paste with less variation in the important characteristics (such as the specific gravity and insoluble solids fraction). This concept could also be extended to tomato paste reformulation where characteristics of specific products would be more repeatable.

4.2 °BRIX, SS, IS AND TS

This section investigates whether there is a relationship between °Brix, soluble solids, insoluble solids and total solids. °Brix is a measure of the soluble solids in the water phase of a product. Soluble solids is the fraction of the whole product that is soluble. At a low concentration of insoluble solids °Brix and soluble solids are very similar (as there is little fibrous portion). However in tomato paste there is a significant difference between these values especially in high solids concentration.

It is ideal to characterise or relate °Brix to soluble solids because if the °Brix is measurable then it can be directly related to the component of soluble solids (one of the components of tomato paste). So if two out of three component amounts are known the other component amount can be determined by the process of elimination. Consequently it is desirable to know the soluble solids fraction as it is a measure of the sugar fraction or the sweetness of the tomato paste, an important functional property considered when processing tomato paste.

4.2.1 Modelling

°Brix (°B) and the fraction of soluble solids (X_{TS}) can be related using the following equations.

$$^{\circ}B = \frac{100 \times x_{SS}}{1 - x_{IS}} = \frac{100 \times x_{SS}}{1 - (x_{TS} - x_{SS})} \quad (\text{Eqtn 4.10})$$

rearranging in terms of X_{TS}

$$x_{TS} = 1 - \left[\frac{100 \times x_{SS}}{^{\circ}B} \right] \quad (\text{Eqtn 4.11})$$

$$\text{where if } A = \frac{x_{IS}}{x_{TS}} \quad (\text{Eqtn 4.12})$$

$$\text{and } x_{SS} = x_{TS} - x_{IS} \quad (\text{Eqtn 4.13})$$

then substituting equations 4.11, 4.12, 4.13 into equation 4.10 gives

$$^{\circ}B = \frac{100 \times (x_{TS} \times (1 - A))}{(1 - x_{TS})} \quad (\text{Eqn 4.14})$$

whose units are

x_{SS} = g soluble solids/g tomato paste

x_{IS} = g insoluble solids/g tomato paste

x_{TS} = g total solids/g tomato paste

$$^{\circ}B = \frac{\text{g Soluble Solids}}{100 \text{ ml Solution}}$$

Graphical representation of this model relationship of $^{\circ}B$ versus the fraction of total solids over typical range of insoluble solids/total solids is shown in Fig 4.6.

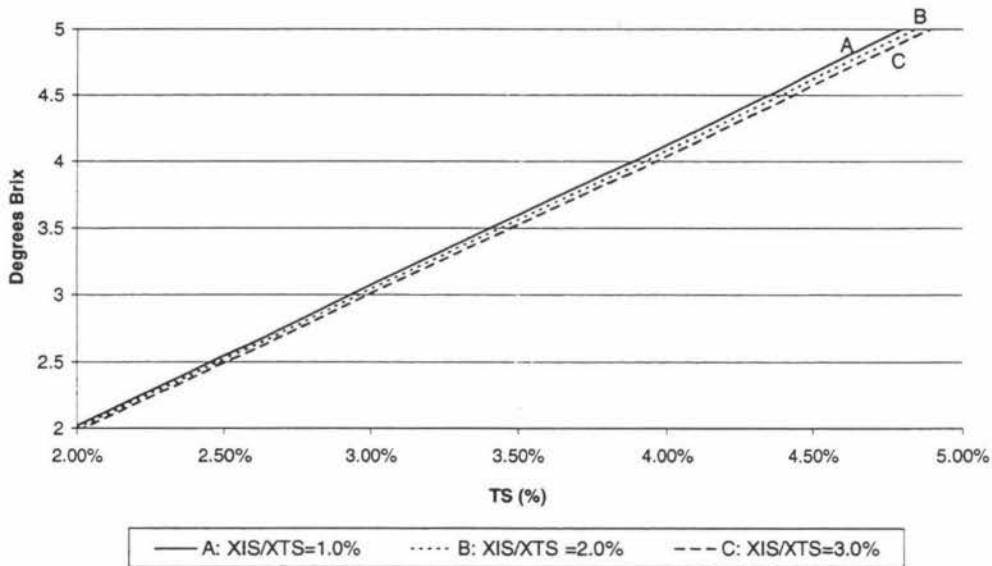


Figure 4.6 $^{\circ}$ Brix versus fraction of total solids (X_{TS}) over a range of X_{IS}/X_{TS} typical of that of warm break tomato paste at 30% total solids.

From the graph it can be seen that $^{\circ}$ Brix does change with the change in soluble solids fraction and also changes over the range of 1%-3% insoluble solids to total solids component.

4.2.2 EXPERIMENTAL

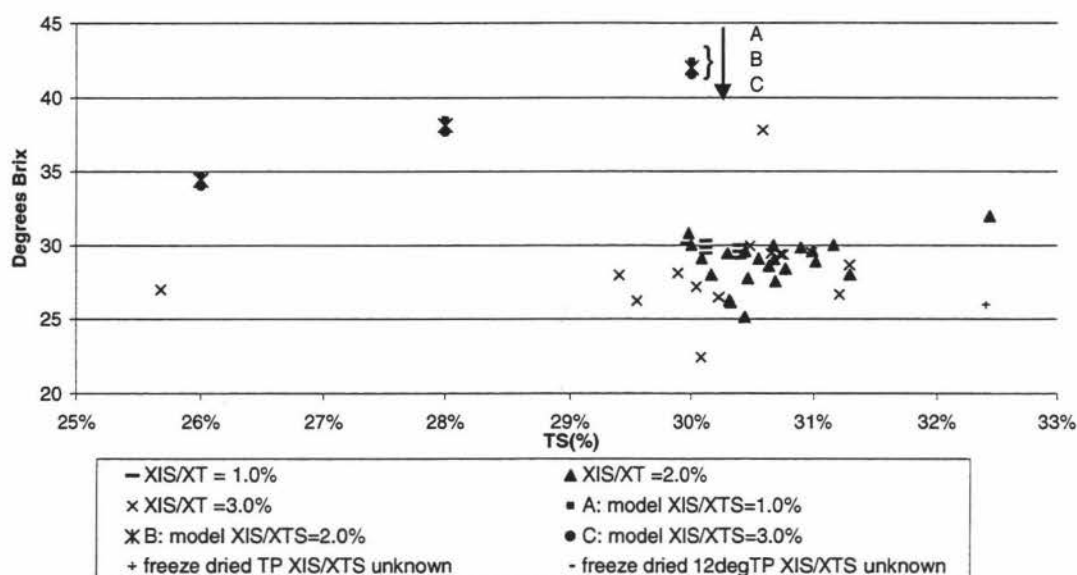


Figure 4.7 °Brix verses total solids fraction at differing IS/TS fractions of experimental data and model data overlaid.

Figure 4.7 shows that the model lays differently than that of the experimental data. The experimental data shows that the °Brix does not strictly correspond to a specific total solids value like the model does. Hence there is no real relationship existing between °B and total solids.

Previously in section 3.4.5 the °Brix has been found to be influenced by the insoluble solids fraction. The experimental data shown is of °Brix of the whole tomato paste. This could be one of the main factors contributing to the variability of the experimental data coupled with the inaccuracies of experimental methods used as the experimental data was actually gathered prior to understanding the best experimental practises to use. Due to this known inaccuracy, the experimental trend between °Brix and total solids should be explored experimentally again using the correct methodologies to get more accurate data which can then be compared to that of the model. The correct methodology for °Brix is covered in detail within section 3.4.5 and suggests that whole paste is not to be used to measure °Brix but instead the insoluble solids material must be separated before a measurement is to be made using the serum or soluble solids fraction. Section 3.5 outlines the correct methodology for total solids whereby the vacuum oven method should be employed to determine the total solids content.

4.3 VISCOSITY

4.3.1 MODELLING

As previously discussed in Chapter 2 (2.6.3), Rao *et. al.*(1981) and Harper & El Sahrighi (1965) demonstrated that the flow behaviours of concentrated tomato products followed the power law model;

$$\eta_{app} = K \times \gamma^{n-1} \quad (\text{Eqtn 2.1})$$

where:

η_{app}	Apparent Viscosity (Pa)
K	consistency index (Pa.s ⁿ)
γ	shear rate (s ⁻¹)
n	flow behaviour index (dimensionless)

The magnitude of 'n' for tomato concentrates ranged from 0.175 to 0.259, depending on tomato variety in the research by Rao *et. al.*(1981) and from 0.3 to 0.45 in the study by Harper and El Sahrighi (1965). The low values of the flow behaviour index (n) indicate that the concentrates were very shear thinning. Rao *et. al.*(1981) showed that the value of 'n' was not significantly affected by temperature and both Rao *et. al.*(1981) and Harper & El Sahrighi (1965) found that the flow behaviour index did not change with concentration.

At a specific shear rate (100s⁻¹) Harper and El Sahrighi (1965) proposed the following model to describe how temperature and concentration affected apparent viscosity.

$$\eta_{app} = \alpha \times x_{TS}^{\beta} \times \exp\left(\frac{E}{R \times T}\right) \quad (\text{Eqtn 4.15})$$

where:

α and β constants

E activation energy (J/mol)

β was found to be 2.4 and E was 7995 J/mol in their study. Rao *et. al.* (1981) found the value of β to be 2.4 to 2.5 for a range of tomato varieties and E was 9623 J/mol. In a

further study by Tanglerpaibul & Rao (1987) it was found that the apparent viscosity is only slightly affected by the serum phase of the tomato concentrate.

The °Brix level of the serum was not important and soluble pectin in the serum contributed to viscosity by only a small amount. They found that the pulp content (as obtained by centrifugation), explained the changes to apparent viscosity of different tomato concentrate samples. They proposed the following equation for the viscosity of tomato concentrates.

$$\eta_{app} = \eta_{serum} + A \times (\text{pulp content})^B \quad (\text{Eqtn 4.16})$$

where:

A=coefficient which reflects the contribution to viscosity by a unit amount of pulp.

B= coefficient which is used to compare the influence of the pulp content on viscosity of concentrates from different cultivars and or processes

and

$$\eta_{serum} = A_2 + B_2 \times (\text{Soluble pectin})^{C_2} \quad (\text{Eqtn 4.17})$$

where:

$$A_2 = 0.00492$$

$$B_2 = 0.0153$$

$$C_2 = 1.483$$

All these variables are referred to as coefficients, where A_2 represents the viscosity of the aqueous medium which contains the dissolved organic acids and salts.

Coefficients of both equations 4.16 and 4.17 are determined by non-linear regression analysis using the VP (%volume pulp), WWP (%wet weight of pulp) and PS (pulp to serum ratio). The pulp content is an indirect measure of the insoluble solids content of the paste sample (x_{IS}), and as stated above the serum viscosity is essentially constant.

From these studies a combined model describing the flow behaviour of tomato concentrate can be developed. The power law equation can be used to describe the effect of shear rate on viscosity. The Arrhenius law can be used to describe the affect of temperature. A simple power law type model can be used to quantify how the insoluble solids concentration affects viscosity.

Such an overall model was proposed in this work;

$$\eta_{app} = k' \times (x_{IS})^{\beta} \times \exp\left(\frac{E}{R \times T}\right) \times \gamma^{n-1} \quad (Eqtn 4.18)$$

where

k' = unknown constant

x_{IS} = insoluble solids concentration (x_{IS}/x_A)

A = ratio of insoluble solids to total solids

β = constant 2.4-2.5

E = activation energy 8000-9600 J/mol

n = flow behaviour index in the range 0.28 – 0.26 J/mol

The raw data reported by Rao et al (1981) was digitised and used to fit a realistic value of k' . Because the insoluble solids content of the pastes used in this study was not reported, the ratio of insoluble solids to total solids was allowed to vary between the tomato varieties. Non linear least squares was carried out to calculate these values resulting in table 4.1 below.

Table 4.1 Variables used in Rao *et al.*(1981)

PARAMETER	VALUE	UNITS
A	New Yorker	0.036575
	Nova	0.049395
	475	0.052037
	#936 CB	0.035296
	#936 HB	0.034909
k'		Pa.s ⁿ
E	9600	J/mol
β	2.5	-
n	0.2	-

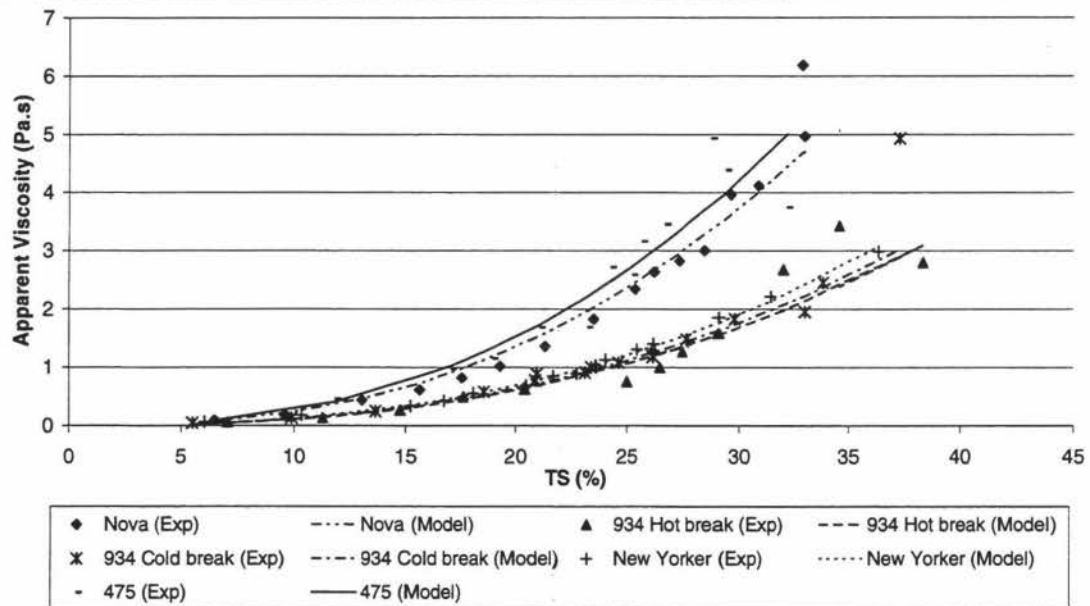
**Figure 4.8** Apparent viscosity vs % total solids (TS)

Figure 4.8 show a clear difference between the tomato varieties and the apparent viscosity they have, in the study by Rao *et al.*(1981). The data shown here was determined by the flow properties of over seventy concentrates made from four cultivars of tomatoes (Nova, New Yorker, #475, #934 hot break and #934 cold break). The flow properties were established by using a concentric cylinder viscometer using the MVI system at $25^{\circ}\text{C}\pm 0.1^{\circ}\text{C}$ (exception being the Nova concentrates determined at 15, 25, 35, 45 and 55°C).

4.3.2 EXPERIMENTAL

4.3.2.1 Method

This section involves the verification of the literature data explained above against real data obtained for the variety of tomatoes used at Heinz Watties Australasia. The experiments involved warm break paste being centrifuged and separated into the soluble solid and insoluble solid components before mixing the components at varying amounts to achieve six pastes of different insoluble solids to total solid ratios ranging from 0 to 0.25. These pastes were then diluted to varying degrees (from 0 to 2:1) and then characterised (for viscosity) using the rheometrics rheometer using a standard cup and bob system at 30°C for a range of shear rates from 0.5 to 500s⁻¹.

An additional temperature scan was carried out on one sample (that is, $X_{IS}/X_{TS}=0.2$, $X_{TS}=0.288$, $X_{IS}=0.0576$) at 1°C/min over a range of 10-50°C at shear rate of 40s⁻¹ to determine the activation energy which could be compared to that introduced by Harper & El Sahrighi (1965) and Rao *et. al.* (1981)

4.3.2.2 Results

4.3.2.2.1 Power Law Model

Firstly the shear rate and viscosity data obtained from experiments using Heinz Watties tomato paste was graphed as shown by Figure 4.9.

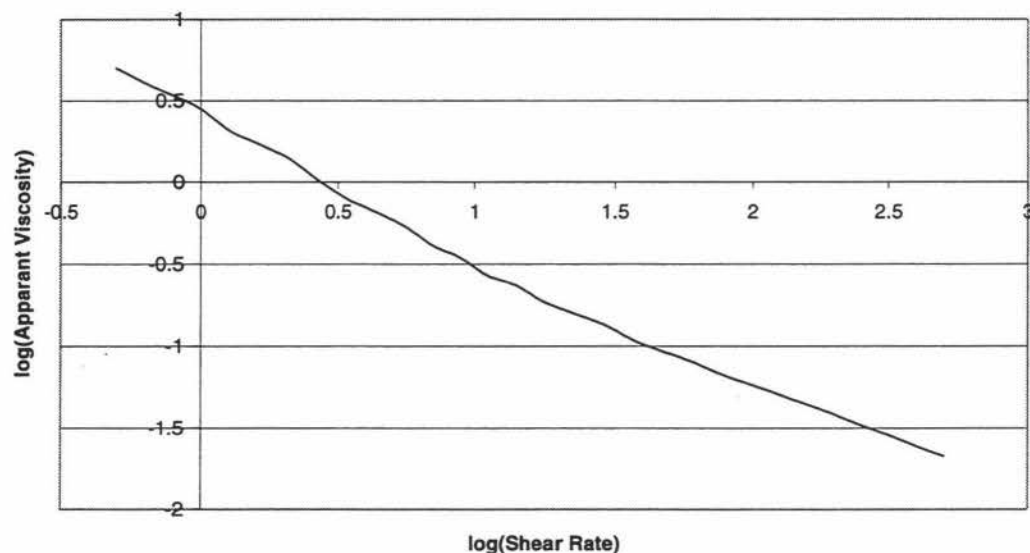


Figure 4.9 Log apparent viscosity vs log shear rate

The chart above (Fig 4.9) shows that the rheology of this sample follows the power law model. Only one sample ($X_{IS}/X_{TS}=0.25$, $X_{TS}=0.288$, $X_{IS}=0.072$) is shown on Figure 4.9 as this is only an example of the linear behaviour exhibited by all the samples, however the samples with low insoluble solids contents (that is, either pure serum samples or very diluted samples) did not give sensible apparent viscosity readings until higher shear rates were achieved. For these samples only the later (linear) range was used to obtain the behavioural index 'n' and flow consistency index 'k'.

4.3.2.2.2 Behaviour Index

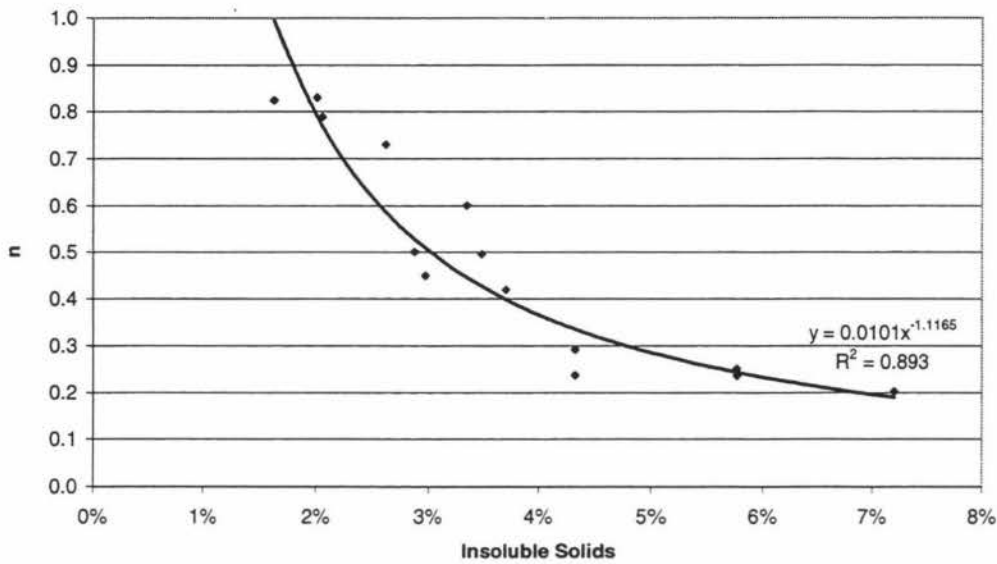


Figure 4.10 Flow behaviour index (n) versus insoluble solid content (%) (X_{IS})

Figure 4.10 above shows how the behaviour index varies with insoluble solids (X_{IS}). The flow behaviour index was also plotted against total solids, however no trend was exhibited. This then suggests that the flow behaviour index is very dependent on the insoluble solids levels in the paste. Hence, flow behaviour becomes more Newtonian as the insoluble solids content (X_{IS}) is reduced, that is as n approaches 1, X_{IS} approaches 0.

This behaviour was not apparent from the literature reviewed and so the model must be further developed to include the prediction of flow behaviour index (n) as a function of insoluble solids (X_{IS}). As seen on Figure 4.10, a simple power law model fits the data reasonably well. Therefore equation 4.11 below can be stated.

$$n = 0.0101x_{IS}^{-1.1165} \quad (\text{Eqtn 4.19})$$

(Where fitted limits are $1.5\% < X_{IS} < 7.5\%$)

If ' n ' is calculated to be greater than 1 then $n=1$, which represents Newtonian behaviour. It can be seen from Figure 4.7 that this behaviour occurs at an approximate insoluble solids level of 1.8%.

4.3.2.2.3 Consistency Index

Figure 4.8 below shows how the consistency index (k) is also dependent on the insoluble solids level of the tomato paste.

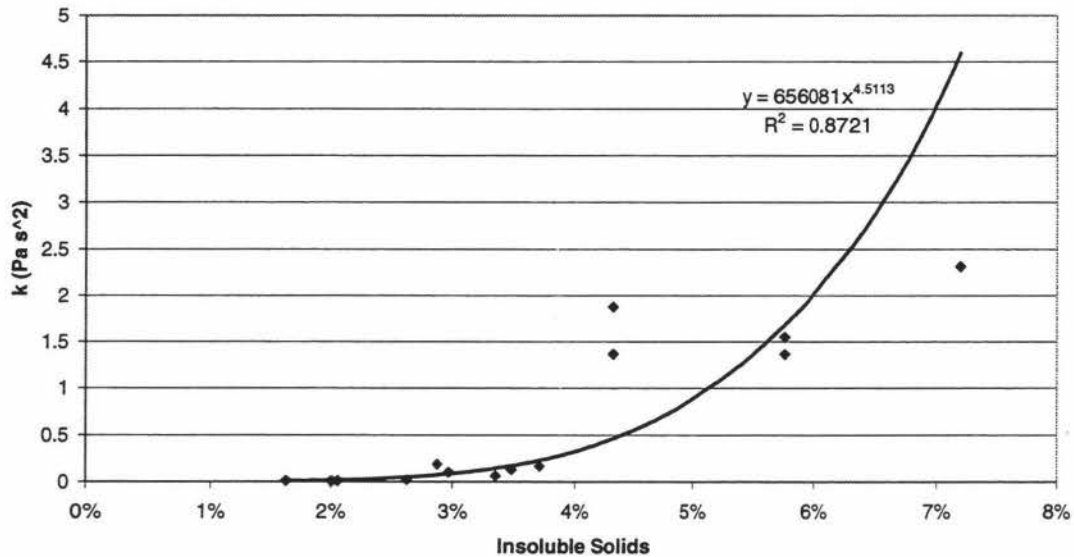


Figure 4.11 Consistency index (k) verses insoluble solids (X_{IS})

This affect illustrated by Figure 4.11 is included in our model derived from literature and again should be explainable using a power law model. In the model illustrated previously by Equation 4.18 as repeated below

$$\eta_{app} = k \times (x_{IS})^{\beta} \times \exp\left(\frac{E}{R \times T}\right) \times \gamma^{n-1} \quad (\text{Eqtn 4.18})$$

The consistency index 'k' is given by

$$k = k' (x_{IS})^{\beta} \exp\left(\frac{E}{RT}\right) \quad (\text{Eqtn 4.20})$$

So the parameter β can be found from a $\log(k)$ verses $\log(X_{IS})$ plot as per equation 4.21 below.

$$\log(k) = \log\left(k' \exp\left(\frac{E}{RT}\right)\right) + \beta \log(x_{IS}) \quad (\text{Eqtn 4.21})$$

Equation 4.21 or the effect on insoluble solids on the consistency index (k) can be seen graphically in Figure 4.12 below.

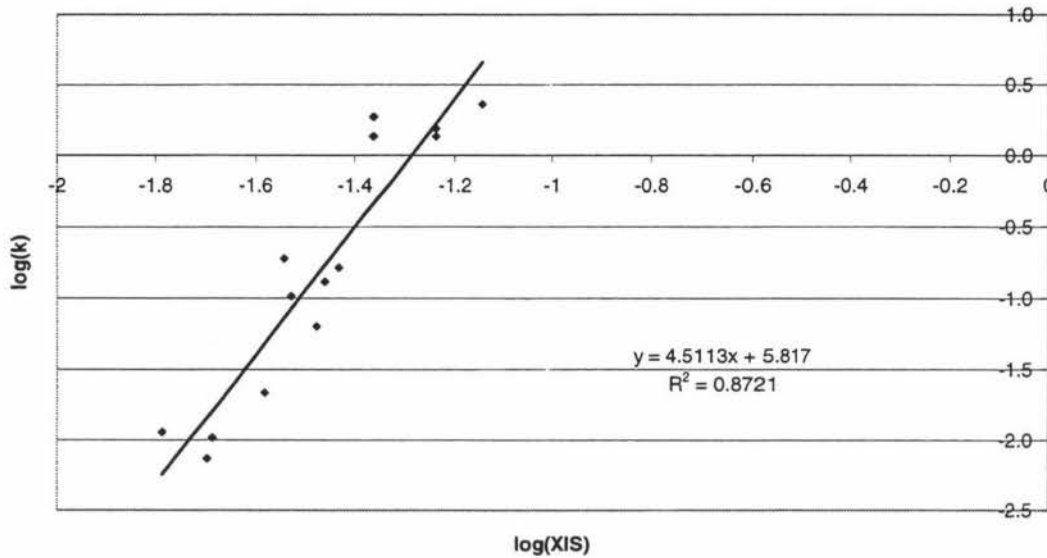


Figure 4.12 Log graph of insoluble solids content (X_{IS}) versus consistency index (k)

Figure 4.12 shows the value of β as 4.5113. As previously mentioned in section 4.3, Harper & El Sahrigi (1965) found β to be 2.4 while Rao *et. al.* (1981) stated β to be in the range of 2.4-2.5 for the range of tomato varieties used in their study. The β value of 4.5113 found in this study is 1.8045 to 1.8797 (5s.f) greater in magnitude than those reported in literature.

A possible reason for this greater magnitude in the β value is the different tomato paste samples used in this study and that of the literature studies. It may suggest that for the tomatoes used in our study, the fraction of insoluble solids are more influential on affecting the viscosity than those in the literature samples.

The plot illustrated by Figure 4.9 also shows that

$$k' \exp\left(\frac{E}{RT}\right) = 10^{5.817} \quad (\text{Eqm 4.22})$$

From this k' can be calculated if the activation energy (E) is found.

The Arrhenius plot (Fig 4.13) below allows the calculation of activation energy (E).

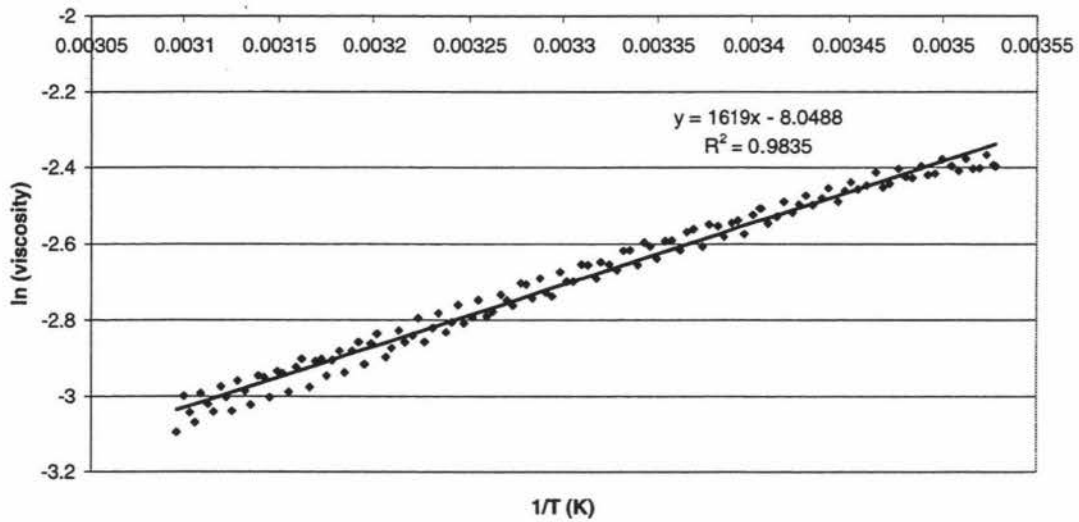


Figure 4.13 Arrhenius plot

Figure 4.13 clearly shows that the experimental data follows the Arrhenius law and from this the value of the activation energy (E) is found to be 13,460 J/mol. This low value of E is typical for the rheological behaviour of tomato paste. Using this value of E, equation 4.22 can be solved for k' .

$$k' = \frac{10^{5.817}}{\exp\left(\frac{13460}{8.314 \times 303}\right)} = 3137.08$$

4.3.3 VISCOSITY CONCLUSION

This therefore provides all the parameters required to predict the apparent viscosity of a tomato paste as a function of insoluble solids, temperature and shear rate, which is represented by Equation 4.18 presented previously as

$$\eta_{app} = k \times (x_{IS})^{\beta} \times \exp\left(\frac{E}{R \times T}\right) \times \gamma^{n-1} \quad (\text{Eqtn 4.18})$$

where

$$n = 0.0101x_{IS}^{-1.1165} \quad (\text{Eqtn 4.23})$$

As a partial validation of this model, the parameters found above were used to predict the apparent viscosity of tomato paste at 500s^{-1} . This is shown below as Figure 4.14.

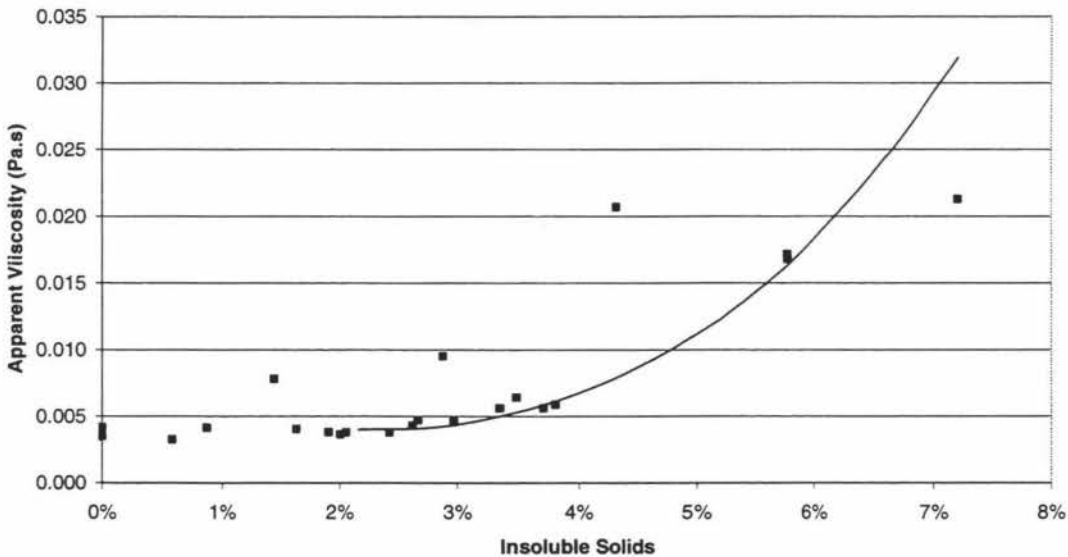


Figure 4.14 Prediction of apparent viscosity versus insoluble solids for tomato paste at 500s^{-1} and actual experimental data overlaid.

Figure 4.14 shows a reasonable fit between that of the prediction of the apparent viscosity and the actual apparent viscosity at differing insoluble solids levels for the tomato paste tested at a shear rate of 500s^{-1} . However more validation on independent samples should be carried out before a justified conclusion can be made.

4.4 CORRELATION CONCLUSIONS

In conclusion, this chapter has found the following:

4.4.1 SG VS TS

The specific gravity or total solids can be correlated if either specific gravity or total solids is known and also if the insoluble solids content is known. This correlation and influence of insoluble solids is shown in Fig 4.2. The insoluble solids fraction is different between different tomato varieties and tomatoes at differing stages of maturity. Experimental data on different samples of Heinz Watties tomato paste show differing specific gravity with total solids. This variation has been shown by Figure 4.4 to be attributed to the varying IS/TS content of the tomato paste and from previous chapters the precision of the total solids and specific gravity methods. If the insoluble solids component is known for the variety and level of maturity of the tomatoes being used as well for the processing conditions used, the specific gravity can be measured and, using the correlation as indicated in equation 4.8 the total solids can be predicted. The modelling and correlation shown here may prove advantageous when factored into an inline mass flow meter within the processing line as an end product which could be characterised may be established.

4.4.2 °BRIX

Based on the experimental data used in this project, there is no clear relationship to that of °Brix and total solids. Firstly the experimental data used whole paste, which as mentioned previously, is significantly influenced by the insoluble solids component that at the time of the experiments was not fully understood. Subsequently those experiment methods used at this time were considered the best experimental practises to use. Also, the experimental methods used were prior to the knowledge of which were the best experimental practises to use. Due to these unknown inaccuracies and variability's at the time of the experiments, the experimental trend between that of °Brix and total solids should be explored further using the correct methods to accurately compare results to that of the model suggested.

4.4.3 VISCOSITY

Experimental data demonstrated that firstly the rheology of the tomato paste at differing insoluble solids levels used at Heinz Watties Australasia can indeed be described by the power law as described in the literature.

Next all the parameters required to predict the apparent viscosity of a tomato paste as a function of insoluble solids, temperature and shear rate (as described by Equation 4.18) were found for the tomato paste used.

$$\eta_{app} = k \times (x_{IS})^{\beta} \times \exp\left(\frac{E}{R \times T}\right) \times \gamma^{n-1} \quad (\text{Eqtn 4.18})$$

The flow behaviour index (n) was found to be able to be described by

$$n = 0.0101x_{IS}^{-1.1165} \quad (\text{Eqtn 4.23})$$

Similarly the consistency index (k) was shown to be dependent on the soluble solids levels (as per Figure 4.8).

β in this study was found to be 4.5113, which is almost twice as large than reported in the literature, but may be due to the differing tomato paste used here where there may be an increased influence on viscosity by the insoluble solids.

The Arrhenius plot clearly followed experimental data and the activation energy (E) was found to be 13,460J/mol, considered typical for the rheological behaviour of tomato paste.

All these values were used (Equation 4.18) to predict the apparent viscosity at differing insoluble solids levels for tomato paste at a shear rate of 500s^{-1} . Experimental data was overlaid and there was a suitable fit between that of the prediction of the apparent viscosity and the actual apparent viscosity at differing insoluble solids levels for the tomato paste tested at a shear rate of 500s^{-1} (as illustrated in Figure 4.11). However more validation on a number of independent samples is highly recommended before a justified conclusion can be made.

Overall more extensive experimental validation based on a longer time period to capture seasonal variation (with respect to the different tomato varieties) and other trends during the production run needs to be completed for all the correlations introduced here in Chapter 4. This is important in order to be able to utilise these correlations in the practicable environment of the production plant.

CHAPTER 5 PROCESS VARIABILITY

In the course of manufacturing products, an inherent variability of end products occur, whether it be due to the actual process (inside stimuli) or outside stimuli (for example: raw materials). This is indeed true of the process of producing tomato paste at Heinz-Watties, which, is one of the reasons for conducting this project. Identifying and characterising the variability is explored within this chapter.

Three difference areas were investigated to explain and characterise the variation in tomato paste from long term to a short term basis.

- Over a season
- Day to day
- Over 20 bags repetitively

5.1 LONG TERM VARIABILITY OVER A TOMATO PASTE PRODUCTION SEASON

The tomato paste production season at Heinz- Watties Hastings typically runs from January to April, however, it is highly dependent on weather conditions to whether the tomatoes are ripe enough to be picked and processed.

Currently the plant has data on the paste production over the season including °Brix, Bostwick, pH and colour, specific gravity, total solids, mould count. Samples at the end of the tomato paste line are taken off every ½ hour to 1 hour and some of the samples are tested every 4 hours for all the properties listed above. Some of the tests such as the pH, colour, °Brix and Bostwick are done immediately by a lab onsite where as the other tests which take a longer time are conducted at another lab within Heinz Watties. An inline °Brix meter also captures the in-line measurement of the tomato paste just prior to its aseptic packaging. This data is recorded to provide data for the whole processing period.

5.1.1 °BRIX

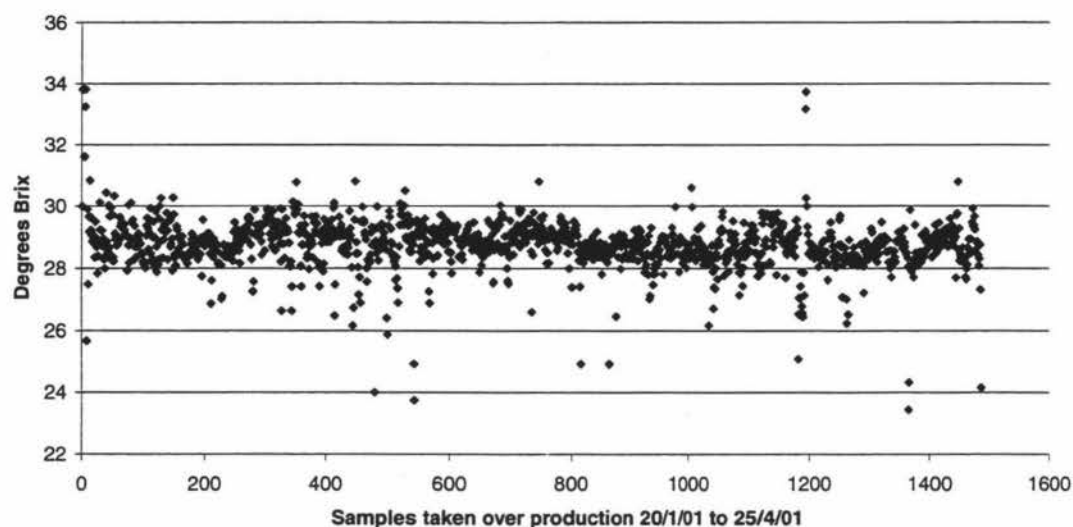


Figure 5.1 °Brix vs samples over the production period of 20/1/01 to 25/4/01

Figure 5.1 shows the °Brix readings for the tomato paste produced from 20th February 2001 to 25th April 2001 at Heinz Watties Hastings. The °Brix readings shown are that of the whole tomato paste. Chapter 3 concludes that the tomato paste should be separated to remove the presence of the insoluble solids which causes a distortion and inherent error of the refractometer readings. This distortion causes a °Brix value to be higher (by approximately 1.6°Brix, as seen in Chapter 3), and with a much larger standard error (± 0.2 °Brix) than that of the serum (soluble solids) fraction over a repeated number of samples. Chapter 3 also shows the decrease in the Quality parameter (obtained from the Bellingham Stanley refractometer) as the insoluble solids fraction increase reiterating the error caused by insoluble solids when measuring °Brix of whole paste. In spite of this inaccuracy associated with the °Brix measurement, Figure 5.1 clearly illustrates that there is a small variation in the °Brix levels over the production season and hence an inherent variability in the tomato paste that is packaged or used in further processing of Heinz Watties products. °Brix is also currently used as the indicator to the quantity of tomato paste in stock.

For example, a quantity of tomato paste at a certain °Brix can be translated into the amount of tomato paste needed within a formulation recipe for producing an amount & quality of spaghetti. The inherent error in the °Brix therefore moves onto an error in the quantity needed to use within the recipe to achieve the finished product at a specified °Brix level. To combat this experience of past history of how much tomato paste to add for a particular recipe is currently used instead of what the theoretical amount, this then affects the final amount assumed to be in stock if stock-taking uses the theoretical values. Hence currently the tomato paste at a higher °Brix level (if the whole tomato paste is measured) corresponds to a higher than actual tomato paste stock level.

5.1.2 TOTAL SOLIDS

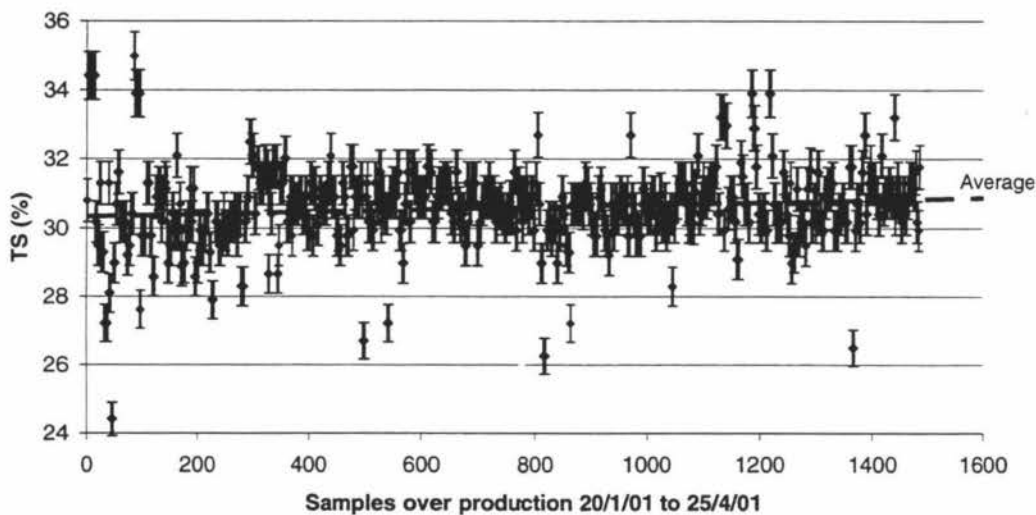


Figure 5.2 Total solids vs samples over the production period of 20/1/01 to 25/4/01

Total solids measurement is carried out more infrequently than °Brix at Heinz Watties Hastings over the production period. Only 2-3 samples a day are actually measured for total solids. As previously mentioned, in Chapter 4, total solids are one of the important measurements to be made in order to properly characterise tomato paste. So if carried out infrequently, the true characteristics of the tomato paste are hard to identify. In addition, total solids were measured by the Forced Air oven method, which was identified in Chapter 3 as to be not the best method for characterising total solids due the large variation between results (hence the 2% error bars on Figure 5.2).

Instead the best method, found in this study, is that of the vacuum oven method which as identified by chapter 3, gave the best repeatability. As illustrated by Figure 5.2 the variability is clearly apparent over a beyond the experimental error (see error bars).

Reasons for this not only include the variability of the test methods used ($\pm 2\%$) but also the variability of the actual tomato paste being produced. One of the areas to control the total solids content is that of the evaporators within the tomato paste production line which dictates the amount of water taken out of the product. If a significant level of control is not achieved in the evaporators, the inconsistency and hence the variability of the final product is increased. This concept is explored further in section 5.3.4.

5.1.3 SPECIFIC GRAVITY

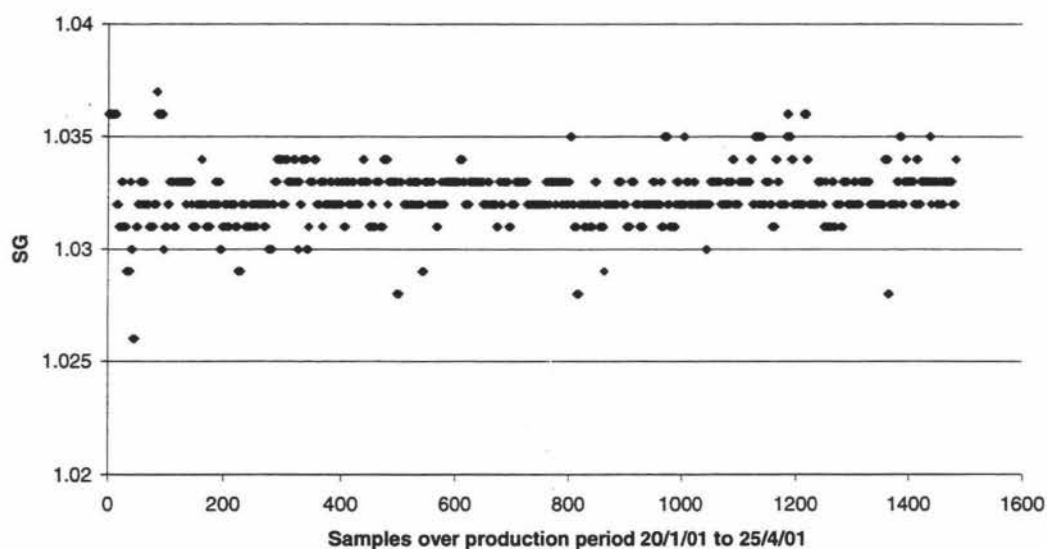


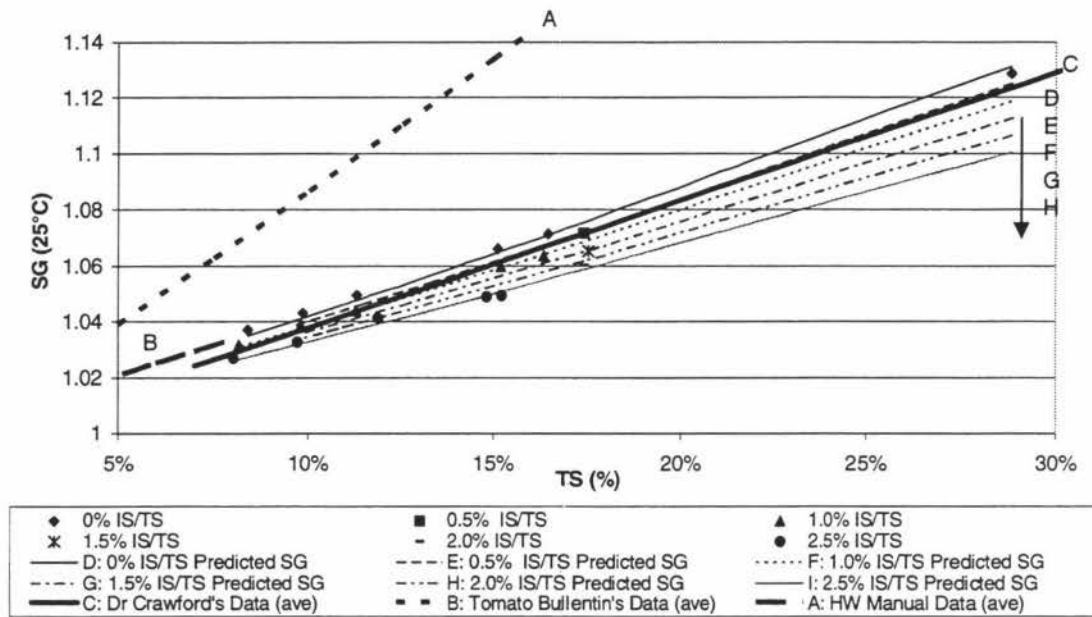
Figure 5.3 Specific gravity (SG) vs samples over the production period of 20/1/01 to 25/4/01

Specific gravity varies over the production period, the data above in Figure 5.3 shows this variation of specific gravity in the samples over a period of production. From studies conducted and concluding upon in Chapter 4, specific gravity is closely correlated to that of total solids, which means that this variation in total solids carries over to a variation in the specific gravity. A variation in total solids also indicates an inherent variation in the insoluble solid and soluble solid components of the total solids portion of the paste.

The correlation between specific gravity and total solids can be seen in the following graph of Figure 4.5 repeated from Chapter 4. The data obtained from Heinz Watties production

has the Literature models (Dr Andy Crawford, Tomato Bulletin data and Heinz Watties analytical manual data) and the Choi & Okos (1986) model overlaid in Figure 5.5.

The clear correlation between specific gravity and total solids of the production data can be seen to be close to that of the literature and Choi & Okos (1986) models which were previously discussed in full in section 4.1.5.



It is advantageous to have this correlation as specific gravity can be measured

Figure 4.5 (repeated from Chapter 4)) Specific gravity (SG) vs % total solids (TS) of experimental values with Choi & Okos model (using CRC Handbook density values) and literature data at differing IS/TS ratios overlaid

instantaneously and total solids can be predicted. If the more precise method of vacuum drying is used then 12 hours is needed.

To avoid every sample having to be tested manually an inline density meter would be the best approach. Temperature would have to be factored in so as to achieve accurate density measurements, but the measurement would be instantaneous and the process could be monitored to ensure more constant total solid levels were being achieved.

5.1.4 BOSTWICK CONSISTENCY

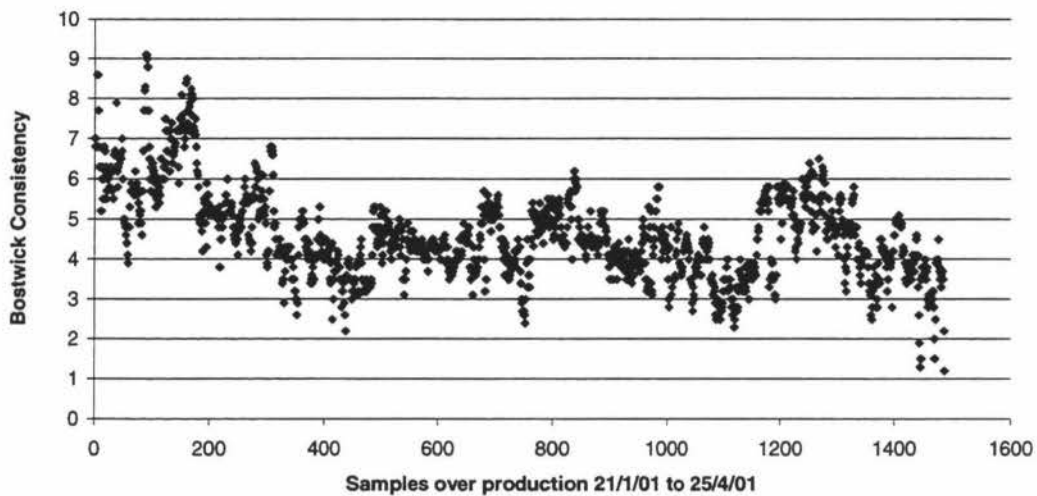


Figure 5.4 Bostwick consistency vs samples over the production period of 20/1/01 to 25/4/01

The Bostwick consistency measurement, which Heinz Watties Hasting use as a measure of viscosity, can be seen to be highly variable over the production period as shown by Fig 5.4. Bostwick consistency is very dependent on temperature, and is also highly dependent on the insoluble solids content. Hence if this measurement was conducted at a constant temperature the main source of variability would be due to the insoluble solids content of the tomato paste. Using the data obtained from Heinz Watties production there is no way of quantifying this variability due to insoluble solids. This is especially due to the inaccuracy of the °Brix measurements (as measurements made using whole paste) and that °Brix and Total solids are not performed on the same sample.

However we may be able to see if Bostwick variation is explained by variation in total solids by comparing Bostwick verses specific gravity (if measurements are carried out on the same sample).

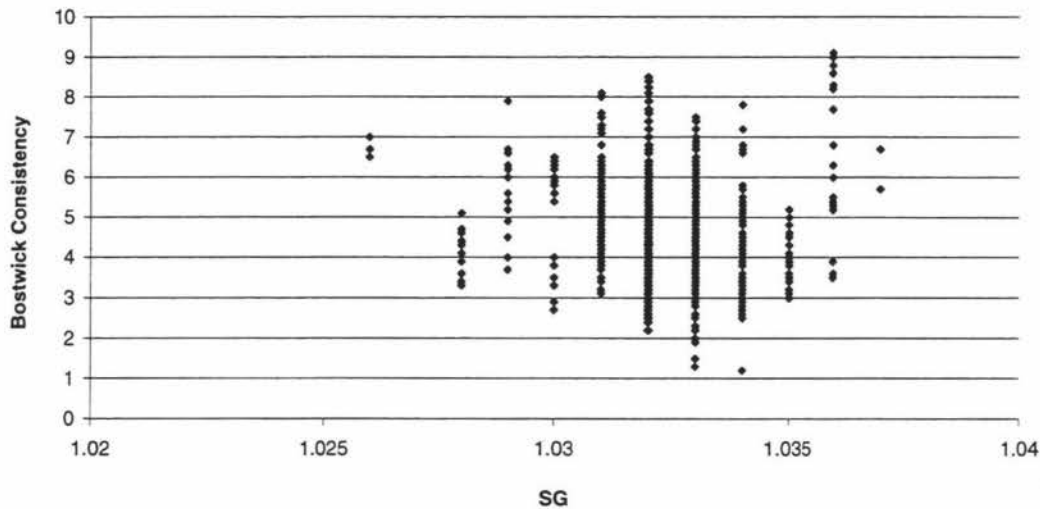


Figure 5.5 Bostwick consistency vs specific gravity over the production period of 20/1/01 to 25/4/01

As can be seen by Figure 5.5 there is no direct correlation between that of Bostwick consistency and specific gravity. The reason for this could be because of both the Bostwick consistency and specific gravity measurements being sensitive to a change in temperature and a change in total solids content within the tomato paste. Another area for variation is the experimental methods used to determine Bostwick consistency and specific gravity. Both measurements use diluted tomato paste. Tomato paste is diluted down to 12.5 °Brix, using a table that bases the amount of water on the original °Brix of the tomato paste, before measuring Bostwick consistency. For the measurement of specific gravity the tomato paste is diluted down in terms on weight. Dilution of 1 part tomato paste to 3 parts water is the procedure for tomato paste of below 35 °Brix, prior to the measurement of specific gravity.

5.1.5 MORE DETAILED EXAMINATION OF IN-PLANT VARIABILITY

Plant records suggest that the insoluble solids levels are varying over the season although the data that is currently collected, does not allow this to be confirmed.

In order to understand the variability a bit better, it was decided to take two hourly samples over a 100hr period of 24hour warm break tomato paste production (from the 17th April 2000 to the 21st April 2000) and characterise the paste using the revised methodologies developed in chapter 3.

Testing involved the determination of the components which make up tomato paste, that of, insoluble solids, soluble solids and water. These components were determined by either direct or indirect measurements and the methodologies for each are summarised as follows.

- Fraction of total solids (X_{TS}) was measured by determining the total solids of the tomato paste using the vacuum oven method.
- Fraction of soluble solids (X_{SS}) was measured by diluting the tomato paste four fold and measuring the °Brix levels. As discussed in Section 4.2, the X_{SS} and °Brix measurements for diluted paste are essentially the same. In this way X_{SS} could be calculated by considering the dilution factor.
- Fraction of insoluble solids (X_{IS}) can be determined indirectly if the other two components are known using a rearrangement of equation 4.7

$$x_{IS} = x_{TS} - x_{SS} \quad (\text{Eqtn 5.1})$$

In each case multiple analyses were taken on each sample. Results from this testing can be seen in Figures 5.6 and 5.7.

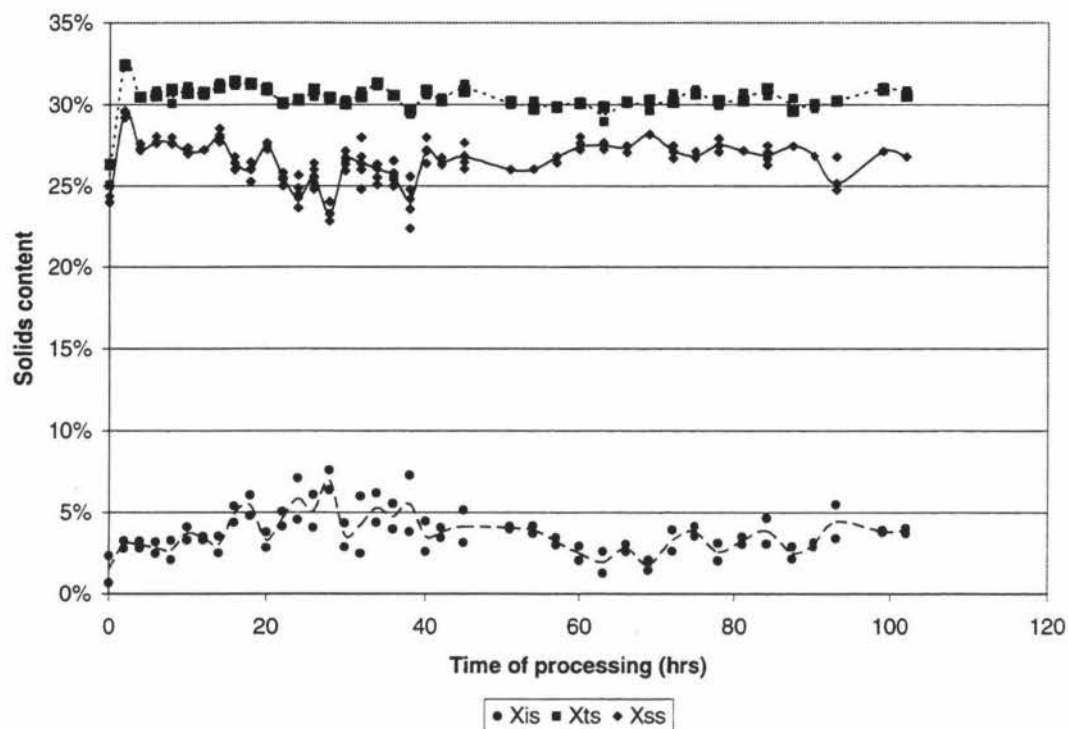


Figure 5.6 Solids content (X_{TS} , X_{IS} , X_{SS}) vs time of processing

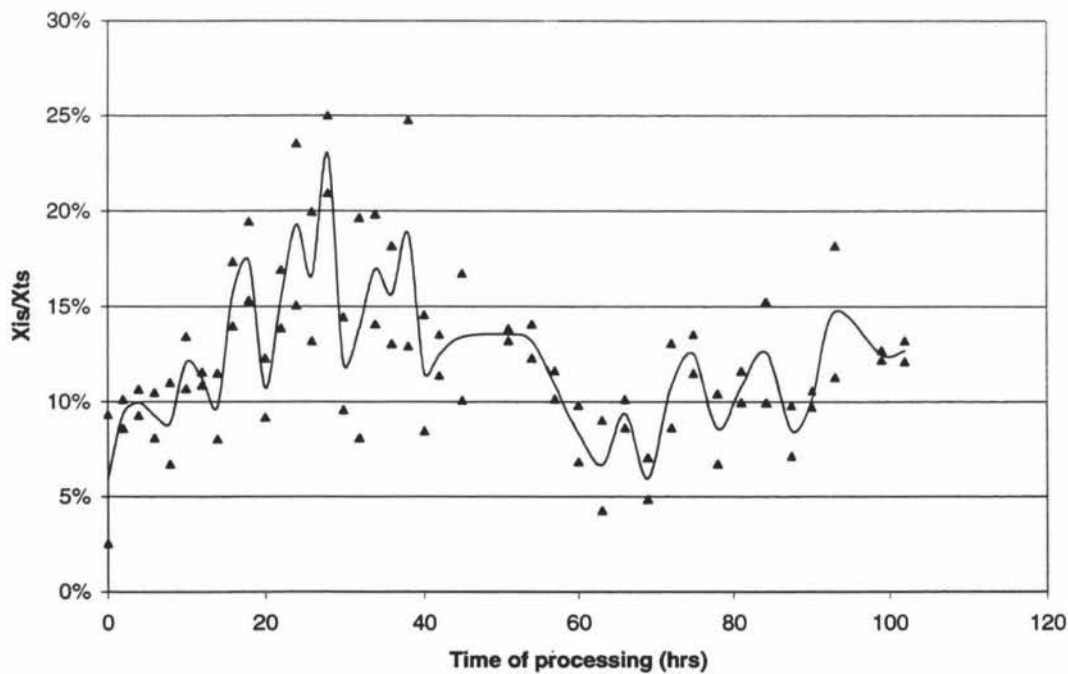


Figure 5.7 Fraction of insoluble solids to total solids (X_{IS}/X_{TS}) vs time of processing

Figures 5.6 and 5.7 show the inherent variation of the individual components that make up tomato paste over 100hrs of production. Total solids are relatively constant over the period indicating good evaporator control. X_{SS} varies a lot in Figure 5.7 hence X_{IS} varies a lot too and consequently viscosity, as viscosity has been found in Chapter 4.3 to be directly related to the insoluble solids fraction. Figure 5.7 clearly shows the variation of insoluble solids content to total solids content (X_{IS}/X_{TS}) being variation 6% to 23%. This is significant especially when producing a base product like paste that is used to make a product with consistent features, such as viscosity and total solids.

To show how fast this variation occurs during production it was decided to collect 20 consequential samples from the line every three minutes (depicting the approximate total time a drum is filled). These samples were analysed in a similar way and the trends are shown in the graph as follows:

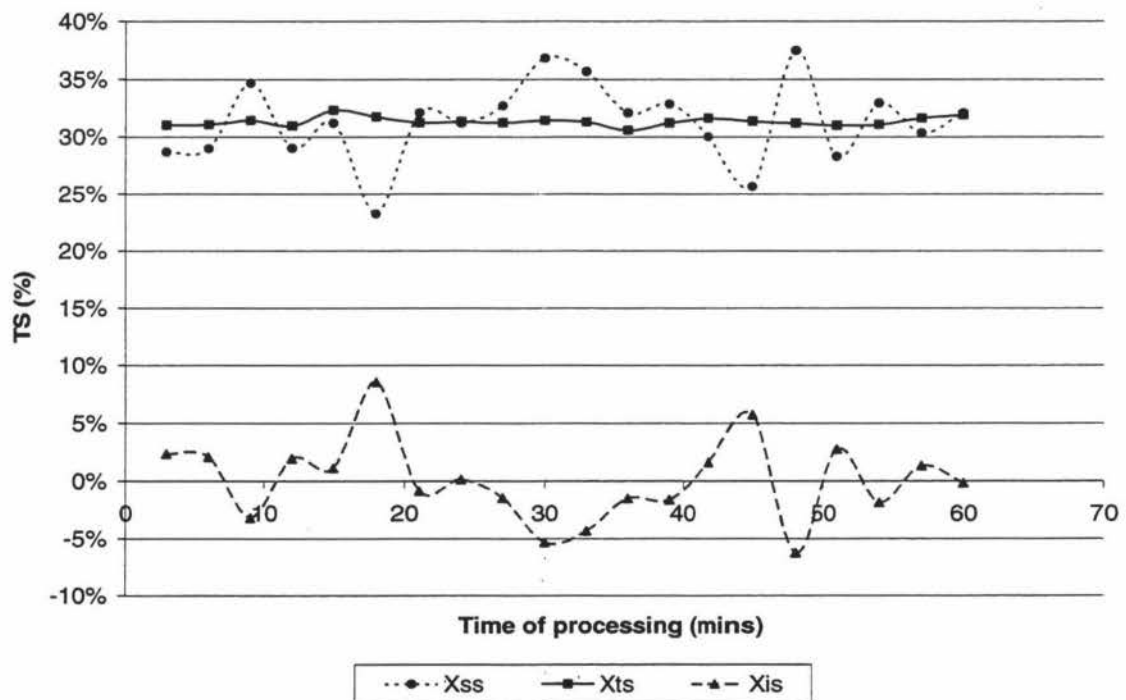


Figure 5.8 % Total solids content (TS) vs time of processing

As can be seen from Figure 5.8 there is variation in the components over processing and in some points the soluble solids are greater than the total solid component hence shows the errors incurred within this method for calculating the insoluble solids component. Instead the viscosity may be used to estimate the insoluble solids however this is beyond the scope of this thesis and validation would have to occur.

5.2 PRELIMINARY INVESTIGATION ON CAUSES ON VARIABILITY IN INSOLUBLE SOLID LEVELS.

From the previous section, the variation has been shown to be in the soluble solids fraction. Within the production process a possible area of variation could be that of the evaporators. The evaporators at Heinz Watties are well controlled but the SS/TS and consequently the IS/TS ratio is variable. From literature this is most likely to be due to the inadequate control over the break process where pectic enzymes hydrolyse the insoluble pectin unless the enzymes are destroyed by heat. The factors affecting the level of enzyme inactivation and pectin hydrolysis in the break tank are explained below.

5.2.1 PECTIN LEVELS IN INITIAL FRUIT

From previous chapters the level of pectin hydrolysis could be potentially the pectin levels in the fruit fed into the process. Shrichantra (2002) showed that pectin levels did vary between fruit, although this was not significantly correlated to fruit colour or ripeness.

5.2.2 RIPENESS OF FRUIT

The fruit ripeness increases the activity of pectic enzymes. This can be seen from figure 5.20 from Shrichantra (2002). As previously mentioned in Chapter 2, the ripeness of the tomatoes are directly related to the activity of the pectinase enzymes. The pectinase enzymes are more prevalent and break up a proportion of the long fibrous pectin chains in the red tomatoes than in the green tomatoes. Thus the insoluble solids content increases as the fraction of green tomatoes increases. Where as if the fraction of red tomatoes are high, the pectinase enzymes have broken down the long insoluble solids pectin chains and created small soluble solids segments, hence increasing the soluble solids (or sugar) component.

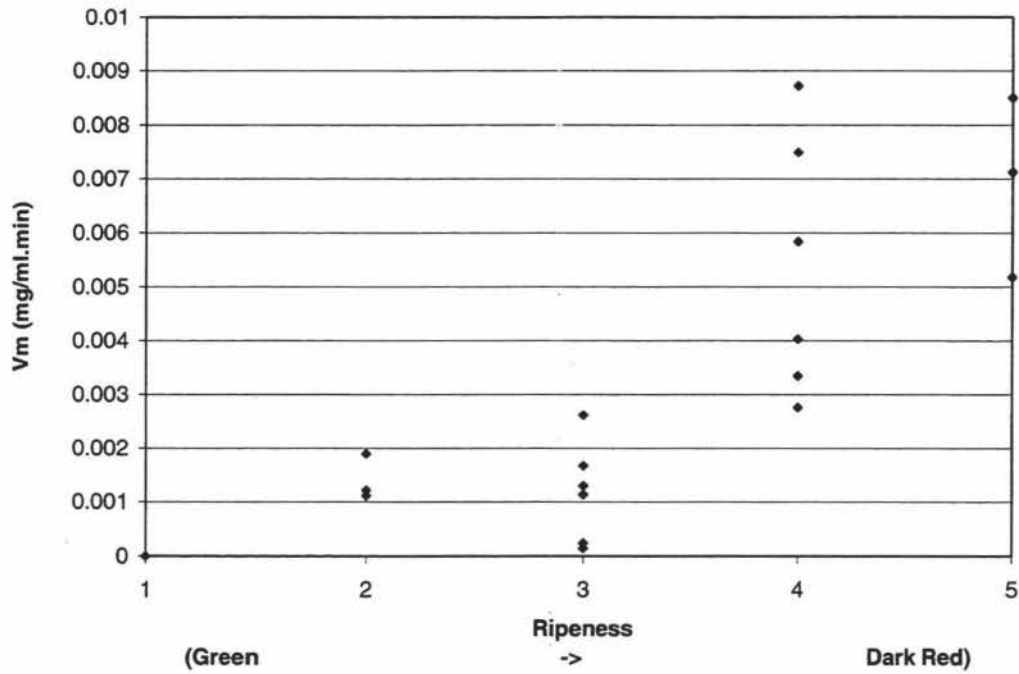


Figure 5.9 Enzyme activity (V_m) vs ripeness of tomatoes entering the tomato paste process

Therefore the degree of pectin hydrolysis is likely to vary as the proportion of green fruit varies over the production period. This is unless the break process is controlled to achieve consistent level of pectin hydrolysis by varying the break temperature and residence time in the break time.

5.2.3 PROPORTION OF FRUIT RIPENESS

Figure 5.10 shows the variation of the changing proportions of green and breaker tomatoes within the truckloads of tomatoes over time entering the production line.

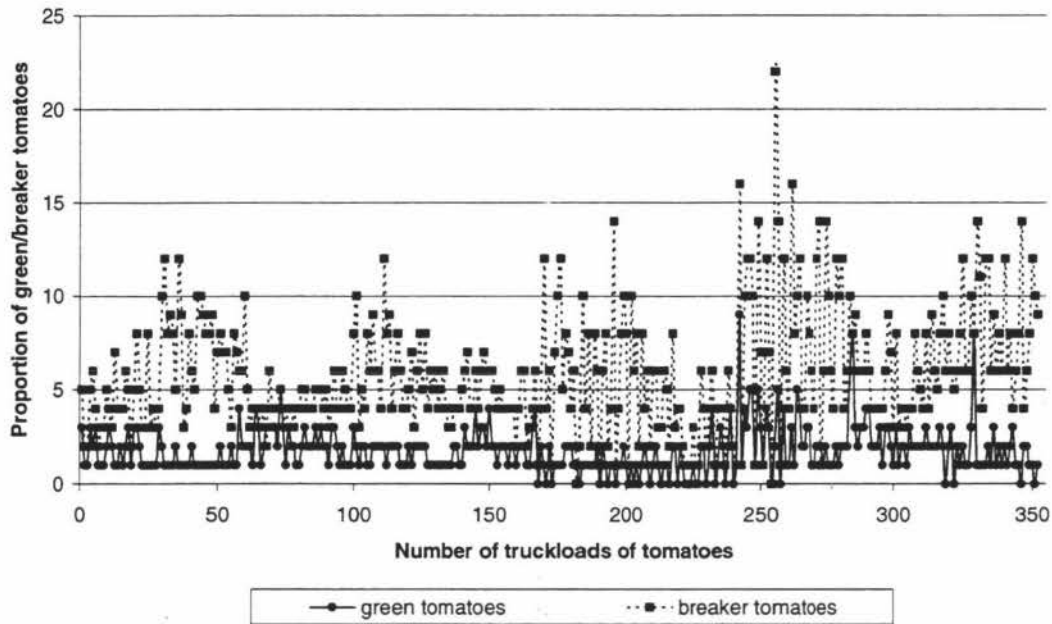


Figure 5.10 Green and breaker tomato proportion within truckloads vs time from 17/4/00 0:05 to 21/4/00 15:11 (approximately 3-4 truckloads per hour)

This variation of green to red tomatoes shown by figure 5.10 causes a variability in the ratio of insoluble solids to total solids. The ratio of insoluble solids to total solids as discussed earlier, is an important measurement in the characterisation of the tomato paste. This insoluble solid to total solids variability adds to the variability caused by the uncontrolled break process accumulating to produce a variable end product.

5.2.4 BREAK TANK OPERATION

It is clear from the literature that control of the break process is crucial to ensuring consistent insoluble solids levels (and hence viscosity) in the finished tomato paste. In addition to the ripeness of the fruit entering the process, several other variables affect the extent of pectin hydrolysis and enzyme inactivation in the break tank. These include varying feed rates (sometimes stopped), varying draw off rates due to evaporator control requirements and set temperature. A companion study (Shrichantra 2002) has been carried out to model these interactions and optimise the process.

5.2.5 FRUIT VARIETY VARIABILITY THROUGH VARIETY DIFFERENCES

Another cause of process or tomato paste variation can be traced back to the tomatoes which is the raw material supply entering the system. Several different varieties are used in tomato paste manufacture at Heinz-Watties as mentioned in Chapter 2. And as discussed in Chapter 4, different tomato variety has different fractions of insoluble solid and soluble solids as established by the different models experimentally modelled. It was seen that the different variety of tomato had different trends of specific gravity to total solids due to the different fractions of insoluble solids to total solids. °Brix was also shown to have an influence by the insoluble solids content. Hence the different variety of tomatoes produce an inherent variability in the insoluble solids entering the tomato paste production process, which in turn causes an inherent variability in the characteristics, used to describe tomato paste.

5.2.6 POST PRODUCTION STORAGE

Tomato paste is stored within an aseptic bag, which is then contained within a 200L drum with a plastic liner. Four drums to a pallet are contained and stacked in several areas around the King Street site of Heinz-Watties, Hastings. The effect of storage was investigated to determine whether there is a change to the tomato paste as it incurs the outside conditions of a summer, autumn, winter and spring seasons.

The trial was carried out in accelerated conditions using sample bags previously collected half-hourly in the 1998-1999 tomato paste production season. Samples were heat-sealed into sections that allowed the testing of the same representative sample over the six month time period. The samples were both of hot break and warm break paste and the tested temperature storage areas used include 2°, 5°, 15°, 20°, 25° and 30°C. During the course of the experiment the samples were tested for the properties that are tested at Heinz-Watties with the methods carried out as per Heinz Watties procedures. The properties tested are what they feel represent the quality of the tomato paste such as the factors of acidity, colour, viscosity and mould count. The other tests determined relate more to the composition of the tomato paste, the amount of water, total solids and the °Brix concentration.

This long term storage trial was found to have no significant changes in the properties of acidity, water content, °Brix, viscosity and mould. The precision is to be questioned here, as this was completed at the initial stages of the project. However the long term storage trial did identify the lack of precision and repeatability in both the °Brix measurement and that of the total solids measurement. As a result of this finding the methods of total solid measurement and °Brix measurement were investigated both by literature and experimental analysis within Chapter 3.

5.3 ONLINE MEASUREMENT OF PROCESS VARIABILITY

Online measurement of tomato pulp and paste composition is useful for both characterising the finished paste and to allow control of the paste production process.

To adequately characterise finished tomato paste products it has been shown that both soluble solids and total solids concentrations are required. In addition it would be useful to have online measurement of the consistency or quality of product in terms of flow behaviour or soluble solids. It is clear from the studies carried out in Chapter 3 that online measurement of °Brix using a refractive index meter is not appropriate to characterise finished paste. The errors induced due to input scatter from the insoluble components of the paste will over estimate the soluble solids levels in the paste and the measurements will have high variance. Accurate measurement of °Brix levels requires sampling of the paste, and separation of the serum fraction as discussed in Chapter 3. This is not possible on-line and should be carried out in the laboratory at regular intervals.

Online measurements of total solids levels in the paste would be very useful. It would provide immediate data which could be used to control evaporator operation as well as being used to characterise the paste for storage and future use. As been previously discussed the best way to measure total solids levels in paste without excessive time delays (for example for drying methods) is to measure specific gravity,, and to calculate total solid levels from the correlations given in chapter 4. If this could be achieved online, for whole paste, the time delays and inaccuracies caused by dilution of the paste in the laboratory method could be avoided.

Density of fluids online is most easily achieved through the use of a Coriolis type mass flow meter. This device works on the principle that a mass flow dependent Coriolis force occurs when a moving mass is subjected to an oscillation perpendicular to the flow direction (www.us.endress.com). One online device of this type (Promass 63I Endress + Hauser Mass Flowmeter) was briefly investigated for use with tomato paste at Heinz Watties Ltd. The specification are given below in Table 5.1

Table 5.1 Specifications for Endress and Hauser coriolis mass flow meter; model Promass 63I

SPECIFICATION SHEET			
FOR PROMASS 63I			
<u><i>Operating Conditions</i></u>			
Normal Flow	2400	Kg/h	
Temperature	20.00	°C	
Pressure	15.00	bar abs	
Viscosity	7000.00	cP	
Density	1200	Kg/m ³	
Vapour Pressure	0.020	bar abs	
<u><i>Sizing & Calculated Results</i></u>			
Connection	DIN		
Meter Size	DN40/DN25FB		
Minimum Pressure Rating	PN16		
Minimum Range 0 to	2250	Kg/h	
Maximum Rang: 0 to	45000	Kg/h	
Pressure Loss	3310	mbar	
Velocity in Tube (s)	1.079	m/s	
Accuracy	0.39	%	
<u><i>Tri-Size Information</i></u>			
	Next Smaller Size	Current Size	Next Bigger Size
Message	Pressure too low	Ideal Size	Flow < min. range
Meter Size	DN25/DN15FB	DN40/DN25FB	DN50/DN40FB
	PN16	PN16	PN16
Minimum Range 0 to	900.0 kg/h	2250 kg/h	3500 kg/h
Maximum Range 0 to	18000 kg/h	45000 kg/h	70000 kg/h
Pressure Loss	12.86 bar	3310 mbar	778.7 mbar
Velocity in Tube(s)	2.428 m/s	1.079 m/s	0.5575 m/s
Accuracy	0.28 %	0.39 %	0.49%

Table 5.1 shows that the precision of the density measurement is of the order of $\pm 0.39\%$. Using this range and Figure 4.5 from chapter 4, it can be estimated that the error in the total solids measurement would be $\pm 1.0\%$. This is acceptable for the purposes of characterising the paste and allowing better control over evaporator performance.

Care must be taken however to calibrate the density measurements of such a device with tomato paste as the density of tomato paste varies with temperature, warranting the need for the calibration to include an adjustment to compensate for variations in temperature. The productive equations explaining the effect of temperature on density given in chapter 4 may be of help for this purpose.

Current practice employs the use of a Bostwick consistometers to characterise the flow behaviour/consistency of the finished paste. Figure 5.6 demonstrates how variable this has been over recent seasons. It was shown previously (Chapter 4) that this variation is principally due to variations in the insoluble solids levels in the paste. Routine manual measurement of Bostwick consistency is of limited value due to the time delays due to the measurement method, inaccuracies resulting in the need for dilution and the fact that total solids levels of the paste can vary.

Online measurement of Bostwick consistency of the total solid levels would as well be very useful to characterise the paste and identify the need for changes to operation procedures to avoid fluctuations. McCarthy and Seymour (1994) found that for dilute tomato products 5 to 8°Brix, Bostwick consistency can be correlated to apparent viscosity. A plot of Bostwick consistency versus $(\eta/p)^{-0.2}$ was linear for all samples. The slope of the correlation $0.0822 \text{ m}^{7/5}\text{s}^{-1}$ agrees to within 2% of that predicted from gravity current analysis. This result suggests that Bostwick consistency can be predicted if the viscosity can be measured online.

One method for measurement of online viscosity is the use of a tubular viscometer. Essentially this can be achieved by measuring the pressured drop over a known length of pipe. Barringer *et. al.* (1998) used this approach to predict Bostwick index online. They obtained linear correlations between Bostwick consistency and reciprocal pressure drop. The correlation was dependent on flow-rate (shear rate) and slightly affected by temperature. This result suggests online prediction of flow behaviour in diluted paste or pulp is certainly possible.

In a tubular viscometer it can be shown that (Macosko, 1994)

$$\eta_{app} = \frac{\pi R^4 \Delta P}{2QL} \left(\frac{n}{3n+1} \right) \quad (Eqn 5.2)$$

where:

- η_{app} apparent viscosity
- R radius of tube from centre (R=0 at centre)
- Q volumetric flowrate
- L length of liquid flow
- ΔP pressure change
- n flow behaviour index

At dilute concentrations it has been shown that the flow behaviour is approaching Newtonian (n=1) and therefore apparent viscosity can be calculated from measured pressure drop (ΔP) and volumetric flow-rate (Q). The volumetric flow-rate can be obtained using the mass-flow and density measurements using the coriolis mass flow meter.

For concentrated tomato paste it is not clear whether the correlations between apparent viscosity or pressure drop and Bostwick consistency holds up. Nevertheless, it should be possible to measure apparent viscosity using the equation 5.2 above. Comparison of measurements of apparent viscosity is complicated by the efforts of shear rate ($\dot{\gamma}$) and total solids levels. If the mass flow rate varies as it is likely to do, then the recorded apparent viscosity must be standardised to a standard shear rate.

It was also shown in section 4.3 that apparent viscosity and the flow behaviour index (n) are also dependent on the insoluble solids (and hence total solids levels). Further work must be carried out to develop this concept to a workable solution for use in the processing plant.

For control of the levels of insoluble solids/total solids ratio (and hence consistency) it is necessary to control the extent of enzyme activity in the break process. To achieve this however, some measure of the insoluble solids/total solids levels in the pulp leaving the break tank must be available. The most likely method to achieve this online is that a tubular viscometer as discussed above be combined with a mass flow meter to provide this information. It is possible that a refractive index meter may be accurate enough to provide a measure of soluble solids in the dilute pulp system to avoid the cost of a coriolis mass flow meter.

5.4 CONCLUSIONS

In conclusion, this chapter has found the following;

The current measurement methods used at Heinz Watties Hastings do not accurately characterise the quality of tomato paste produced, and give inaccurate records of quantity. The problem identified is in the existing procedures of measuring °Brix which has an inherent error if the whole tomato paste is measured and thus is highly variable over the production season. Total solids have a high variability over the production season as well as within the method used. Specific gravity is also variable over the production season and this data shows specific gravity can be correlated to that of total solids as seen in Chapter 4. The Bostwick consistency measurement, (measure of viscosity) has been shown to be variable due to the inconsistency of the insoluble solids fraction over the production period.

Revised methodologies for °Brix and total solids adapted from Chapter 3 allow the accuracy of the measurements to increase and allow the quantification of the insoluble solids to total solids ratio. As previously mentioned the insoluble solids to total solids ratio has a profound affect on that of the Bostwick consistency measurement, which is a measure of viscosity at Heinz Watties Hastings. More accurate measurements of °Brix, total solids and viscosity would allow the more accurate knowledge to describe paste quality and quantity.

With the ability to characterise the insoluble solids to total solids ratio better the optimisation or better control of the break process can be investigated and achieved, thus ensuring a more consistent paste quality can be attained.

CHAPTER 6 FORMULATION

6.1 INTRODUCTION

Tomato paste is a product sold in its pure form, but is most often diluted with water as a base ingredient for as many as 21 of the major food brands such as the formulated products, for instance, pasta sauces, ketchup or baked beans sauce. It is estimated that tomato paste has an input value of \$4.8 million per annum in factories around New Zealand. During reformulation a recipe is normally followed where the paste is diluted to a specific °Brix level or total solids level. Calculation of the amount of water required relies on accurate data characterising the paste (the subjects within chapters 3 and 4) and using the correct dilution equation.

It was shown in Chapter 5 that tomato paste quality varies, over the season due to differences in tomato ripeness and operation of the break and evaporation processes. This results in variation of the ratio of insoluble to total solids. A consequence of this reformulation is that if the paste is diluted to a specified °Brix level, the viscosity, colour etc could be variable. Similarly if a paste is diluted to a specified total solids level, the °Brix level could be variable between batches.

This chapter is aimed at deriving a set of appropriate dilution equations to show how paste composition and physical properties change upon dilution. These equations will then be used to demonstrate the expected variability in physical properties after dilution. Access to these dilution equations should also allow product development technologists to specify an amount of tomato paste with an appropriate basis for dilution for a new product by considering which principle properties the paste will contribute to the reformulated product. The equations will also be used to demonstrate the inherent errors resulting in calculated dilutions from inappropriately characterised paste.

6.2 DERIVATION OF EQUATIONS

6.2.1 DILUTION OF TOTAL, SOLUBLE AND INSOLUBLE SOLIDS

It is relatively simple to derive expressions for dilution of paste characterised on a whole paste basis. The following definitions are made in subsequent derivations.

Subscript (u) corresponds to undiluted tomato paste, that is, tomato paste before dilution.

Subscript (d) corresponds to diluted tomato paste.

In 1kg of undiluted paste there are:

s kg of sugar

i kg of insoluble solids

And (1-i-s) kg of water

If W kg of water is added per kg of undiluted tomato paste then;

$$X_{TS(u)} = s + i \quad (\text{Eqtn 6.1})$$

$$X_{TS(d)} = \frac{s + i}{1 + w} \quad (\text{Eqtn 6.2})$$

Therefore

$$X_{TS(d)} = \frac{X_{TS(u)}}{1 + W} \quad (\text{Eqtn 6.3}) \quad \text{or} \quad W = \frac{X_{TS(u)}}{X_{TS(d)}} - 1 \quad (\text{Eqtn 6.4})$$

Similarly it can be shown that for soluble solids levels

$$X_{SS(d)} = \frac{X_{SS(u)}}{1 + W} \quad (\text{Eqtn 6.5}) \quad \text{or} \quad W = \frac{X_{SS(u)}}{X_{SS(d)}} - 1 \quad (\text{Eqtn 6.6})$$

and for insoluble solid levels

$$X_{IS(d)} = \frac{X_{IS(u)}}{1 + W} \quad (\text{Eqtn 6.7}) \quad \text{or} \quad W = \frac{X_{IS(u)}}{X_{IS(d)}} - 1 \quad (\text{Eqtn 6.8})$$

6.2.2 DILUTION WITH RESPECT TO °BRIX

It is common to dilute tomato paste of known °Brix ($^{\circ}B_{(u)}$). Equations are therefore required to relate the before and after dilution °Brix levels to the amount of water added per kg of tomato paste (W). However, this equation is complicated by the insoluble solids levels in the tomato paste, which has been previously discussed in Chapters 4 and 5.

Using the same basis as in the previous section (6.2.1) we can define

$$^{\circ}B_{(u)} = \frac{100s}{1-i} \quad (\text{Eqtn 6.9})$$

$$\text{and } ^{\circ}B_{(d)} = \frac{100s}{1-i-W} \quad (\text{Eqtn 6.10})$$

$$\text{which then becomes } ^{\circ}B_{(d)} = \frac{^{\circ}B_{(u)}(1-i)}{1-i+W} \quad (\text{Eqtn 6.11})$$

because $i = X_{IS(u)}$ (Eqtn 6.12) we can write

$$^{\circ}B_{(d)} = \frac{^{\circ}B_{(u)}(1 - X_{IS(u)})}{1 - X_{IS(u)} + W} \quad (\text{Eqtn 6.13})$$

$$\text{and } W = \left(\frac{^{\circ}B_{(u)}}{^{\circ}B_{(d)}} - 1 \right) (1 - X_{IS(u)}) \quad (\text{Eqtn 6.14})$$

We can see this graphically below:

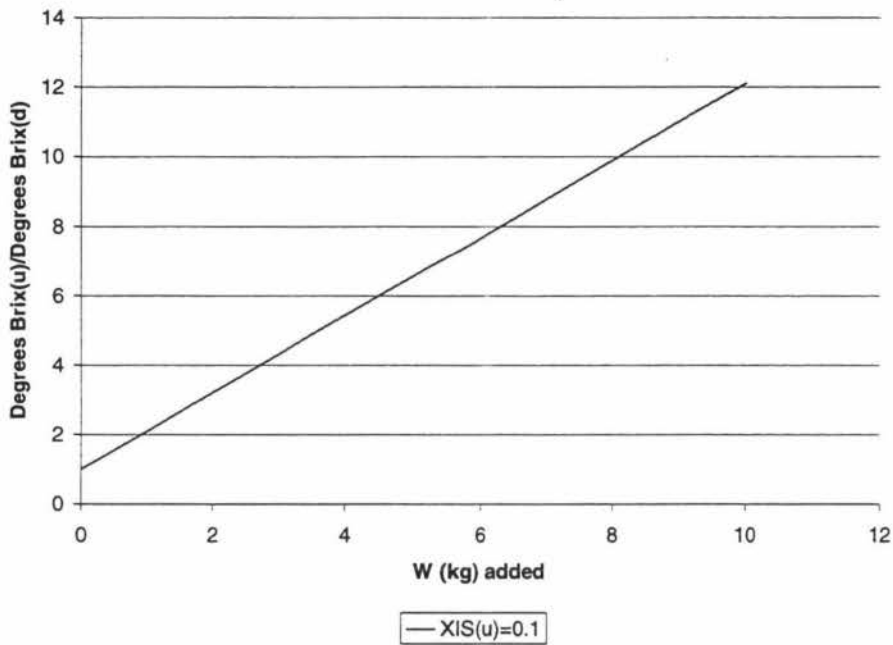


Figure 6.1 °Brix(undiluted)/°Brix(diluted) vs water added (W)

Often the insoluble levels are not known and it is more convenient to express this calculation in terms of the fraction of total solids that are insoluble (r), that is:

$$r = \frac{X_{IS(u)}}{X_{TS(u)}^*}$$

It can be shown that this fraction can be calculated from known total solids levels and °Brix levels of paste as follows:

$$r = \frac{100X_{TS} - ^\circ B}{100X_{TS} - ^\circ B X_{TS}} \quad (\text{Eqtn 6.15})$$

using the relationship:

$$X_{TS} = rX_{TS(u)} \quad (\text{Eqtn 6.16})$$

and the equation relating °Brix to total solid levels previously obtained;

$$\frac{^\circ B_{(u)}}{100} = \frac{(1-r)X_{TS(u)}}{1 - (rX_{TS(u)})} \quad (\text{Eqtn 6.17})$$

Then the following expressions can be arrived at by substitution and rearrangement.

$$^{\circ}B = \frac{{}^{\circ}B_{(u)} \times (1-r)}{(1+W) - r \left(1 + W \left(1 + \frac{{}^{\circ}B_{(u)}}{100} \right) \right)} \quad (\text{Eqtn 6.18})$$

or

$$W = \left(\frac{{}^{\circ}B_{(u)}}{{}^{\circ}B_{(d)}} - 1 \right) \left(\frac{(1-r)}{1-r \left(1 - \frac{{}^{\circ}B_{(u)}}{100} \right)} \right) \quad (\text{Eqtn 6.19})$$

We can see this expression (as per Eqtn 6.18 or 6.19) graphically in Figure 6.2.

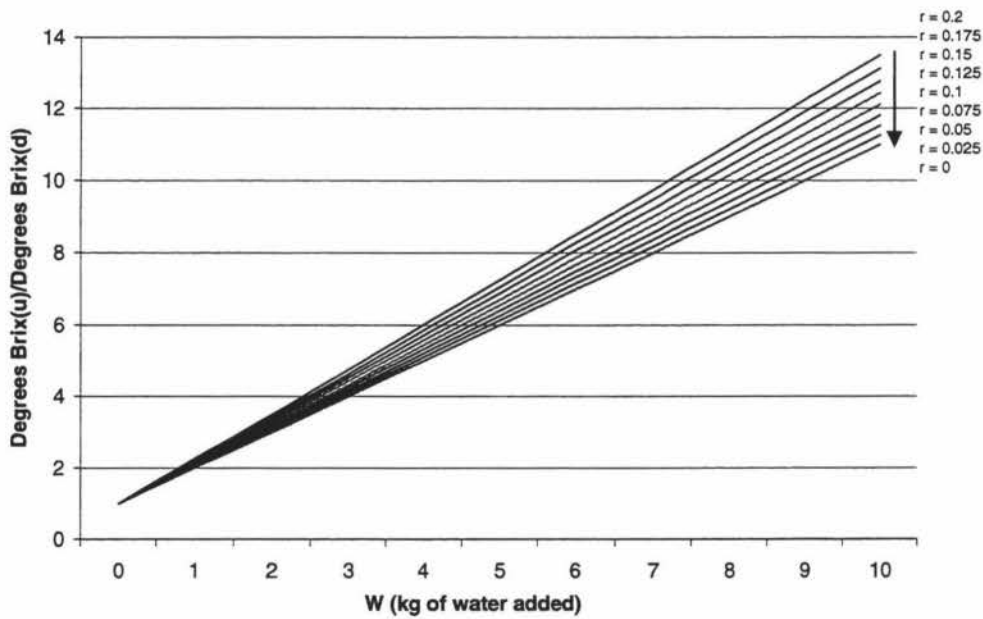


Figure 6.2 $^{\circ}\text{Brix}(u)/^{\circ}\text{Brix}(d)$ ratio vs water added (W) with different insoluble solids contents ($r = X_{\text{IS}(u)}/X_{\text{TS}(u)}$) of the original paste changing

6.2.3 EFFECT OF DILUTION ON SPECIFIC GRAVITY (DENSITY)

The dilution of tomato paste will cause significant changes in specific gravity or density. From chapter 4 it was shown that

$$\frac{1}{\rho_{TP(u)}} = \frac{(1-r)X_{TS(u)}}{\rho_{sugar}} + \frac{rX_{TS(u)}}{\rho_{fibre}} + \frac{1-X_{TS(u)}}{\rho_{water}} \quad (Eqtn 6.20)$$

$$\text{or } = X_{TS(u)} \left(\frac{(1-r)}{\rho_{sugar}} + \frac{r}{\rho_{fibre}} - \frac{1}{\rho_{water}} \right) + \frac{1}{\rho_{water}} \quad (Eqtn 6.21)$$

$$\text{Now after dilution } X_{TS(d)} = \frac{X_{TS(u)}}{1+W} \quad (Eqtn 6.22)$$

Therefore

$$\frac{1}{\rho_{TP(d)}} = \frac{X_{TS(u)}}{1+W} \left(\frac{(1-r)}{\rho_{sugar}} + \frac{r}{\rho_{fibre}} - \frac{1}{\rho_{water}} \right) + \frac{1}{\rho_{water}} \quad (Eqtn 6.23)$$

If the density of the undiluted paste is known then it can be shown that the following equation applies.

$$\rho_{TP(d)} = \frac{(1+W)}{\frac{W}{\rho_{water}} + \frac{1}{\rho_{TP(u)}}} \quad (Eqtn 6.24)$$

$$\text{or } SG_{(d)} = \frac{(1+W)}{\left(\frac{1}{SG_{(u)}} + W \right)} \quad (Eqtn 6.25)$$

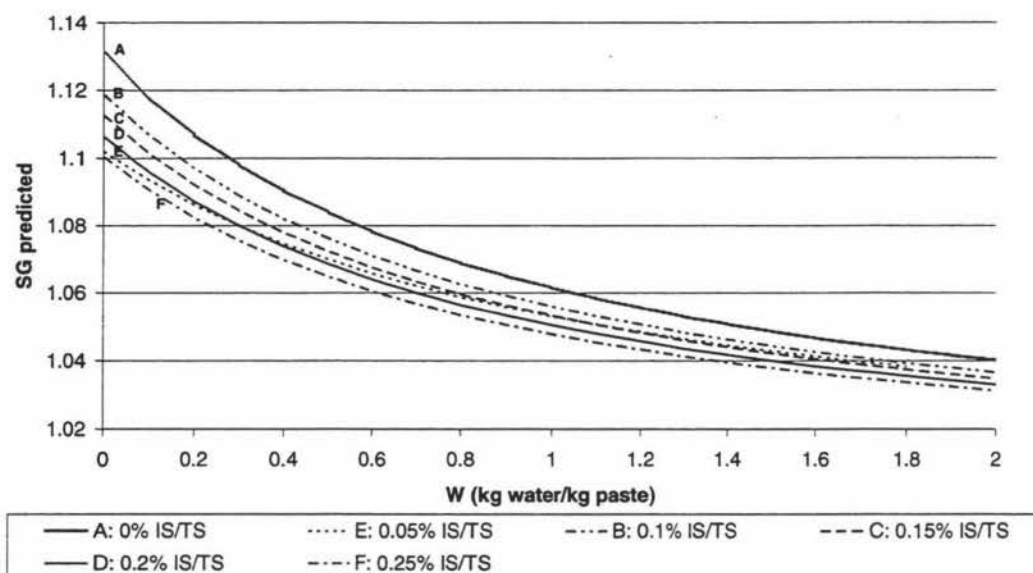


Figure 6.3 Specific gravity predicted (SG) vs water added (W) at differing IS/TS content

As shown above in Fig 6.3, the specific gravity is also dependent on the composition of the tomato paste in terms of the insoluble, solid and water components. Equation 6.23 and Chapter 4 explains that the density of tomato paste is a function of the individual fractions divided by the density of the particular component. This relationship reiterates the concept already explored and recognised in this thesis that the tomato paste has to be properly characterised, that is, knowing the insoluble solids levels and the other properties as discussed in Chapter 3 prior to measuring characteristics properly and as seen in prior to dilution.

6.2.3 EFFECT OF DILUTION ON APPARENT VISCOSITY

It was shown in Chapter 4 that viscosity is strongly dependent on the concentration of insoluble components in the paste. It therefore stands to reason, that the viscosity of tomato paste will be dramatically affected by the addition of water. A relationship between apparent viscosity before and after dilution can be obtained by considering the model for viscosity developed in chapter 4.

$$\eta_{app(u)} = k'' \times (x_{IS(u)})^\beta \times \exp\left(\frac{E}{R \times T}\right) \times \gamma^{n-1} \quad (\text{Eqtn 6.26 adapted from Eqtn 4.10})$$

As shown in section 6.2.1 the insoluble solids fraction in the paste after dilution is given by

$$X_{TS(d)} = \frac{X_{IS(u)}}{1+W} \quad (\text{Eqtn 6.22})$$

therefore

$$\eta_{app(d)} = k'' \times \left(\frac{x_{IS(u)}}{1+W}\right)^\beta \times \exp\left(\frac{E}{R \times T}\right) \times \gamma^{n-1} \quad (\text{Eqtn 6.27})$$

Dividing equation 6.27 by equation 6.26 above gives

$$\frac{\eta_{app(d)}}{\eta_{app(u)}} = (1+W)^{-\beta} \quad (\text{Eqtn 6.28})$$

or

$$W = \left(\frac{\eta_{app(u)}}{\eta_{app(d)}}\right)^{1/\beta} - 1 \quad (\text{Eqtn 6.29})$$

It should be noted that this relationship suggests the fractional decrease in viscosity brought about by dilution is independent of temperature and shear rate.

Figure 6.4 below graphically represents this behaviour

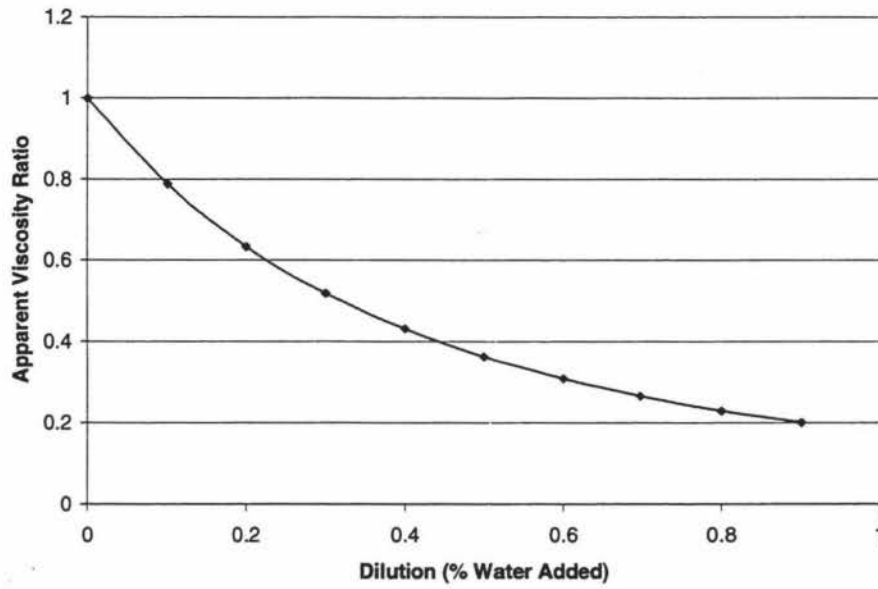


Figure 6.4 Apparent viscosity ratio vs dilution

6.3 EXPERIMENTAL VALIDATION OF DILUTION EQUATIONS

Experiments were carried out on warm break tomato paste in order to validate the dilution equations introduced in section 6.2.

6.3.1 *DILUTION OF TOTAL, SOLUBLE AND INSOLUBLE SOLIDS*

In order to validate the dilution equations introduced in section 6.2.1, the components (total solids, insoluble solids and soluble solids) of warm break tomato paste were determined prior to the addition of different ratios of distilled water to a sample of tomato paste. The total solids, insoluble solids and soluble solids were again determined at each dilution of the tomato paste. The dilution equation for total solids (equation 6.3) was then used with the original component values of the tomato paste to determine the value of total solids when the same additions of different ratios of distilled water were added (model). The experimental data (represented by 4 groups of points) and model (represented by lines) can be seen in Figure 6.5.

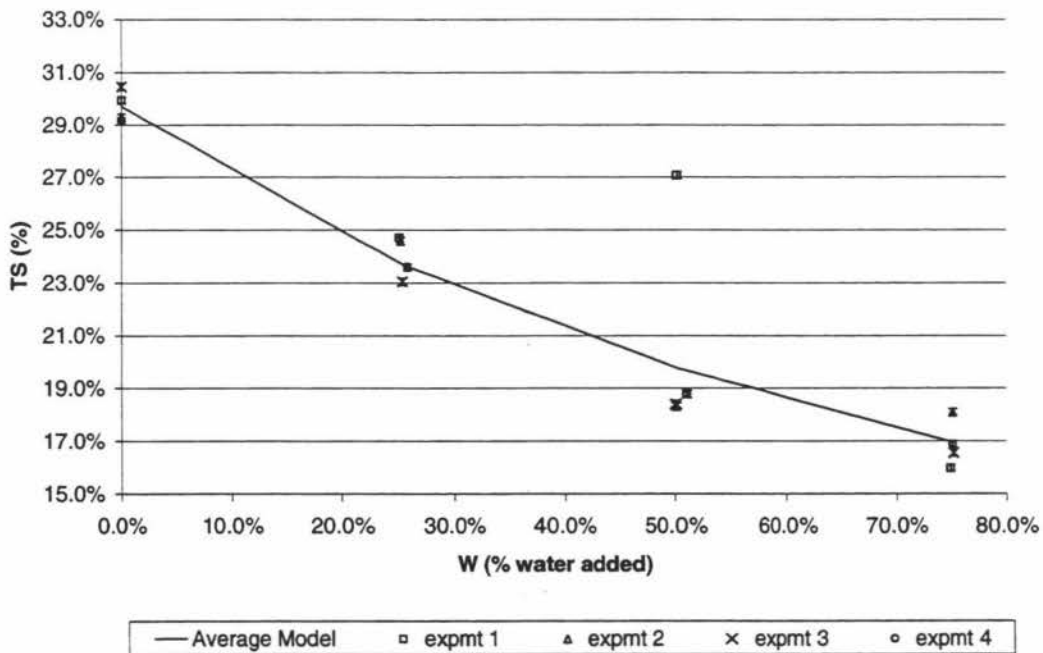


Figure 6.5 % Total solids (TS) vs % water added (W) with average model overlaid

As can be seen from Figure 6.5 above, the model (based on the dilution values of the experiments) closely represents the actual trend of the diluted tomato paste determined experimentally. Hence the model can be used to predict the total solids level when a certain dilution is made.

6.3.2 DILUTION WITH RESPECT TO °BRIX

A similar experiment to that discussed in 6.3.1 was completed for dilution with respect to °Brix. Here, different ratios of distilled water were added to warm break tomato paste and the °Brix value was determined. Model values were then determined using the tomato paste components and dilution values determined experimentally using equation 6.18 in section 6.2.2. The comparison can be seen in Figure 6.6 below where the experimental values are as points and the model values are represented by a line.

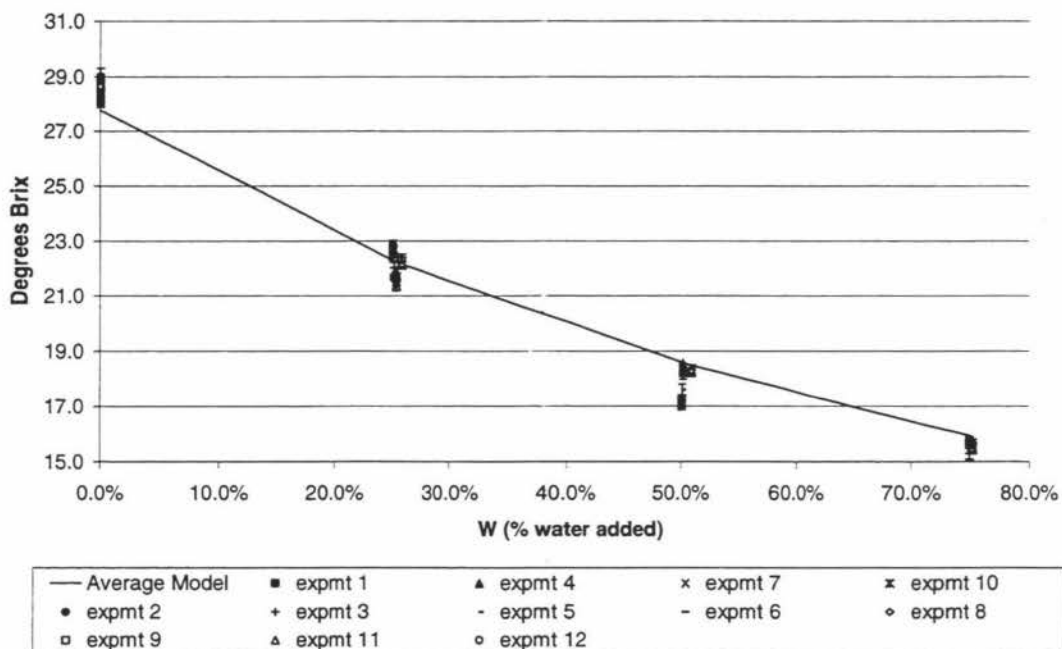


Figure 6.6 °Brix vs % water added (W) with average model overlaid

Figure 6.6 above shows that the twelve experimental data groups are close to that of the predicted model calculated from the values of dilution used in the experiments.

6.3.3 EFFECT OF DILUTION ON SPECIFIC GRAVITY (DENSITY)

Warm break tomato paste was centrifuged, the serum separated and the total solids and °Brix (28.8°Brix) determined. The decantant left was washed, re-centrifuged and the insoluble solids were separated and diluted 3 fold (to wash the remaining serum from the insoluble solids) before testing for total solids (75.5% via vacuum oven method) and °Brix. From this varying amounts of solids and serum were mixed to give six different pastes with known total solids and r (ratio of IS/TS), ranging from 0 to 0.25. These six pastes were then diluted with water to give different levels of dilution and the specific gravity was experimentally determined.

These experimental values were then compared to model predictions, which used equation 6.25 as introduced from section 6.2.3. Model values were based on the original components of the six warm break tomato paste combination used. The experimental data (represented by measured SG I, II and III of points) and model (represented by lines predicted SG I, II and III) can be seen in Figure 6.7.

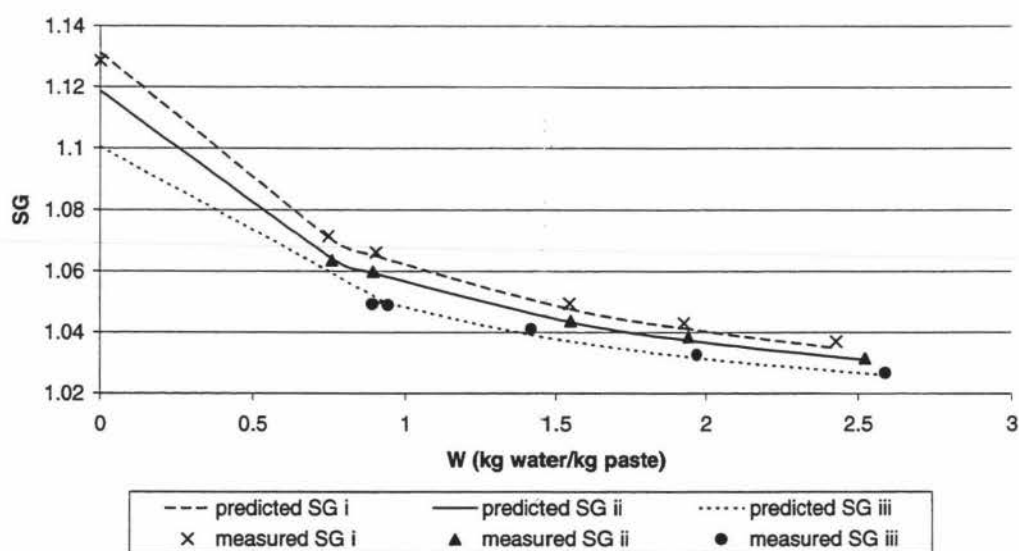


Figure 6.7 Specific gravity (SG) vs water added (W)

6.3.4 EFFECT OF DILUTION ON APPARENT VISCOSITY

Again a similar experiment to that previously described in 6.3.1 and 6.3.2 was completed to show the effect of dilution on apparent viscosity. Different ratios of distilled water were again added to warm break tomato paste of distilled water were again added to warm break tomato paste and the apparent viscosity was measured. Model values were to be calculated based on the experimental values using equation 6.28 or 6.29 as described in Section 6.2.4, however during the course of this experiment, the flow behaviour index (n) was found to change during dilution. Therefore the equation for the effect of dilution on apparent viscosity is shown in equation 6.30.

$$\frac{\eta_{app(d)}}{\eta_{app(u)}} = (1+W)^{-\beta} \gamma^{(0.006 X_{IS}^{-1.2475})((1+W)^{1.2475}-1)} \quad (Eqtn 6.30)$$

Figure 6.8 shows the comparison between that of the model (shown as a line) and the experimental values (shown as points).

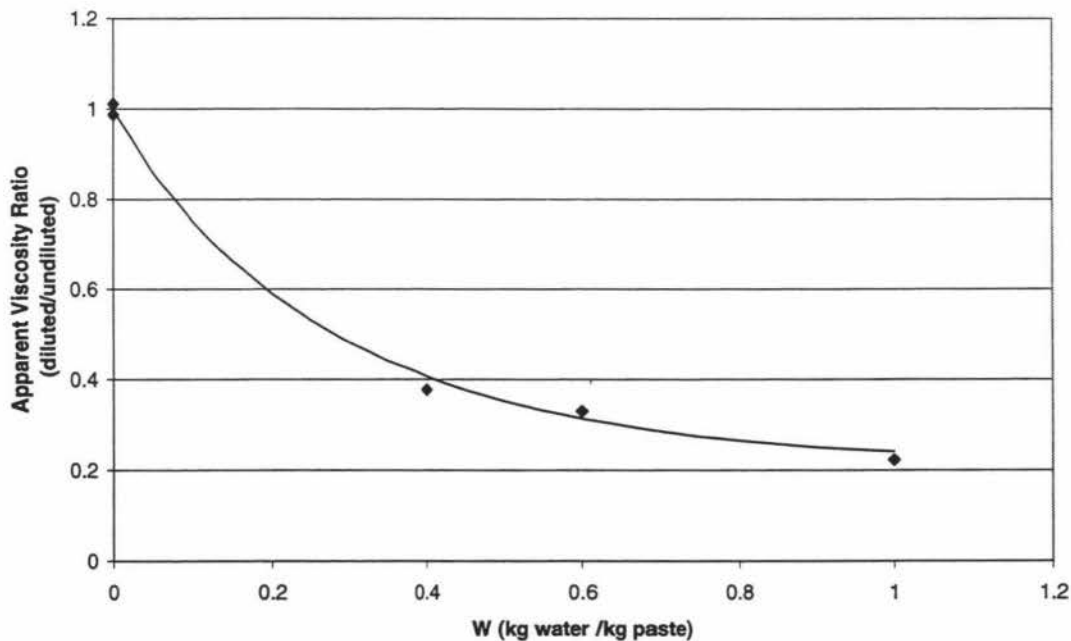


Figure 6.8 Apparent viscosity ratio of diluted tomato paste/undiluted tomato paste vs water added (W)

The Figure 6.8 shows that the experimental values closely represent the behaviour predicted by that of the dilution. Further experimental validation should occur to build up a library of the trends which different tomato varieties and stages of the production season may have on the apparent viscosity when dilution occurs.

6.4 CONCLUSION

The optimal utilisation of the tomato paste is reliant on the following issues:

- i) The adequate control of the paste quality during paste manufacture.
- ii) The accurate recording of stock levels in terms of quantity and quality of the stored product
- iii) The appropriate calculation of the amount of paste used during the formulation of the final products.

Each of the aspects listed above are dependent on the accurate characterisation of the tomato paste that is produced. This requires appropriate measurement methods to be used that are repeatable, have the accuracy needed and are suitable for use in an industrial environment. If such methods are available then the stock levels would accurately reflect the amount of tomato paste ingredient is in storage and the manufacturing process could be better controlled to produce more consistent paste quality. In addition to this the most appropriate measure of the paste composition could be used to calculate the amount of paste needed to achieve required formulated product functionality (in terms of such aspects as flavour and colour).

The specific aims of this project were to firstly determine the most appropriate measurement methods for complete tomato paste characterisation. These methods were then used to assess the degree of variability of tomato paste production during the 2000 season at Heinz-Watties Australasia, King Street, Hastings. The project also investigated how physical and compositional properties of tomato paste are correlated and how they can be related to the functionality of the formulated product.

Section 6.2 introduced the derivation of a set of equations that model the change in physical properties (in particular to that of the °Brix, SG and apparent viscosity) when diluting tomato paste. The models were then found to follow the actual dilution behaviour of the physical properties of °Brix, SG and apparent viscosity when diluting tomato paste.

Hence the following set of equations can be used by production development technologists to predict the change of tomato paste when diluting in order to achieve a reformulated product with the desired composition and physical properties.

➤ Dilution with respect to °Brix

$${}^{\circ}B = \frac{{}^{\circ}B_{(u)} \times (1-r)}{(1+W) - r \left(1 + W \left(1 + \frac{{}^{\circ}B_{(u)}}{100} \right) \right)} \quad (\text{Eqtn 6.18})$$

or

$$W = \left(\frac{{}^{\circ}B_{(u)}}{{}^{\circ}B_{(d)}} - 1 \right) \left(\frac{(1-r)}{1-r \left(1 - \frac{{}^{\circ}B_{(u)}}{100} \right)} \right) \quad (\text{Eqtn 6.19})$$

➤ Dilution with respect to density or specific gravity (SG)

$$\rho_{TP(d)} = \frac{(1+W)}{\frac{W}{\rho_{water}} + \frac{1}{\rho_{TP(u)}}} \quad (\text{Eqtn 6.24})$$

$$\text{or } SG_{(d)} = \frac{(1+W)}{\left(\frac{1}{SG_{(u)}} + W \right)} \quad (\text{Eqtn 6.25})$$

➤ Dilution with respect to apparent viscosity

$$\frac{\eta_{app(d)}}{\eta_{app(u)}} = (1+W)^{-\beta} \quad (\text{Eqtn 6.28})$$

or

$$W = \left(\frac{\eta_{app(u)}}{\eta_{app(d)}} \right)^{1/\beta} - 1 \quad (\text{Eqtn 6.29})$$

CHAPTER 7 CONCLUSIONS & RECOMMENDATIONS

As the base ingredient to many of the 21 major food brands Heinz Watties supply in New Zealand, tomato paste optimisation in terms of its production, storage and use is important to understand. This thesis describes the work carried out to show how to characterise tomato paste products, correlations between variables, process variability and formulation. This thesis reviewed the literature in terms of the fundamental chemical and physical composition of tomatoes and of tomato paste. This understanding was broadened into the chemical changes which occur within tomatoes as they ripen and during processing with particular emphasis on enzyme activity. The main enzyme activity is the breaking up of the pectin bonds is determined by the ripeness as well as the break temperature of the tank which in turn influences the ratio of insoluble solids and soluble solids the produced tomato paste has.

Within literature and currently within Heinz Watties, °Brix, TS, and colour are physical properties considered important and were introduced in Chapter 2. Density predictions and rheology as per the literature and assumptions were also introduced within this chapter. However they have been expanded on within the scope of the thesis work. Chapter 2 also introduced the actual process of producing tomato paste at Heinz Watties, which involves, tomatoes being received from the field then prepared for processing prior to hot or warm breaking then through an evaporator before being packaged aseptically for later use (reformulation) if not used directly. The measures in place and literature about the quality of both tomato paste and tomatoes were lastly summarised.

From this literature and methods used at Heinz Watties an understanding of the six important functional and quality parameters of tomato paste for use in paste derived formulations were established. These are:

- Flavour
- Sweetness
- Viscosity
- Colour
- Acidity
- Microbial Stability

Chapter 3 outlines the work done to identify which compositional or physical properties best characterise tomato paste quality during manufacture and in tomato paste formulation and how they are best measured.

In order to measure soluble solids, centrifugation of the tomato paste is needed to separate the soluble solids from the insoluble solids. The soluble solids (serum) content can be established by drying via a vacuum oven with diatomaceous earth for 12 hours at 70°C. The concentration (°of sweetness) of the soluble solids can be measured with the °Brix scale using a digital refractometer under constant temperature and time.

Insoluble solids content can be established by the drying of the washed insoluble solids component (remaining from the centrifugation of the tomato paste after decanting the serum). The insoluble solids can be dried under the same conditions as the soluble solids, vacuum oven at 70°C for 12 hours.

Total solids can be measured directly by drying. The Vacuum oven method at 70°C for 12hours has been found to give the most repeatable and the lowest variation in results in this investigation.

The pH value (acidity level) can be directly read via a pH meter, which is designed and calibrated for pH values around pH 4-5 (which is the usual acidity of tomato paste). Samples of tomato paste must be kept at the same temperature at which the pH meter is calibrated (usually 25°C).

When measuring colour, a good colorimeter should be used which has standard colour systems being measured (L, a and b or Y, x and y) and calibrated against a white tile. The colour variance must be tracked and should be compared to that of standard values specified for the production of tomato paste (a/b (yellowness to redness scale) =1.9 or above for first grade tomato paste).

Controlling the microbial activity is a vital part of any food processing and therefore frequent measurements should be conducted during processing to ensure that the tomato paste is within standards. However the current test method, the Howard Mould count does not have a high level of repeatability. Due to this other methods beyond this thesis should be explored. In addition to this ensuring that the raw material is graded properly and the process lines are kept clean from material build-up will contribute to a low microbial activity.

Therefore in order to properly characterise tomato paste in terms of its flavour, sweetness, viscosity, colour, acidity and microbial stability, soluble solids, insoluble solids, total solids, pH, colour and the Howard mould counts should be measured.

Correlations between variables was explored in order to determine whether correlations could be used without having to measure a large number of variables (which as identified in Chapter 3, tomato paste cannot be properly characterised by only one variable. Also correlations are advantageous if the variables are difficult and time consuming to measure (for example, total solids take 12 hrs in a vacuum oven). Modelling was carried out from the knowledge of the components that exist within tomato paste and then experimental validation was sought. The correlations that were explored were that of specific gravity and total solids; °Brix, soluble solids, insoluble solids and total solids; viscosity.

Specific gravity and total solids

Literature shows three studies of SG vs TS, that of the Tomato Bulletin Data (1992), Heinz Watties Analytical Manual Data (1999) and Dr Andy Crawford's Data (1998). Modelling (using a simple model suggested by Choi and Okos (1986) whereby

$$\frac{1}{\rho} = \sum_{i=1}^I \frac{x_i}{\rho_i} \quad (\text{Eqn 4.1})$$

as in Eqn 4.1, the density of a product can be related to the composition of each component, was shown to closely relate to the data of Dr Andy Crawford and that of Heinz Watties analytical manual data. However it was also noted in the modelling that the correlation changes as the IS levels change. TS was seen to vary 2.2-2.6% if the IS/TS ratio varied 1-3% (typical of tomato paste).

Therefore the insoluble solids ratio needs to be known. Similarly the SG varies ± 0.005 which from experimental methods in chapter 3 showed that TS $\pm 2.5\%$ which is comparable.

Also the correlation is better if IS is known and measuring SG then using the correlation to determine the TS content is a lot quicker than conventional methods of measuring total solids.

SG is also influenced by temperature. The modelling of SG vs TS was again investigated by a change in temperature as SG is dependent on the temperature. Temperature was found to have a large effect on the SG reading (± 0.0024 or 0.22% (2 s.f.)) that in turn causes TS to range by 1.2% . Therefore ensuring the temperature is constant when measuring SG is important if the correlation is to be used effectively.

Experimental data shows that SG increases with increased amount of insoluble solids and over the range of 0-2.5% IS/TS covers Tomato Bulletin data and Dr Andy Crawford's data but reiterates the fact for knowledge of the insoluble solids component before accurate correlations of TS and SG can be made.

An inline mass flow meter is a suggested tool for establishing a continuous SG reading which at a specific temperature and IS content (both of which would need to be measured) would be used in the correlation to determine TS amount indirectly.

°Brix, SS, IS and TS

The correlation between °Brix, SS, IS and TS was explored. If the °Brix is measurable, then it can be directly related, via correlation, to that of the SS content as has been shown in this thesis that the °Brix is highly influenced by the presence of IS. Modelling was carried out by the use of related °Brix (a measure of the soluble solids in the water phase of a product). Graphical representation (Fig 4.5), showed that °Brix does change with the change in SS fraction and how it also changes over the 1-3% IS/TS range.

Experimental data showed no real relationship between °Brix and Total solids however this experimental data was that of °Brix of whole tomato paste which as previously mentioned the IS fraction could have been a contributing factor to the variability of the experimental data.

Experimental data was gathered prior to the knowledge of the correct methodologies therefore the experimental trend between °B and TS should be explored again using the correct methodologies to accurately compare the experimental with that of the model.

Viscosity

Chapter 2 discussed the flow behaviours of concentrated tomato paste and an overall model was proposed as seen in Eqtn 4.18.

$$\eta_{app} = k' \times (x_{IS})^{\beta} \times \exp\left(\frac{E}{R \times T}\right) \times \gamma^{n-1} \quad (\text{Eqtn 4.18})$$

The model equation was established by describing tomato paste in terms of three different parts, the effect of shear rate on viscosity was described by the power law equation, the Arrhenius law to describe the effect of temperature and the simple power law which was to quantify how IS concentration affects viscosity. The constants and parameters were experimentally determined based on Heinz Watties warm break tomato paste and were found to be as follows

$$n = 0.0066x_{IS}^{-1.2475} \quad (\text{Eqtn 4.23})$$

$\beta = 4.9062$, which is greater in magnitude than in literature. This difference could be due to the different tomato variety to that in literature, which may suggest that the tomatoes at Heinz Watties are more influential on affecting viscosity than those in literature.

$$k' = 10,048.73$$

$E = 13,460$ J/mol, which is typical for the rheological behaviour of tomato paste.

Experimental validation shows a reasonable fit between predictions of apparent viscosity and actual, however more validation on independent samples is advised.

Overall Chapter 4 concludes that more extensive experimental validation based on a longer time period and greater experimental sample population needs to be completed for all the correlations before these correlations can be utilised in the plant. However these results do show that the models or correlations mentioned relate closely to those of the limited experimental data, therefore these are a basis for these behaviours and characteristics.

In the course of manufacturing tomato paste an inherent variability (inside or outside stimuli) exists as with manufacturing any product. This was explored with tomato paste from a long term to a short term basis in Chapter 5 within three different areas.

- Over a season
- Day to day
- Over 20 bags repetitively

It was found that the current measurement methods used at Heinz Watties Hastings do not accurately characterise the quality of tomato paste produced, as well as giving inaccurate records of quantity. °Brix has an inherent error if the whole tomato paste is measured and thus is highly variable over the production season. Total solids has a high variability over the production season as well as within the method used. Specific gravity is also variable over the production season and this data shows specific gravity can be correlated to that of total solids as seen in Chapter 4. The Bostwick consistency measurement, (measure of viscosity) has been shown to be variable due to the inconsistency of the insoluble solids fraction over the production period.

Revised methodologies for °Brix and total solids adapted from Chapter 3 allow the accuracy of the measurements to increase and allow the quantification of the insoluble solids to total solids ratio. As previously mentioned the insoluble solids to total solids ratio has a profound affect on that of the Bostwick consistency measurement, which is the viscosity measure of choice at Heinz Watties Hastings. More accurate measurements of °Brix, total solids and viscosity would allow a more accurate knowledge to describe paste quality and quantity.

With the ability to characterise the insoluble solids to total solids ratio better the optimisation or better control of the break process can be investigated and achieved, thus ensuring a more consistent paste quality can be attained.

As previously mentioned tomato paste can be sold in either its pure form or diluted with water as a base ingredient for many formulated products such as pasta sauces and tomato sauces. At Heinz Watties Hastings in a recipe formulation the basis is to dilute the tomato paste mixture to a specific °Brix or TS level. Chapter 6 showed that the calculation of the amount of water required relies on an accurate tomato paste characterisation (as discussed in Chapter 3) and using correct dilution equations which take into account all the paste composition and physical properties which change upon dilution. Derivation of a set of equations that model the change in physical properties, (in particular to that of the °Brix, SG and apparent viscosity) when diluting tomato paste, were introduced in Chapter 6. These models were then tested and found to follow the actual dilution behaviour of the physical properties of °Brix, SG and apparent viscosity when diluting tomato paste. Therefore this set of equations (as indicated below) can be used by production development technologists to predict the change of tomato paste when diluting in order to achieve a reformulated product with the desired composition and physical properties.

➤ Dilution with respect to °Brix

$${}^{\circ}B = \frac{{}^{\circ}B_{(u)} \times (1-r)}{(1+W) - r \left(1 + W \left(1 + \frac{{}^{\circ}B_{(u)}}{100} \right) \right)} \quad (\text{Eqtn 6.18})$$

or

$$W = \left(\frac{{}^{\circ}B_{(u)}}{{}^{\circ}B_{(d)}} - 1 \right) \left(\frac{(1-r)}{1-r \left(1 - \frac{{}^{\circ}B_{(u)}}{100} \right)} \right) \quad (\text{Eqtn 6.19})$$

- Dilution with respect to density or specific gravity (SG)

$$\rho_{TP(d)} = \frac{(1+W)}{\frac{W}{\rho_{water}} + \frac{1}{\rho_{TP(u)}}} \quad (\text{Eqtn 6.24})$$

$$\text{or } SG_{(d)} = \frac{(1+W)}{\left(\frac{1}{SG_{(u)}} + W\right)} \quad (\text{Eqtn 6.25})$$

- Dilution with respect to apparent viscosity

$$\frac{\eta_{app(d)}}{\eta_{app(u)}} = (1+W)^{-\beta} \quad (\text{Eqtn 6.28})$$

or

$$W = \left(\frac{\eta_{app(u)}}{\eta_{app(d)}}\right)^{1/\beta} - 1 \quad (\text{Eqtn 6.29})$$

In conclusion this thesis has identified that tomato paste needs to be characterised properly in terms of its important functional and quality parameters (flavour, sweetness, viscosity, colour, acidity and microbial stability) by measuring insoluble solids, °Brix soluble solids, total solids, colour, pH and Howard mould counts. This will accurately not only describe tomato paste but accurately account for it in terms of quantity. Not all of these variables need to be measured, for example SG can be measured instead of TS (as long as IS is known) therefore correlations can be used to save time and equipment usage. Though further experimental validations using Heinz Watties tomato paste needs to occur.

Also identified was the use of dilution equations which model the actual behaviour of the tomato paste characteristics when dilution occurs in an effort to create a more consistent reformulated final product, of which it's functional and quality parameters can be predicted.

In addition the current process of producing tomato paste at Heinz Watties was characterised to identify the extent and cause of process variability. The work above has showed that although total solid levels are well controlled, the ratio of insoluble solids to total solids is not. The cause of this was most likely due to poor control over the break process and the extent of enzymatic pectin hydrolysis that occurs. Some suggestions on online measurement options to enable better control of this were made.

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APPENDICES

APPENDIX ONE.**VARIETIES OF TOMATOES USED BY HEINZ WATTIES LTD, HASTINGS****Table 1: Varieties of Tomatoes used by Heinz Watties Ltd, Hastings (Kale, 1999)**

Variety	Properties		
	pH	°Brix	Viscosity
Morse	high	high	medium
225	medium	low	medium to high
9665	medium	low	medium to high
9775	medium	low	medium to high
230		medium	medium

APPENDIX TWO.***TOMATO PASTE PROCESS FLOW CHART******Definitions Used in Flow Chart******Fruit***

Green Tomato fruit are 70-100% green in colour

Breaker red These tomato fruit are turning from green to red in colour. They are usually orange or pink in colour. The number of breaker fruit to be removed from the production of tomato paste is dependent on the colour of the rest of the batch of tomatoes and the type of paste to be produced. For example: For Warm Break the colour must be bright red. If the trailer load of tomatoes entering the process consists of many red –ripe tomatoes more breaker fruit could be added. In contrast, a trailer load of a little number of red-ripe tomatoes, the number of breaker fruit to be left in would be more constricted.

Paste Types

Hot Break This involves rapid heating to 95°C after crushing of the tomato pulp. This method allows the retention of natural pectins yielding a thicker product which is used in such products as sauces which require thick consistency. Evaporator performance is low when producing Hot Break Paste so the maximum soluble solids content that can be achieved is approximately 30-32% of the paste.

Warm Break This process involves slow heating to 75°C in the hot break tank. However higher evaporator performance is achieved due to the lower residence time in the hot break tank because of the use of the cold break equipment. The soluble solids content achievable is between 32-34%. This type of paste is thinner in consistency in comparison to the Hot Break paste, hence is used in such products as soups, spaghetti and baked beans.

Cold Break This process involves low heating (75°C) of the crushed tomato pulp reducing the pectin activity and thickness, hence cold break paste is used for products that do not need thickness, like tomato juice. With this method evaporator performance is good, achieving a soluble solids content of 36-40%.

Aseptic filler

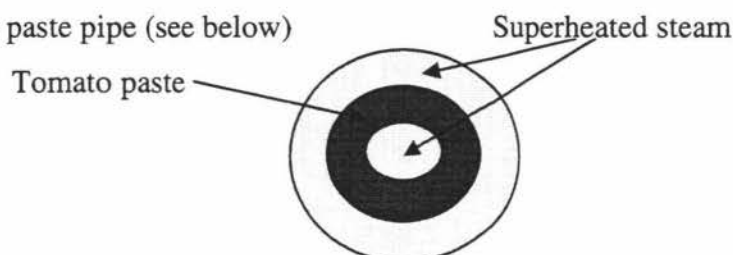
Gamma Sterilised Bags Scholle 200 L PM Aseptic Single bags dosed with min of 15kgray or 1.5 megarads of irradiation for sterilisation. Made from HF and PE material with an inner liner material of Poly 100µm .

Aseptic Filler

The aseptic machinery at Heinz-Wattie Ltd. Hastings is a Fenco system with a design capacity of 8 tonnes per hour. A ELPO aseptic filling head is used to fill the 200 L Scholle aseptic bags. Approximately 27,000 drums p.a. are produced with an operational capacity of approximately 3-4 tonnes per hour. (Packaging Specification Sheets 1999 & Eagleton, 1999)

Aseptic System

This system is the sterilising step before packaging occurs and consists of a holding tank, heating section, holding section and a cooling section. From the holding tank the paste is heated by superheated water within an annular pipe system, where the water flows around and inside the tomato paste pipe (see below)



After the heating section the tomato paste is held for approximately 1.9 minutes at 106°C in the holding section in order to achieve sterilisation of the product. If the tomato paste does not reach this temperature or if the level within the holding tank is too low or failure of the filler occurs, recycling of the tomato paste occurs. The tomato paste is recycled back to the beginning of the aseptic system, the holding tank and continues through again.

Immediately before the product is filled into the aseptic bag, the tomato paste is cooled to approximately 30°C by water in another annular pipe system. Filling occurs through an aseptic head at 112°C (head at saturated steam temperature ensuring sterility) with the only contact made by the tomato paste is the bag plug which is steam flushed before and after connection to the nozzle which fills the bag with tomato paste.

Flow Chart (Chambers, 1994)