Design of a process for the manufacture of Beef Stock

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Abstract

This work deals with the development of a process for the production of commercial stock from beef bones using a formal food process engineering analysis instead of random experimental trials of potential processes. The major difference between a food and a traditional chemical process engineering analysis is the inclusion of the food functional, textural and/or sensory properties besides the yield and efficiency in the optimal design. These properties often interact with the process and equipment design.

The bones were extracted with hot water and the kinetics of extraction determined by following the changes in soluble solids over time. Extraction curves measured at several temperatures between 80 and 120°C could be modelled using first order rise to an equilibrium concentration and the effect of extraction temperature could be measured using the Arrhenius law.

Despite the presence of gelatine in the aqueous stock extracts, which is known to produce strongly time-dependent non-Newtonian solutions, they were found to be Newtonian for temperatures above 20°C. Thus the Newtonian viscosity of the aqueous extracts was measured as an indicator of stock texture. Textural changes due to exposure to high temperatures over time were determined for temperatures between 60 and 120°C and found to follow first order kinetics. The effect of temperature followed the Arrhenius law.

An equilibrium curve for bone extraction in hot water at 120°C and a maximum yield of extractable solids non-fat were also determined.

A mathematical model was constructed on an Excel platform using the kinetics of extraction and textural changes as well as the equilibrium data. It is based on a novel method of analysis of multi-stage solid-liquid extraction called “stage wise iterative analysis” and gave a profile of soluble solids concentration and viscosity during the extraction and concentration phases of the manufacturing process that fell within less than 10% of experimental measurements. Simulations showed that soluble solids concentration, viscosity, yield and processing time all impacted on the optimum design.

These analyses highlighted the significant importance of reducing the run time from the current 6 days to 5 hours as it has the potential to increase the production rate and therefore revenue ten-fold with a minimum change in equipment. The higher extraction rate can be achieved by increasing the extraction temperature from the current 92°C to 120°C. While the rate of losses of viscosity and therefore texture is increased with the higher process

temperature, the model showed that the great reduction in processing time more than compensates for the temperature effect and the viscosity of the final stock extract is greater than that found in the current industrial operation. It was also found that the yield of extracts from the bones could be improved significantly by conducting a multi-stage semi-counter current extraction instead of a single stage extraction for the same overall extraction time. Preliminary considerations were given to the use of secondary product streams, high quality tallow and calcium phosphate to improve further the financial returns of the process. Finally a process modification was considered to improve the consistency of the flavour properties of the stock. It was proposed that separating the meat from the bones and roasting it in a smaller oven to allow quick and separate extraction of the flavour components found in the commercial stock. These can be added back to the bone extracts in standardised quantities to produce a product of consistent flavour.

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1 Introduction

Stock for soups and sauces have been manufactured in homes for centuries. But early commercial stock was marketed to households in dried form with a high salt content. Stock of good flavour and textural quality was supplied mainly to restaurants and caterers. This work originated from a request by Essential Cuisine Limited (EC), a small manufacturer of stocks and sauces for technical assistance. They had two requests:

1. Increase the volume of production for concentrated beef stock 10 fold from 1,500 L per week to 15,000 L per week.

2. Increase the thickness of the stock texture. The colour and flavour of the current product were well liked and needed to be maintained.

A visit to the manufacturing premises showed that the process was heavily batch and lasted more than 3 days. A quick check of the literature further showed that there was little information on the on textural changes in concentrated stock.

A literature review is covered in Chapter 2. Chapter 3 provides a review of the current EC operations and also includes experimental work conducted at Massey University to obtain a fuller characterisation of stock currently manufactured by Essential Cuisine and detail the outcome of their current extraction process. Chapter 4 outlines the research objectives for a new process. The experimental work for the new process is presented in Chapters 5 and 6 including the kinetics of textural changes of bone extract (Chapter 5), the kinetics of extraction under different operating conditions, and an equilibrium distribution curve of the extractable material between the solid and liquid phases (Chapter 6). Chapter 7 presents the generation of a model that combines the kinetics of extraction and textural changes along with analysis using the equilibrium curve to quantify textural properties, solids content and yields. The model is used to highlight key issues in process design. The model is also used to demonstrate in a quantitative manner how objectives of this project can be achieved.

2 Literature Review

2.1 Introduction

This literature review was conducted in order to identify and understand previous work related to stock manufacture. This information was necessary for the formulation of a research plan but should also provide good background information for the sponsor. Specifically the literature was reviewed in order to identify the raw materials used for the production of stock, the composition of stock and key attributes of stock in particular flavour, colour and texture. Manufacturing processes for stock were reviewed in order to understand the key operations and process alternatives. Details of key processes are presented along with design variables and equipment for such processes.

2.2 Terms and definitions

McEvoy (2004) describes stock as the flavourful liquid resulting from extraction and concentration of fats, oils, juices and liquid compounds from various organic sources. Generally, bones, vegetables, meats and fishes are the primary sources. Spices, herbs and aromatics often are added to create more complex flavours.

The terms broth and stock are often used interchangeably and both are manufactured by simmering meat and/or bones in water with seasoning.

Bouillon is the French word for stock and essentially means the same thing. It is often used in the case of stock cubes but can apply to stock in the liquid or powdered form.

Consommé is another word describing stock but specifically refers to stock or bouillon that has been clarified to remove all minute particles, which cloud or float in the liquid.

A double consommé is a regular consommé that has been reduced by half its original volume to double the intensity of the flavour. Adding unflavoured gelatine and perhaps some port or other spirits makes a jellied consommé.

2.3 Uses of Stock

Stock is generally used as an ingredient for cooking, for example it is often used as a base ingredient for gravies, sauces and soups. Other ingredients are added to the stock in order to provide flavour and texture. The stock is generally heated and the other ingredients are added. The resulting product is often served hot.

The quality of the final product depends heavily on the quality of the stock i.e. its flavour profile, clarity or lack of depending on the end requirements and finally its textural characteristics (thickness, smoothness, creaminess and viscosity).

2.4 Raw materials

Bones have been used for the production of stock and soups for centuries. According to Ochi (1981) fresh bones should be collected for high quality materials. Those bones that are not used immediately should be kept under refrigeration at < 4°C for short term storage, or stored at -25°C if not used within 2-3 days.

Bones used in the manufacture of stock include some attached meat and this will vary depending on the type of bones used and previous processing. Ockerman & Hansen (2000) report that bone comprises 7.5-12% and 7-12% of the live weight for pork and beef, respectively. Typical bone composition is presented in Table 2-1 for pork and beef, but variations occur depending on bone type and age of the animal.

Table 2-1 Bone composition (Ockerman & Hansen, 2000)

	Pork (% of bone weight)	Beef (% of bone weight)
Moisture	43	32-50
Protein	20.6	20.6-29.0
Fat	12.4	15.2-22.0
Ash	21.4	13.0-29

Bones contain a significant amount of minerals as indicated by the high ash content. Calcium makes up 37% of the ash component (Ockerman & Hansen, 2000). The protein present in bones, 20-29%, (Table 2-1) contains a significant proportion of collagen. Ockerman & Hansen (2000) indicate that gelatine yields for wet bones are 10-16% indicating that half of the protein present in bones is collagen. Collagen comprises 30-33% of the total protein in humans and animals and is wide spread in the body including, bones, cartilage material and skin. A review on collagen is provided by Swan and Torley (1991) while Ockerman & Hansen (2000) and Johnston-Banks (1990) discuss collagen as the raw material used to make gelatine. Because collagen is such a key component of stocks it has been extensively studied and a good understanding of its chemistry and behaviour exists.

The collagen molecule exists as a triple helix, comprised of three discrete α-chains that adopt a three dimensional structure (Johnston-Banks, 1990) and a molecular weight in the range of 345,000 to 360,000 (Ockerman & Hansen, 2000). As reported by Johnston-Banks (1990) the

repeated amino acid sequence in the collagen chains is glycine-X-Y and therefore glycine makes up 33% of the residues. The X and Y components contain a high proportion of proline and hydroxyproline.

Collagen also contains the rare amino acid hydroxylysine which makes up 1% of the amino acid residues (Johnston-Banks, 1990). Johnston-Banks (1990) state that because glycine has no side chains it is a compact amino acid and allows close association with hydroxyproline and proline residues on the other two chains providing an ideal geometry for hydrogen bonding. As glycine occupies every third residue in the chain, numerous sites are available for hydrogen bonding creating extensive cross linking, i.e. good ability to form gels.

In most structures collagen is arranged in bundles of four to five molecules to form quaternary structures known as fibrils which are further associated with other nearby fibrils to make further bundles of large diameter (Johnston-Banks, 1990). The intermolecular cross-linking produces a highly stable structure that is insoluble in water and immune from attack by most enzymes.

Details of the manufacture of gelatine are provided by Johnston-Banks (1990), Swan & Torley (1991) and Ockerman & Hansen (2000). Processes for its manufacture include heating of the collagen solution to increase the solubility and digestibility. Heat induces denaturation of collagen in a two-step process; (1) break down of helical structure followed by (2) disassociation of the polypeptide chains. Rates of denaturation and increased solubility can also be manipulated by pH and the use of enzyme treatments. The commercial production of gelatine is carried out using acid or alkali conditions.

2.5 Composition of Stock

The composition of stock depends highly on the raw materials used and the manufacturing processes. Meat extracts may be taken from different species, different cuts and from meat and/or bones.

Placing bones in hot-water or steam results in the leaching of compounds from the bones to the water/steam due to a concentration gradient. Typically the solids leached include fat, protein, short chain peptides, amino acids and minerals. The relative amounts of these materials depends on the raw materials, degree of flesh removed from the bones, processing conditions for extraction and further processing which may involve separation and/or concentration. Addition of salts to stock is also common resulting in a higher mineral content than that which is extracted.

Ockerman and Pellegrino (1988) provide extensive data on a variety of meat extracts from different authors and this is summarised in Table 2-2. Typical solids contents for concentrated stocks are between 65-69%. Given that typical fat free solids contents from extraction processes is reported to be between 1 and 10% there is significant concentration. Powdered stocks are typically 95% solids. Comparison of different stocks should be made on a solids basis because of the variation in moisture contents. However, addition of salts to stock affects reported composition data and can make comparisons difficult.

Table 2-2 Chemical composition of natural pork, ham, meat (pork/beef) Stocks/broths naturally flavoured (Ockerman & Pellegrino, 1988)

Typical Chemical analysis	Range wet basis (g 100 g^{-1} wet basis)	Range dry basis (g 100 g^{-1} dry basis)
Total solids	65-69	
Nitrogen	8.7-9.7	13.3 – 14.0
Protein (Nitrogen × 6.25)	56-60	83 – 88
Fat	<1	<1.5
Ash	9.6-11.7	14 - 18
Salt	8.5-9.2	12 – 14.

Analysis of the data presented by Ockerman & Pellegrino (1988) reveals that stock is comprised mostly of protein, typically 80-90% of the solids. Fat levels vary depending on how much fat is skimmed off but typical values are 1% of the total solids. Ash levels and salt levels vary depending on the process, material source and finally whether salts are added to the extract. Typical values for sodium chloride are 13% of the dry solids, but it can be as high as 20% of the dry solids, while the total mineral content (ash) can be up to 30% total solids for commercial meat extracts.

Table 2-3 Chemical Analysis of No. 1 meat extract (17.28% moisture and 13.21% Protein) (Ockerman & Pellegrino, 1988)

Components		% of dry weight.	N (% of total weight)
Amino acids	3-Methylhistidine	Tr	
	Alpha-alanine	1.32	
	Serine	0.1	
	Methionine	0.01	
	Isoleucine	0.08	
	Leucine	0.08	
	Histidine	0.03	
	Taurine	0.32	
	Citrulline	0.26	
	Total	2.20	0.22
Peptides	Carnosine	3.70	0.92
	Anserine	0.75	0.16
	Imadazole peptide	1.88	0.47
Guanidines	Creatine	4.80	1.54
	Creatinine	5.51	2.04
	Methylguanidine	0.1	
	Guanidine	0.1	
Purines, etc.	Hypoxanthine	1.90	0.78
	Inosine	0.70	0.15
	Inosinic acid	Tr.	
Protein (14.9% N, 0.1% Ash)		10.92	1.65
Organic acids	Lactic acid	14.60	
	Glycollic acid	0.98	
	Succinic acid	1.26	
	Beta-Hydroxybutyric acid	(<1)	
Other Compounds	Carnitine	3.3	0.29
	Choline	Tr	
	Urea	0.11	0.05
	Ammonia	0.42	0.35
Inorganic mutter (8.95% K; 7-3% $P_2 0_5$)			
	Coloring matters	18.30	4.23

Major non-volatile compounds reproduced from Ockerman & Pellegrino (1988) are presented in Table 2-3. The data shows that amino acids are not widely present as free amino acids, but rather are part of peptides such as carnosine (3.70% dry weight) or the guanidines; creatine and creatinine which are present at 4.8% and 5.5% respectively (Table 2-3). Without knowing the amino acid profile it is impossible to say what proportion of protein in the sample is gelatine. Lactic acid is also present in a highly significant quantity, up to 14.60% and will likely affect flavour. The non-volatile components do affect flavour and these are further discussed under the flavour section.

Ockerman & Pellegrino (1988) provide the amino acid composition for stocks prepared from beef and pork and this is presented in Table 2-4.

Table 2-4 Amino acid analysis of natural meat (pork/beef) stocks/broths naturally flavoured (Ockerman & Pellegrino, 1988).

Amino Acid	% of Protein(meat/stock broth)	
	Average	Variance
Alanine	10.08	0.64
Arginine	2.64	1.76
Aspartic acid	6.27	0.44
Cystiene	0.59	0.03
Glutamic acid	11.93	0.57
Glycine	20.73	1.29
Histidine	0.55	0.05
Hydroxyproline	9.59	0.22
Isoleucine	1.32	0.04
Leucine	4.11	0.10
Lysine	5.9	0.25
Methionine	0.97	0.02
Phenylalanine	2.95	0.43
Proline	11.67	0.45
Serine	2.34	0.60
Threonine	1.84	0.29
Tryptophan	0.59	0.002
Tyrosine	3.42	0.85
Valine	2.3	0.44

Glycine is the most abundant amino acid, while glutamic acid, proline, alanine and hydroxyproline are also in significant quantities. Such data is consistent with the presence of substances extracted from collagen for which glycine is the most abundant amino acid, while proline and hydroxyproline are also highly significant. According to Duerr & Earle (1974), the collagen of an extract from beef bones is determined by multiplying the hydroxyproline by 7.25. Applying this calculation to the 9.59% hydroxyproline as a percentage of the protein would indicate that about 70% of the protein is from collagen. High percentages of proline and glycine also support this. The presence of sulphur amino acids cystine and histidine show that non collagen proteins are also present.

Mineral composition is provided by Ockerman & Pellegrino (1988) (Table 2-5) and shows a high proportion of phosphorus, calcium and magnesium.

Table 2-5 Mineral composition of dried soup stock (Ockerman & Pellegrino, 1988).

Component	Beef stock	Pork stock
Fat (%)	2.2	0.4
Cholesterol (mg 100 g^{-1} fat)	362.0	194.0
Sugar (%)	0.2	0.2
Phosphorus (ppm.)	437.0	983.0
Total nitrogen (%)	15.5	15.9
Calcium (ppm.)	280.0	84.0
Sodium (%) .	0.8	0.9
Potassium (%)	0.4	0.7
Iron (ppm.)	6.6	6.6
Magnesium (ppm.)	590.0	560.0
Total solids (%)	94.5	94.9
Ash (%)	3.3	3.8
Carbohydrate	0.0	0.0

The volatile compounds for stock were investigated by Wood and Bender (1957) and are thought to be precursors for meat-like flavour. Later studies have identified and quantified the volatiles that are present and their contribution to flavour. These are discussed under the section on flavour.

2.6 Stock Attributes

Stock provides definite functionality to the final product they are used in. Visual appearance, thickness, consistency, smoothness, creaminess and flavour are included in the sensory characteristics of stock.

Colour, flavour and texture were considered as key attributes and are important in providing the sensory characteristics in stock. These are discussed individually below in order to understand the components and mechanisms that provide these attributes in stock and to try and identify optimum measures for these attributes.

2.6.1 Colour

According to Ockerman & Pellegrino (1988) colour is strongly influenced by processing conditions and a dark brown colour is seen as traditional and preferable to a lighter colour. Stock that is concentrated solely by vacuum evaporation is lighter in colour than that concentrated by a combination of vacuum and open pan evaporation.

McEvoy (2004) states that high temperature processing, such as retorting, can cause natural colours to fade or change, leaving shades of grey and brown.

The Maillard reaction contributes to the development of brown colours and changes of flavours in processed foods (Van Boekel, 2001). The Maillard reaction, often referred to as non-enzymic browning, is a complex series of chemical reactions between amino acids and reducing sugars. The rate of reaction is affected by temperature, pressure, water activity and pH. The rate of reaction is rapid at high temperatures such as those experienced in processing, but can also occur at a slower rate at lower temperatures causing significant changes in colour of products during storage and distribution.

2.6.2 Texture

Sensory descriptors such as thickness, consistency, mouth-feel and smoothness are often used to describe a product's texture. Flow properties of a fluid such as viscosity relate to these sensory descriptors and can be quantified by instrumental methods. Such properties may also be referred to as rheological properties.

According to McEvoy (2004) a great stock has a velvety viscosity when heated but sets as a gel at low temperatures. Such a texture is provided by the presence of gelatine. During extraction and processing the heating conditions aided by acids naturally present, break down the

cartilage, collagen, elastin and other connective tissues in the meat and/or bones, forming gelatine.

McEvoy (2004) also states that if stock is extracted using high temperatures and short time processing conditions poor rheological properties often result. Specific temperatures and times are not provided but the explanation for the statement is that short extraction results in a low concentration of gelatine in the extract, while high temperatures breakdown the gelatine structure of the extract resulting in poor rheological properties. Therefore other gums and starches are added to products but this creates a "rubbery," "chewy" gravy, that is undesirable and never experienced with traditional stocks (McEvoy, 2004).

Gelatine and its derivation from collagen has been extensively reviewed by several authors (Johnston-Banks, 1990; Swan and Torley, 1991 Ockerman & Hansen, 2000). Gelatines are water soluble proteins prepared from the purest collagen by processes that destroy the tertiary, secondary and to some extent, the primary structure of the native collagen.

Gelatine has many applications because of its ability to form a gel. Research into this process is summarised by Johnston-Banks (1990) showing the process involves random coiled structures forming secondary and tertiary structures of peptides and aggregating together through hydrogen bonding, in a similar fashion to that found in raw collagen.

Gelatine's properties and characteristics are provided by Johnston-Banks (1990). Gelatines are characterised by gel strength 'bloom', viscosity of solution, gel setting and melting temperatures. Gelatine properties vary widely and are dependent on the collagen source, method of manufacture and processing conditions.

Gel strength or bloom is measured as the force required for a probe to penetrate 4mm into a gel made with 6.66% gelatine that has been conditioned for 18 hours at 10°C (Johnston-Banks, 1990).

Setting time is strongly influenced by the high molecular weight fractions as these are associated with the initial conformations necessary for the onset of gelation (Johnston-Banks, 1990).

Melting point is related to several features, one being the proportion of low molecular weight peptides that cannot take part in the forming of the gel network (Johnston-Banks, 1990).

Gel solution viscosity is measured using a 6.66% solution at 60°C for characterisation. Johnston-Banks (1990) state that at most temperatures gelatine acts as a Newtonian fluid, but

just above the gel setting temperature the viscosity becomes markedly time dependant owing to the degree of aggregation taking place. The Newtonian behaviour is confirmed by Marcotte *et al,* (2001) who found Newtonian behaviour for 2, 3 and 4% gelatine solutions at 20, 40, 60 and 80°C. As the temperature of the solution increases, viscosity decreases. An equation for the temperature and concentration dependency of viscosity for gelatine solutions was presented by Croome (1953) who determined a straight line relationship between log viscosity and the inverse of absolute temperature in the temperature range of 40°C to 65°C for 4, 5 and 6% gelatine solutions.

At low temperatures viscosity will increase markedly with time if aggregation occurs. While at very high temperatures thermal degradation of the peptide chains could cause further decrease in viscosity (Marcotte, et al., 2001)

Holding a gelatine solution at high temperature markedly decreases its viscosity over time. Johnston-Banks (1990) demonstrates a 15-45% decrease (depending on pH) in solution viscosity over a 15 hour period for a 6.66% solution held at 60°C. The rate of viscosity decrease is very rapid between 0-5 hours, but is considerably less after 15 hours.

Increasing the concentration of gelatine is reported to cause an exponential increase in gelatine solution viscosity (Johnston-Banks, 1990).

The effect of pH on viscosity of gelatine solution was also considered by Johnston-Banks (1990). The solution viscosity was found to vary with pH although this was not as noticeable at higher gelatine concentrations and with the addition of sodium chloride, i.e. increased ionic strength. The viscosity is always at a minimum at the iso-electric point, and increases either side of this pH as the overall charge on the molecule becomes more positive or negative up to some minimum and maximum pH at which it starts to decrease.

Every sample of gelatine has unique properties depending on its origin and processing conditions. Gelatine solutions will degrade when subjected to heat and extremes of pH Johnston-Banks (1990) hence raw material and processing conditions will affect the properties of the manufactured gelatine. Extremes of pH are used for processing collagen into gelatine. Acid hydrolysis is a milder treatment and tends to break the cross links between the chains; the peptide bonds are attacked less often. In contrast alkaline hydrolysis tends to cleave the peptide bonds rather than selecting the chain cross links.

2.6.3 Flavour

The flavour of meat and extracts derived from meat results from complex heat induced chemical reactions. Raw meat has a blood like taste and a weak odour (Gasser & Grosch, 1988). The characteristic flavour of meat develops during heating and arises from different volatile and non-volatile flavours. Compounds that are said to be precursors to the flavour development of meat due to cooking are widely reported.

Studies of the volatiles and non-volatiles are often reported separately in the literature for meat, meat broth, and meat bouillon flavour.

In a review of numerous studies Farmer and Patterson (1991) state that odour is generally caused by low molecular weight volatile compounds, while taste substances are usually larger and water soluble, although the role of larger compounds in meat flavour seems to be a point of contention amongst researchers. Farmer and Patterson (1991) also discuss a further class of compounds described as flavour enhancers that do not necessarily possess a taste or an aroma themselves, but enhance the flavour of other compounds.

The development of desirable characteristic flavour compounds in stock is a function of the Maillard reaction (Varnam & Sutherland, 1995). Mottram (1998) also identifies the Maillard reaction as being responsible for most of the cooked flavours in meat, i.e., the roasted, boiled, and savoury flavours. Pentoses, in particular ribose, and the sulphur containing amino acid cysteine are important precursors for the flavours in cooked meat. Furanthiols and furan sulphides are very important compounds with exceptionally low odour threshold values, which are responsible for characteristic meaty aromas.

Cooking methods and temperatures have an important effect on the formation and stability of both volatile and non-volatile compounds and consequently on meaty flavour. For example, the formation of Maillard reaction products is enhanced at higher cooking temperatures but also increases the rate of protein and fat oxidation (Imafidon & Spanier, 1994).

Wasserman (1972) describes the chemical changes that occur as a result of heating meat. Protein degradation begins with temperatures as low as 30°C, and small fragments may be split off some proteins. Between 35 and 50°C actomyosin fibres unfold, increasing the number of imidazolium groups, which results in a pH increase from 5.5 to about 6.0. As a result of the protein unfolding the number of –SH groups increases. Most proteins are coagulated between 55 and 85°C. The –SH groups are oxidised to disulfide bonds above 80°C, and at temperatures above 90°C hydrogen sulphide is released from the –SH groups of the myofibrillar protein.

Browning reactions begin at 90°C and increase with time and temperature. The amount of browning depends on the glucose content in the meat. On exposure to dry heat, evaporation of water from the surface of the meat concentrates tissue constituents, creating conditions that are more favourable for the browning reaction (Pedenko, et al., 1980).

2.6.3.1 Aroma Compounds

Wood and Bender (1957) carried out a preliminary examination of the flavour of meat extract and identified the volatile compounds present in beef extract (Table 2-6). Large peaks were found for acetylaldehyde, hydrogen sulphide and methyl mercaptan. However, the compounds were not quantified and no work was carried out to determine the sensory threshold for any of the compounds. Over 1,000 aroma compounds are produced during the thermal treatment of meat (Imafidon & Spanier, 1994).

Table 2-6 Composition of volatile components of beef extract (Wood & Bender, 1957)

Component	Peak
Hydrogen sulphide	Large
Methyl mercaptan	Large
Ethyl mercaptan	Small
Dimethyl sulphide	Small
Acetaldehyde	Large
Propionaldehyde	Small
Isobutyraldehyde	Small
Acetone	Medium
Isoaleraldehyde	Small
Methyl ethyl ketone	Small
Methonal	Small and only in some samples
Ethanol	Small and only in some samples

Research has been conducted in order to determine which of these compounds contribute significantly to the flavour of meat (Wasserman, 1972; Pedenko, et al., 1980; Farmer & Patterson, 1991; Cerny & Grosch, 1992, 1993; Guth & Grosch, 1994). One technique used to determine which of the compounds significantly contribute to flavour is the extract dilution analysis (EDA) as used by Cerny and Grosch (1992). Flavour compounds of cooked meat or broth are extracted with a solvent and analysed by high resolution gas chromatography-olfactometry also described as sniff port analysis. Gas Chromatography separates the compounds and the odour is sniffed by an observer who can describe the odour. The

separated compounds can also be identified by further analytical techniques. The extract is diluted in a stepwise fashion to determine the dilution at which the flavours could not be detected. In order to quantify the potency of the compound a factor referred to as the FD factor is calculated as the highest dilution at which the substance can be smelled. For example a dilute value of 20 means that 1 volume of the initial substance was diluted by 19 volumes of diethyl ether. Following the identification with flavour dilution analysis, models with pure compounds can be constructed. Once a model odour has been established omission experiments can be carried out, to determine which of the compounds contribute to aroma (Guth & Grosch, 1994).

Gasser and Grosch (1988) found that 40 compounds were highly significant to the flavour of cooked beef (boiled) which was defined by an FD factor of 4 or greater. Seventeen compounds were found to have FD factors in the range 64-512, 15 of which were identified. Two of the compounds 2-methyl-3-furanthiol and bis-(2-methyl-3-furyl) disulphide where characterised as having a meat like flavour.

The same research group also studied roasted beef flavour (Cerny & Grosch, 1992) and identified 22 out of 25 compounds that were significant to the aroma but these did not include the two compounds that were identified in boiled cooked beef.

Guth & Grosch (1994) studied the odour of stewed beef juice that was roasted for 10 minutes followed by stewing for 4 hours at 200°C. Extract dilution analysis was used to identify significant compounds and model flavour systems were developed based on these results. It was found that the odour of meat could be successfully reproduced with 12 compounds at the levels identified by extract dilution analysis added to a gelatine solution. It was therefore concluded that 12 compounds contributed to the aroma of stewed beef juice.

Farmer & Patterson (1991) studied the volatiles of cooked meats by the method of Gasser & Grosch (1988) and found in addition to Bis-(2-methyl-3-furyl), four other compounds significantly present in heart tissue but only present in trace amounts in semimembranosus and psoas major cuts of beef.

A summary of these important aroma compounds as shown by Farmer (1994) is presented in Table 2-7 with descriptors of the compounds, possible precursors and reaction mechanisms.

Table 2-7 Important aroma compounds in cooked beef (Farmer, 1994)

Compound	Odour	Precursor(s)	Mechanism
Trans-2-nonenal*	Tallow, fatty	n-6 Fatty acids	Thermal Oxidation
Trans-trans-2,4-decadienal*	Fatty, fried potato	n-6 Fatty acids	Thermal Oxidation
1-Octen-3-one*	Mushrooms	n-6 Fatty acids	Thermal Oxidation
2-Acetyl-1-pyrroline*	Roasty, sweet	Proline	Mallaird reaction
Methional*	Cooked potaotoe	Methionine	Strecker degradation
Phenyl acetaldehyde*	Honey-like sweet	Phenylalanine	Strecker degradation
2-Methyl-3-furanthiol*	Meat-like, sweet, sulphurous	Cystine and ribose or Thiamin	Maillard Reaction or thermal degradation
Bis-2-methyl-3-furyl disulphide*+	Meat-like, oxo	Cystine and ribose or Thiamin	Maillard Reaction or thermal degradation
2 Methyl-3-fyrul 2-furfuryl disulphide++	Roasted, meat like		
β-Ionone*	Violet-like	β-Carotene	Oxidative degradation

*Gasser & Grosch (1988), +Grosch & Schieberle (1991), ++ Farmer & Patterson (1991)

While the reactions for flavour are complex there are two identified by Farmer (1994) as being important; the Maillard reaction and the oxidation of lipids during heating. The Maillard reaction between amino acids (peptides) and reducing sugars is a complex series of reactions which yields high molecular weight brown coloured products and volatile aroma compounds (Farmer, 1994).

Lipids break down via oxidation of the fatty acids to give volatile compounds which contribute to both desirable and undesirable flavours (Farmer, 1994). It was identified that some of these compounds were created by the use of cooking oil in the roasting process.

It may be argued that separation of fat will remove the precursors for the development of flavour compounds from oxidation of fat compounds. However, roasting and processing prior to extraction will enable the conversion of precursors into flavour compounds which then may be extracted from the roasted meat/bones and may or may not be removed during the fat separation process. Therefore these flavour compounds may be present after a fat removal process.

2.6.3.2 Non-volatile compounds

Warendorf & Belitz (1992) and Warendorf et al. (1992) studied the non-volatile flavour of bouillon prepared according to a recipe for double consommé from 500 g of beef. Quantitative analysis of bouillon by gel permeation chromatography and reverse-phase-HPLC and sensorial analysis was carried out on non-volatiles present to establish taste qualities and thresholds. It was found that many non-volatiles were present above their threshold. Free glutamic acid and 5'-inosine monophosphate in combination with some sour and salty components were demonstrated to be the most important flavours. In addition the contribution of gelatine to the overall impression was significant. Concentrations of glutamic acid and 5'-inosine monophosphate were found to be lower in commercial bouillon.

Kono *et al.* (2005) compared the flavours of 14 plain Chinese bouillons and 14 plain Japanese bouillons. Significant differences were seen in the quantities of flavour compounds such as glutamic acid, taurine, and potassium between Chinese and Japanese bouillons. Principal component analysis showed that the 3 stock samples fell into 3 distinct groups. Discriminate analysis then confirmed that the 3 groups were discriminated on the basis of the flavour component analysis, especially aspartame, glutamine, methionine, phenylalanine, histidine and calcium. The 3 groups of stocks were also discriminated by their aroma sensory patterns. Results indicated that Chinese chicken bouillon and Japanese chicken bouillon differed to some extent in respect of flavour and aroma although both were made from similar materials. It is suggested that Chinese and Japanese people differ in their preference for flavour and aroma.

Cambero *et al* (2000) studied the development of beef broth flavour. Variables included the ratio of extract liquid to meat, sodium chloride concentration in the extraction solution, meat size and cooking temperature and time. Flavour was measured by sensory using descriptive profile analysis, rank order test and triangular differentiation test. It was concluded that the best meat broth flavour was obtained by heating minced meat in a 7.5 g L^{-1} solution of sodium chloride solution (1:2, w/v) at 85°C for 60 minutes. It was concluded that accurately determining the heat treatment was important and that the temperature plays a more important role than cooking time.

Cambero *et al* (2000) reports that differences in flavours development in meat products are mainly due to different cooking temperatures and water content of the meat. The flavour of boiled meat produced in the presence of water at temperatures around 100°C or below is different to the flavours produced by roasting which are generated at temperatures over 100°C in relatively dry conditions. Wasserman (1972) makes the observation that when meat

is roasted at a temperature of about 190°C the interior temperature varies from around 60°C to 80°C depending on the intensity of cooking. The temperature at the surface was not reported, but this would remain at the wet bulb temperature until the moisture diffusing to the surface of the meat cannot replace the moisture that is being removed at the surface. Then the surface temperature would rise above 100°C and the roasting flavours will develop. Therefore, the flavour of roasted meat is essentially derived from the surface.

2.7 Manufacturing process for stock

Stock is produced commercially on a large scale and supplied to consumers and the food service industry. Some chefs prefer to make their own stock because of particular quality requirements.

The common basic process for the manufacture of stock involves (1) extraction of material from meat and/or bones, (2) separation and filtering of unwanted components followed by (3) concentration processes. If the final form is to be a dry product then a drying step is also necessary.

2.7.1 Chefs' process

The principles used by chefs are outlined by Corriher (1997)and McEvoy (2004) and discussed below.

According to McEvoy (2004) the extraction process is started with a cold liquid. Starting the extraction process with boiling water would save time, however, the heat would cause blood and other compounds to coagulate within the bones, sealing in valuable compounds rather than extracting them. Corriher (1997) also suggests starting the extraction with cold water but in his reasoning it was done to maximise the extraction of flavour.

Corriher (1997) suggested using a narrow tall pot to hold a lot of bones while minimising the surface area of the simmering liquid. The advantage is that you do not have to constantly replace evaporated water.

According to McEvoy (2004) gentle convection simmering rather than boiling is preferred to allow fat to float to the top enabling complete separation. Low temperature simmering creates gentle convection currents that keep small particles suspended; preventing the scorching that would occur if they were to settle to the bottom. Additionally many heat-driven reactions are prevented or reduced with the use of low temperature.

Natural clarification is used by skimming impurities from the surface continuously during cooking. Continuous skimming removes fats and other compounds that may burn, create off flavours and poor texture. McEvoy (2004) suggests that it is better to use naturally occurring albumin and other proteins along with gentle convection currents to clarify the stock and suggests this yields a far clearer and better tasting product than filtering the liquid.

The chefs process is time consuming and labour intensive.

2.7.2 Industrial process

Industrial processes for the manufacture of stock are discussed by numerous authors (Mehl & Seebeck, 1978; Ochi, 1981; Ockerman & Pellegrino, 1988; Varnam & Sutherland, 1995; Ockerman & Hansen, 2000). A process flow diagram for the manufacture of bone extracts (Ochi, 1981) is given in Figure 2-1. Industrial processes tend to produce lower quality stock but they are more efficient.

In order to make high quality stock fresh bones should be used for the manufacture of a quality stock (Ochi, 1981).

Previous meat extraction studies have focused on combinations of specific temperature and time combinations and meat/bone to water ratios (Duerr & Earle, 1974; Ochi, 1981; Ockerman & Pellegrino, 1988; Mikkelsen, 1996). The data seems largely empirical and shows that the solids non-fat extracted from bones increases with temperature and time up to a maximum of 10 to 12 g per 100 g of bones. Duer and Earle (1974) characterised the end of the extraction process by measuring nitrogen, collagen and non-protein nitrogen and deriving the non-collagen proteins. Other authors simply measure total solids.

Some studies provide an evolution of solids extracted over an extraction period. A study reported by Ockerman and Pellegrino (1988) provides a time series of cooking bones in 1:1 ratio with water. No temperature is reported. This showed an increase in yield over an 8 hour period of 3% although it is not clear what that yield represents. Their graph indicates that equilibrium has not been achieved after 8 hours. Mickelson (1996) also provides a time series for the evolution of solids from bones boiled for up to 30 hours. The graph of solids versus boiling time indicates that the rate of solids extracted had slowed after 10 hours but did not show a levelling off even up to 30 hours as would be expected in an equilibrium process. Ockerman and Pellegrino (1988) provide solids data for 100 kg of bones cooked in three times their weight water. The bones are removed and replaced with fresh bones every 30 minutes for 6 cycles i.e. 6,000 kg of bones were used and this yielded a solution of 1% solids and

38.5 kg of solids or 0.64 kg per 100 kg of bones. This seems very dilute and is low yielding for the bones.

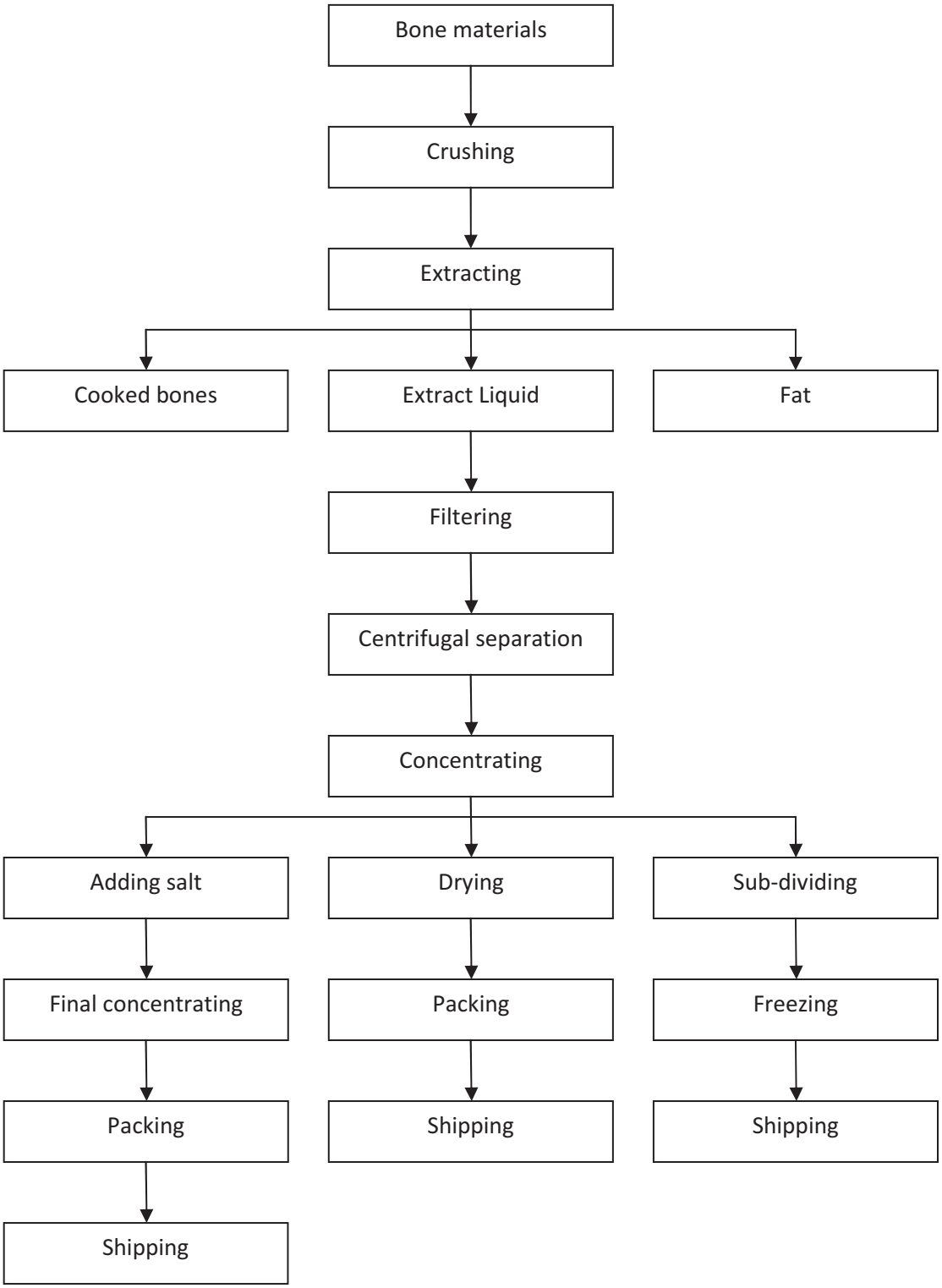

Figure 2-1 Process for manufacturing bone extracts (Ochi, 1981)

Smaller sized solid particles allow more rapid diffusion of solution through the particles and generally have a higher surface area to volume ratio, thus increasing the rate at which solution moves from the surface to the bulk phase. Therefore smaller particles give a greater rate of extraction. Mikkelsen (1996) used cow bones and found that cutting into pieces to less than 50 mm thick resulted in a faster rate of extraction than whole cow leg bones (about 200 mm long), but that going from a size of 20-50 mm down to 5-10 mm made little difference. There is also a limit to size reduction which is determined by the ability of equipment to separate the un-dissolved solids from the liquid phase.

Reported industrial extraction processes use hot water and in some cases steam. Prior to extraction bones may be reduced in size in order to aid the extraction. The temperature, time of extraction and ratio of water to bones are key process variables for extraction. Duer and Earle (1974) used a 1 hour extraction time for bones in a 1:1 ratio with water found that as the temperature of extraction was increased from 50°C to 125°C the solids extracted increased from 1 kg per 100 kg of bones to 5 kg per 100 kg of bones. They also found the amount of collagen increased substantially when the temperature was above 100°C.

Increasing the water to bones ratio increased the total solids removed from the bones but results in a more dilute solution (Ockerman & Pellegrino, 1988).

Three alternative processes of extraction presented by Ochi (1981) are compared in Table 2-8 and demonstrate that higher yields are achieved at higher temperatures, but colour and flavour is compromised, particularly with temperatures above 143°C. The best flavoured stocks are produced by hot water extraction, but these are the most expensive.

Table 2-8 Alternative extraction processes (Ochi, 1981)

Parameter	Steam and high pressure extraction	Water and high pressure extraction	Hot water Extraction
Processing time (hours)	2	1.5-2	20-40
Pressure (MPa)	0.59	0.39	
Temperature (°C)	158	143	90-100
Extract yield per 100 kg of bones	43.3	66.67	167
Solids content of extract kg 100 kg^{-1}	20	10	5
Solids yield per 100kg of bones	8.6	6.7	8.3
Water removal required for 100 kg of extract at 60% solids	200 L	500 L	1100 L
Cost	Lowest		Highest
Flavour	Can be bitter		Best
Colour	Can be too dark		

From the studies presented in the data none indicate that the maximum amount of extractable material had been achieved, and none quantified the maximum amount of material that can be extracted from the bones. Other authors provided analysis of the extract at the end point of extraction (Duerr & Earle, 1974). Extraction time series data to provide some idea of the extraction kinetics were found (Mikklesen, 1996; Ockerman & Pellegrino, 1988) but for limited conditions. Such can provide an idea of how long an extraction process needs to be to ensure an efficient process. Fundamental extraction kinetics are based on equilibrium theory in which the extraction process is described as an equilibrium between the solvent and the solute (Earle, 1966). No published equilibrium curve for any of the components of meat or bone extract was found. Likely the reason for this would be the expensive analysis for each component.

Prior to concentration bones are taken out of the extract and the fat is removed by skimming or centrifuging. For skimming, stock is kept at 98°C for 15 minutes to allow the fat to rise to the surface. The remaining liquid is gravity filtered at 82°C to remove suspended solids (Ockerman & Pellegrino, 1988).

The filtrate is transferred to a refining tank and boiled for 1 hour in order to coagulate various components that are removed by skimming and additional filtration. This is essential to ensure that the reconstituted stock is a clear solution. If the stock must be held before processing equipment becomes available, it is usually maintained at 95°C. In the coagulation tank the pressure is raised to 241 kPa and the temperature to 135°C, which requires 10-15 minutes come up time. Once the temperature is reached it is maintained for 6-8 minutes. The pressure is then released and the stock is transferred to a flash tank where it is boiled for 15 minutes. The product is allowed to settle and the fat is skimmed off. The stock is filtered again at a minimum temperature of 80°C. The filtered stock is transferred to holding tanks held at 71°C until it can be transferred to the evaporator (Ockerman & Pellegrino, 1988).

The most extensive report of the industrial evaporation process for meat extracts is provided by Ockerman and Pellegrino (1988). The description is somewhat confusing and the writing appears repetitive. The best interpretation of it is presented here. It appears that concentration involves several steps of evaporation. From the initial solids content which is not clear the extract is concentrated to about 50% total solids using vacuum evaporation. Conditions for the evaporator are 75 to 88 kPa vacuum corresponding to an evaporation temperature of 50-65.5°C. In a typical evaporator this is achieved in 5-6 hours. The authors refer to a continuous single effect evaporator (e.g. Buflovac) as being state of the art for the

operation. Given the long residence time this would suggest re-circulation, but this is not clear.

After concentration to 50% solids the stock is sterilised by boiling at 103°C or put through a continuous steriliser with a discharge temperature of 102.8°C. The stock can then be placed into a helical coil pre-concentrator or an open pan. A helical coil pre-concentrator is described as troughs with coils filled with water at 65°C that rotate at 6-7 rpm until the stock reaches 78% solids. It is suggested that this takes 7 to 14 hours.

Open pan evaporation uses a large pan which is heated with low pressure steam to maintain a stock temperature between 61-65.5°C. The open pans generally contain paddles that rotate at 12 rpm. The stock reaches a final concentration of 84% solids.

A third option is to concentrate using a vacuum evaporator operated at 70-75°C, but further details of this are lacking.

In summary it appears that traditional processes like open pans use very long processing times at high temperatures. It would seem that a faster rate of evaporation and the use of lower temperatures is desirable for a quality product. The effects of a high viscosity on vacuum evaporation are not commented on, but this may reduce the evaporation rate. Also of concern is the colour development which is covered by Ockerman & Pellegrino (1988) who point out that concentration entirely under vacuum results in stock of a lighter colour than stock concentrated with open pan evaporation. This is probably due to the shorter processing times.

Ockerman & Pellegrino (1988) also refer to two patents for continuous processing of bones. (US patent No. 3,368,906 (Coffin & Hockenburg), and 3,368,907 (Miller).

Coffin & Hockenburg's patent breaks the bones, then feeds them into a pressure chamber at a ratio of water to bones of 0.5-1.5. The bones are extracted for 5-30 minutes at temperatures ranging from 135°C to 163°C at a pressure that prevents the water from boiling. In this pressure cooker the water flows in the opposite direction to the bones and the bones are fed into a second pressure compartment. In the second compartment, the bones (liquid to bone weight of 1.5:3.5) are cooked in the stock liquid at a temperature of 135-163°C at a pressure which prevents the liquid from boiling. The stock is concentrated to over 60% solids and 9% salt is added to stabilise the product.

Miller (1968) feeds the bones into a container where the bones are heated in sufficient water to cover for approximately 15 minutes at 99°C. The fat is skimmed off, and then the bones are

placed under pressure (345kPa) and the mixture is heated to approximately 149°C for 30-45 minutes. The pressure is then released, the stock removed and fresh water (4-5 parts water to 1 part bone) is added to the remaining bones, which are heated for approximately 30-60 minutes at a temperature of 93-99°C and then the liquid stock is separated from the bones.

In both cases of continuous extraction, the liquid is later concentrated either by pan and/or vacuum evaporation.

2.8 Conclusion

The manufacturing process for stock includes the extraction of the desired components from bones, meat and vegetables with water or steam, clarification of the resulting liquid, concentration of the liquid, thermal treatments of the stock followed by filling and packing.

Extraction methods appear to vary, be empirically based and lack optimisation based on kinetic data. Concentration and preservation process appear to utilise thermal processing methods and while specific processes are described, many details are lacking.

Key attributes of stock include texture, colour and flavour. The texture or thickness of stock is largely due to proteins derived from the collagen found in the raw materials. The characteristic brown colour is attributed to the Maillard browning reaction a complex reaction influenced by processing conditions. The flavour of stock is very complex involving volatile and non-volatile compounds that are developed from precursors with the elevated temperatures of processing.

It is evident that there is a large amount of information on the composition and flavour of stock, but little in the way of specific, quantifiable data that could be used for the development of a process to produce beef stock. There is therefore the need to produce data that could be firstly used to modify the existing Essential Cuisine process to enable the company to increase throughput 10 fold without deleteriously affecting the physico- chemical properties of the stock. Secondly be used to predict the consequences to the physico chemical properties of any changes to the extraction sequence, extraction time and temperature of any proposed process.

3 Documentation of current process and characterisation of the current products

The purpose of this Section is to establish the scientific data linked with the current commercial process for Essential Cuisine (EC) beef stock and characterise the product currently produced with instrumental as well as sensory measurements.

3.1 Methods and Materials

3.1.1 Evaluation of current commercial beef stocks

A final year student at Massey University was assigned a project supervised by the author to compare EC beef stock with others on the New Zealand Market, namely Signature Range Beef Stock and Campbell's Beef Stock. The stocks were evaluated for solids, Brix, pH and viscosity as well as sensory characteristics by a trained sensory panel.

3.1.2 Documentation of current process

In order to determine and document the current process a visit was made to the premises of Essential Cuisine to view the process and meet with the company owner and processing staff. The process was then described using a process flow diagram.

3.1.3 Characterisation of stock

Five batches of liquid beef stock were provided by Essential Cuisine with best before dates (BB) of 22/9/2007, 1/10/2007, 5/10/2007, 8/10/2007, 10/10/2007. All stock was manufactured by Essential Cuisine as part of commercial production. The date of production is 4 months before the best before dates. Samples were transported to Palmerston North by refrigerated truck and stored at 4°C before being analysed within 2 weeks of receipt.

A portion of the samples were combined in order to establish the relationships between solids and Brix and solids and density. Samples of different solids level were prepared by either concentrating the combined solution to different solids levels using a rotary evaporator or by diluting the sample with water.

A roto-vacuum evaporator Buchi Rotovapor R-215 with a Buchi V850 vacuum controller and a Buchi B-491 heating bath was used with the following procedure. 250 mL of Essential Cuisine stock was placed into a 1 L flask that was attached to the vacuum evaporator. The flask was heated by partial submersion in a water bath operating at 60°C. The vacuum for the evaporator was maintained using a high flow of cold water through a venture ejector. Cooling of the condenser was achieved by a low flowrate of cold water. The sample flask was rotated

during the operation between 50 and 120 rpm. The sample was heated by the water bath and allowed to boil under vacuum for 10-20 minutes to give 30-45°Brix solutions.

Samples were diluted by adding a known amount of distilled water at room temperature. Samples were mixed and allowed to stand at room temperature for 2 hours prior to any measurements.

3.1.3.1 Soluble Solids (°Brix)

The soluble solids (°Brix) were determined using a hand held Otago PAL-1 refractometer (0-53°Brix) that was calibrated with distilled water. Five measurements were taken for each sample.

3.1.3.2 Solids content

Solids content were determined using a gravimetric method with an air oven at 108 ± 2°C (AOAC 930.15). Aluminium moisture dishes were dried and then weighed at room temperature. Then 3-6 g of sample was placed into the dishes and weighed.

Samples were transferred to an air oven at 108 ± 2°C and dried to a constant weight. On completion of drying, dishes were cooled to room temperature inside desiccators held at 0% relative humidity with sodium silicate, and then weighed. Dishes were then transferred back to the air oven and the cycle repeated until the weight became constant. The % weight loss of for each dish was calculated as the moisture content from which the solids content could be calculated. Triplicate measurements were made for each sample and the standard error was less than 0.2%.

3.1.3.3 Density

Density was determined by using a density bottle or a measuring cylinder of known volume and weighing the sample. A 25 mL bottle was used, although a 10 mL measuring cylinder was used for the high concentration stock that has a high viscosity making it difficult to fill the 25 mL bottle. Measurements were carried out in triplicate. The method was calibrated by measuring the density of distilled water at 20°C. It was found to be 998.2 ± 0.7 kg m^{-3} which is in agreement with the value of 998.0 kg m^{-3} given by Cooper and LeFerve (1969).

3.1.3.4 pH

The pH of solution was determined at room temperature using an Orion SA520 pH meter (Thermo Scientific). The meter was calibrated with standard buffer solutions (pH 7 and pH 4).

3.1.3.5 Colour

Colour was determined with a Konica Minolta colourimeter CM-2600d. The colourimeter is fitted with an illuminate C light source. Colour was determined through a clear Petri dish. The sample depth was 20 mm, and was held in the petri dish by a steel 50 mm pipe. Measurements were carried out at room temperature with samples that had been equilibrated to room temperature. Parameters L*, a* and b* values were determined.

3.1.3.6 Rheological determination

3.1.3.6.1 Equipment

The rheometer used was a Paar Physica MCR 301, a computerised rotational controlled shear stress rheometer serial number 876728 (Physica Messtechnik, GmbH, Stuuttgart). Temperature control was performed through an in-built Peltier system attached to an Anton Paar Viscotherm T2 water bath. The spindle geometry used was a cup and bob (CC27-SN6298 measuring system) supplied with the equipment requiring 20 mL of sample.

3.1.3.6.2 Determination of reliable range for the rheometer

Experience in the Institute of Food Nutrition and Human Health, Massey University shows that the reliable range of controlled stress rheometers is often much smaller than claimed by the manufacturers (Trinh et al, 2005). Thus to avoid artefacts introduced by the rheometer, which are all too often wrongly interpreted as evidence of new exciting physical behaviours of the sample measured, it was necessary to determine carefully the reliable range of speed (shear rate) and torque (shear stress) associated with the MCR 301.

The principle of the method used by Trinh et al. (2005) is to measure the flow curve of a fluid with known Newtonian behaviour. A plot of viscosity against shear rate or shear stress must therefore be a flat horizontal line. Any departure from this line represents a potential problem.

An example is shown in Figure 3-1 for a mineral oil of viscosity 7.03 cP at 50°C. The three replicates runs made by the author in 2007 do not coincide well below a shear rate of 10 s^{-1} but otherwise show remarkable agreement at higher shear rates. This does not mean however that the data reported by the rheometer at shear rates above 100 s^{-1} is correct since the viscosity of a Newtonian fluid needs to be constant. Thus in this case reproducibility alone is no guarantee of correctness.

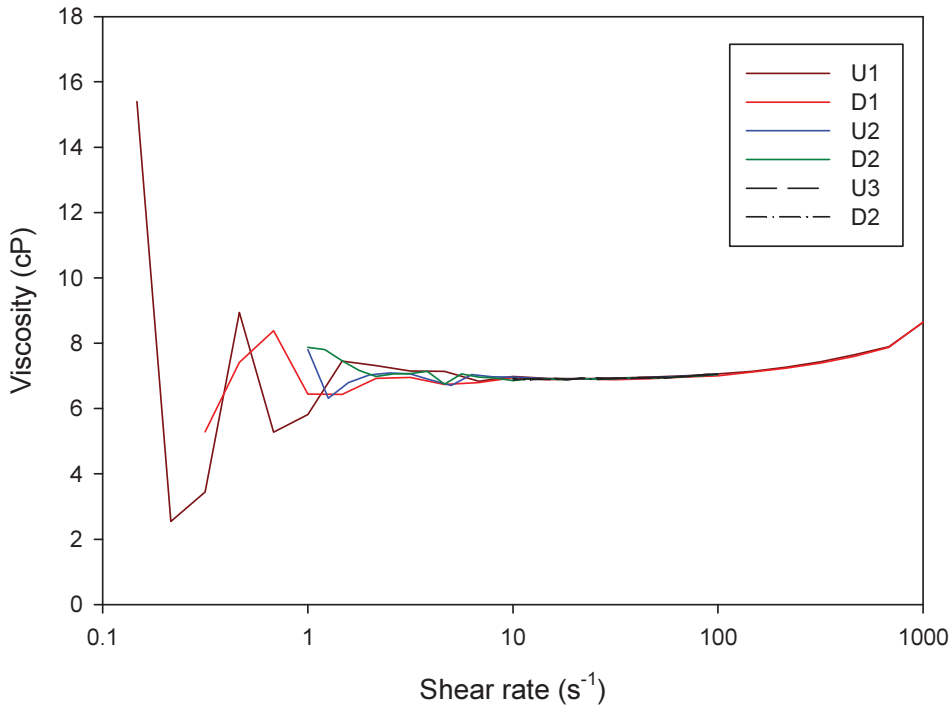

Figure 3-1 Viscosity curves for mineral oil at 50°C, 3 runs of shearing Up (U) and shearing Down (D).

The data from these three replicate runs is averaged and re-plotted as departure from its stable Newtonian viscosity in Figure 3-2.

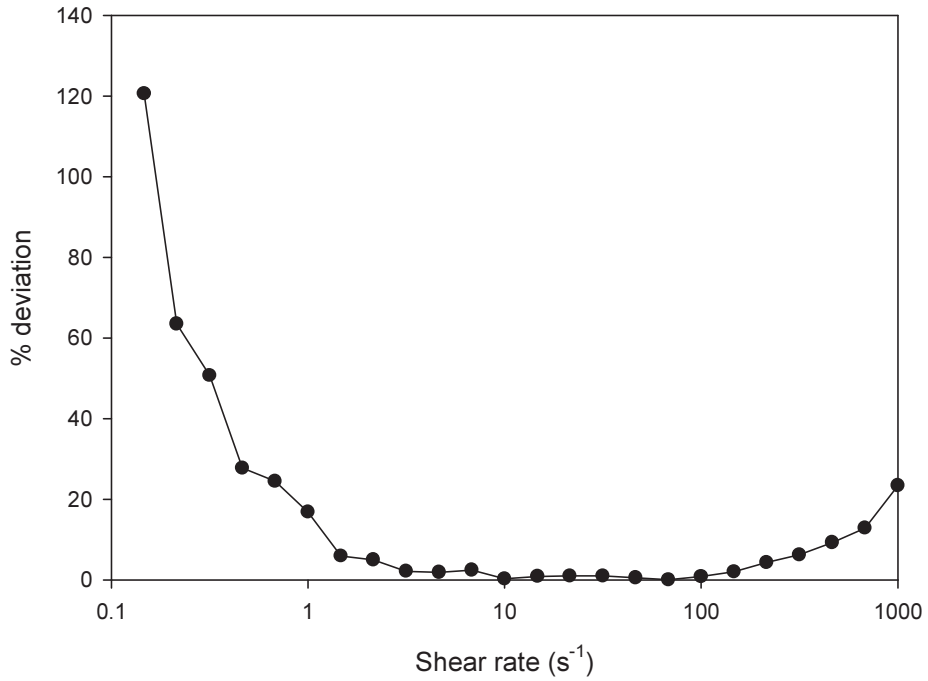

Figure 3-2 Deviation from true viscosity as a function of shear rate for mineral oil at 50°C

As discussed in greater detail by Trinh et al. (2005) at low shear rates the rheometer wrongly reported a shear-dependent viscosity for this Newtonian oil. At higher shear rate, the reported increase in viscosity can be attributed to the energy consumed by eddies, particularly Taylor vortices. This extra energy is wrongly interpreted by the rheometer as an increase in viscosity. Thus this data indicates that for this viscosity the range of reliable shear rate of the MCR301 is only 3-100 s^{-1}.

A more complete mapping of the reliable range of shear rates for this rheometer was later made by several fourth year students using standard cannon oils and sugar solutions in projects co-supervised by the author and his supervisor (Figure 3-3)

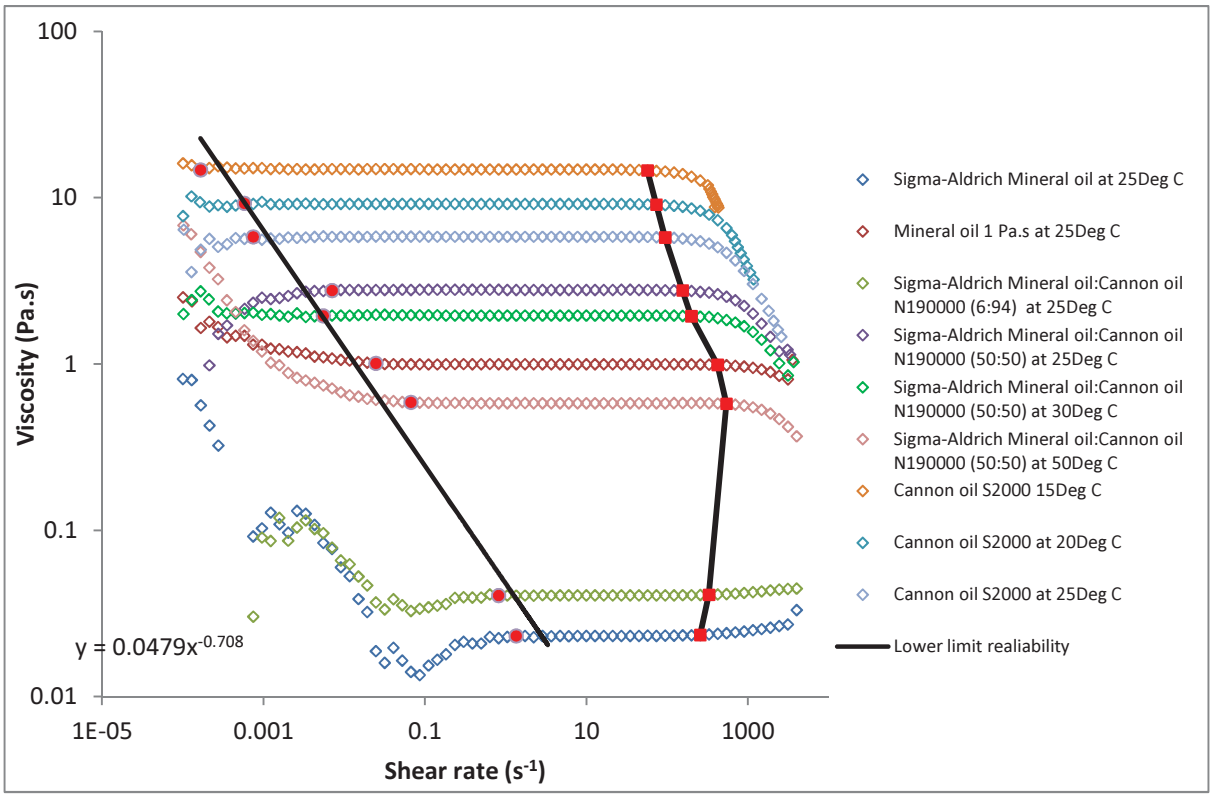

Figure 3-3 Range of reliable shear rates for the MCR 301 Paar-Physica (Lim, 2012)

It is also necessary to determine the minimum reliable torque (or shear stress) and minimum measuring time before rheological characterisation of the stock can be made reliably. For this experiment, runs were made by requesting a constant torque and reports of 100 data points taken at 1 s intervals. Torque values between 0.1 and 10 µNm were used and a plot of normalised viscosity versus time for each different torque is given in Figure 3-4. The plot shows that for a torque greater than 0.5 µNm a stable reading was achieved within 60 s, while for a torque less than 0.5 did not produce a stable reading within 60 s.

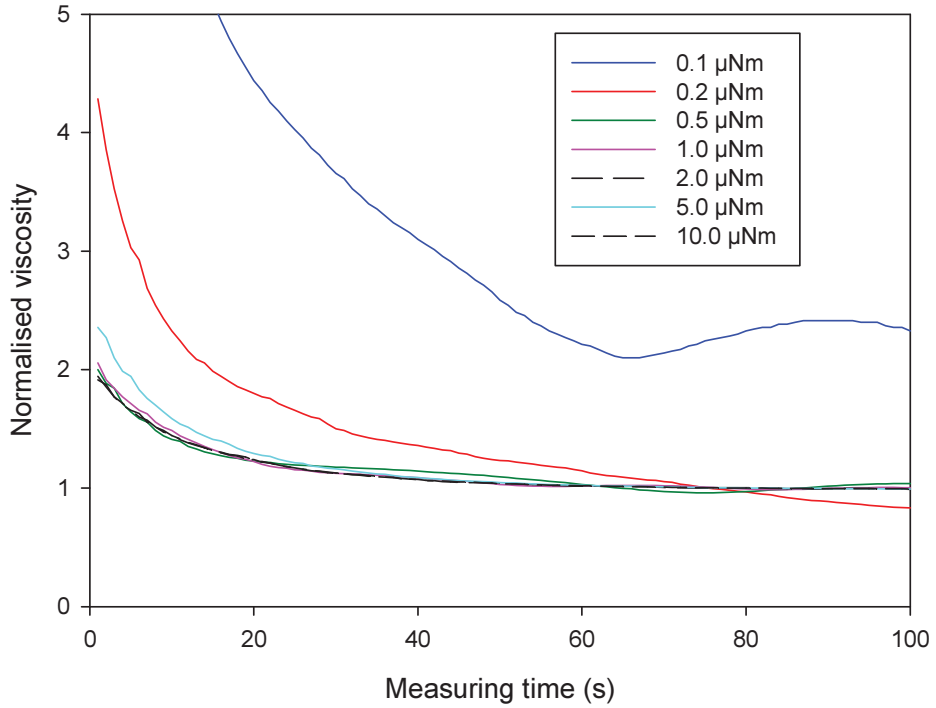

Figure 3-4 Normalised viscosity response for different torques applied to mineral oil at 50°C

The easiest way to identify an acceptable minimum torque and measuring time from this data is to calculate a coefficient of variation (COV). For the different torque settings the coefficient of variation for viscosity from the time period 60 to 100 s of the readings is plotted in Figure 3-5. The plot shows that a torque greater than 1 µNm was required to provide a COV of less than 0.01.

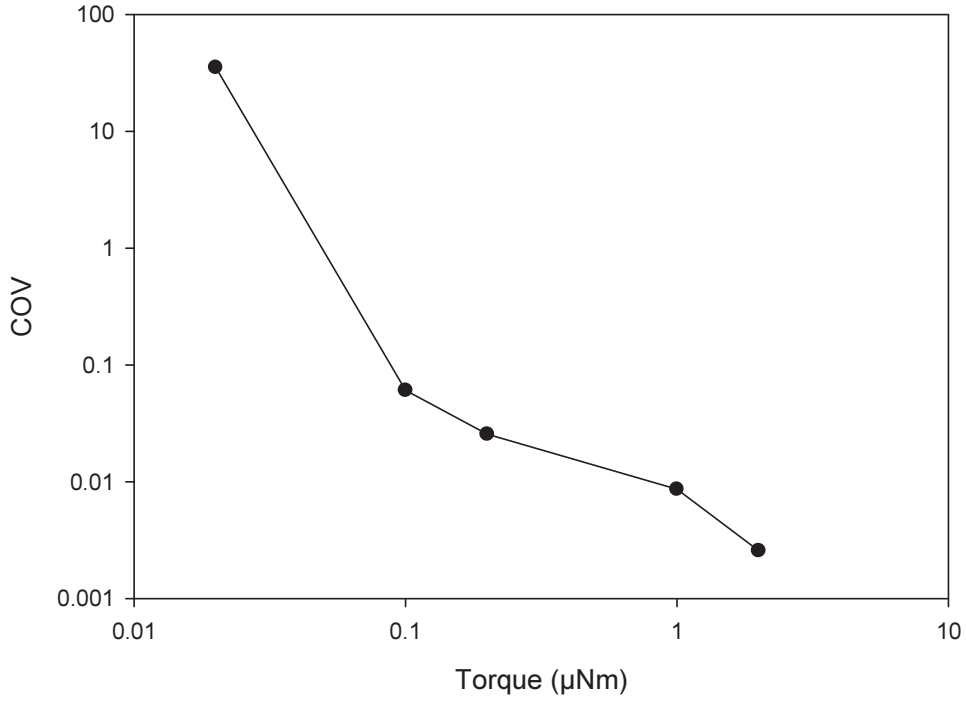

Figure 3-5 Coefficient of variation for viscosity as a function of torque for oil at 50°C

From the data it was concluded that the minimum torque of 1 µNm be specified. At a torque of 1 µNm the speed of the rheometer for mineral oil was about 2 RPM.

3.1.3.6.3 Procedure for the rheological measurement for stock

The rheometer was used in controlled shear rate mode and a shear sweep was performed for shear rates between 2 and 120 s^{-1}, by shearing up for 200 s, holding at 120 s^{-1} for 15 s and then shearing down for 200 s. Measurements were recorded at 5 s intervals. The reason for shear up and down was the expectation that the gelatine would make the stock time dependent and it was important to have a record of the hysteresis loop area.

Shear sweeps were performed for each batch of stock at measurement temperatures of 20, 30, 40, 50 and 60°C.

The following Hershel-Bulkley model was fitted for each of the shearing up and shearing down legs of the sweep

$$\tau = y_0 + K\dot{\gamma}^n \quad (3.1)$$

where τ is shear stress (Pa), y_0 is the yield stress (Pa) or the stress required to cause the liquid to flow, and $\dot{\gamma}$ is the shear rate (s^{-1}). K is the consistency coefficient (Pa s^n) and is an indication

of how thick the sample is, while *n* is the flow index giving an indication of the deviation from Newtonian behaviour (Trinh, et al., 2007).

The hysteresis area between the shear up and shear down legs of the sweeps was divided into squares and triangles in a grid pattern and the sum of these were calculated using Excel.

3.2 Results and Discussion

3.2.1 Evaluation of currently available commercial beef stocks

Table 3-1 reports current properties of beef stock. It was found that the solids content of the EC stock was found to be three times higher than other liquid stocks on the market resulting in a 5 fold higher apparent viscosity.

Table 3-1 Physical evaluation of current commercial beef stocks

Beef Stock brand	Solids Concentration (g $100g^{-1}$)	Brix	pH	Apparent viscosity (Pa.s)
Essential Cuisine	17.29	21.0	5.95	0.039
Campbell's	4.66	5.8	5.20	0.0080
Signature Range	2.49	2.3	6.03	0.00075

The descriptors generated by the trained sensory panel are provided in Table 3-2.

Table 3-2 Sensory descriptors generated by a trained sensory panel

Attribute	Descriptor	Definition	Low	High
Appearance	colour	how light or dark	light	dark
	viscosity	how thick	thin	thick
	transparency	how see-thru	clear	cloudy
	oily	how much oil sits on the surface	absent	extreme
	particulates	how many particulates are in solution	absent	extreme
Aroma	burnt	aroma of burnt meat	weak	strong
	mushroom	aroma similar to a mushroom sauce	weak	strong
	onion	aroma of onions being cooked	weak	strong
	vegetable	aroma of casserole vegetables	weak	strong
	beef	aroma of roasted beef	weak	strong
	pepper	aroma of black pepper	weak	strong
	overall	initial impression of 'beef' intensity	absent	extreme
Flavour	herb	the flavour strength of garden herbs	weak	strong
	beef	the flavour strength of roasted beef	weak	strong
	salt	the flavour strength of salt	weak	strong
	onion	the flavour strength of cooked onion	weak	strong
	soy	the flavour strength of soy sauce	weak	strong
	pepper	the flavour strength of black pepper	weak	strong
	marmite	the flavour strength of marmite spread	weak	strong
	burnt	the flavour strength of burnt meat	weak	strong
	overall	the total impact of the 'beef' flavour	absent	extreme
Mouth Feel	oiliness	degree of slipperiness of the liquid in the mouth	not	very
	thickness	the viscosity of the liquid in the mouth	thin	thick
After Taste	bitter	the extent to which the bitter notes linger	weak	strong
	burnt	the extent to which the burnt meat notes linger	weak	strong
	beefy	the extent to which the roasted meat notes linger	weak	strong
	marmite	the extent to which the marmite notes linger	weak	strong
	salty	the extent to which the salty notes linger	weak	strong
	overall	the total impact of the lingering aftertaste	absent	extreme

The sensory evaluation results for the three stocks from the trained panel are shown in Table 3-3. The trained sensory panel was able to distinguish between the stocks for many of the descriptors.

Table 3-3 Sensory scores for attributes and descriptors from trained sensory panel*

Attribute	Descriptor	Essential Cuisine	Campbell's	Signature Range
Appearance	Colour	7.98 ± 0.04[a]	6.73 ± 0.16[b]	2.98 ± 0.16[c]
	Viscosity	5.00 ± 0.06[a]	3.50 ± 0.20[b]	3.02 ± 0.21[c]
	Transparency	7.94 ± 0.07[a]	6.08 ± 0.24[b]	6.60 ± 0.33[c]
	Oily	4.13 ± 0.09[a]	3.69 ± 0.30[b]	2.60 ± 0.22[c]
	Particulates	5.85 ± 0.11[a]	4.04 ± 0.26[b]	2.73 ± 0.22[c]
Aroma	Burnt	7.94 ± 0.07[a]	5.02 ± 0.33[b]	2.79 ± 0.25[c]
	Mushroom	6.00 ± 0.12[a]	5.02 ± 0.35[b]	3.04 ± 0.30[c]
	Onion	4.04 ± 0.08[a]	4.42 ± 0.28[a]	2.79 ± 0.22[b]
	Vegetable	5.10 ± 0.16[a]	4.08 ± 0.30[b]	3.13 ± 0.27[c]
	Beef	7.75 ± 0.20[a]	5.56 ± 0.36[b]	2.94 ± 0.24[c]
	Pepper	3.19 ± 0.14[a]	4.46 ± 0.41[b]	2.42 ± 0.18[c]
	Overall	7.58 ± 0.25[a]	6.15 ± 0.35[b]	3.38 ± 0.26[c]
Flavour	Herb	3.06 ± 0.07[a]	4.58 ± 0.27[b]	3.19 ± 0.30[a]
	Beef	7.94 ± 0.07[a]	5.90 ± 0.33[b]	3.15 ± 0.21[c]
	Salt	4.94 ± 0.09[a]	6.44 ± 0.22[b]	5.35 ± 0.34[a]
	Onion	4.02 ± 0.09[a]	4.54 ± 0.35[b]	3.25 ± 0.25[c]
	Soy	5.06 ± 0.09[a]	4.85 ± 0.29[a]	2.96 ± 0.28[b]
	Pepper	3.04 ± 0.08[a]	5.10 ± 0.43[b]	2.63 ± 0.22[a]
	Marmite	4.13 ± 0.14[a]	5.00 ± 0.36[b]	2.81 ± 0.35[c]
	Burnt	7.23 ± 0.13[a]	4.58 ± 0.34[b]	2.56 ± 0.22[c]
	Overall	7.96 ± 0.08[a]	6.35 ± 0.24[b]	3.58 ± 0.30[c]
Mouth feel	Oiliness	6.75 ± 0.14[a]	4.40 ± 0.32[b]	3.15 ± 0.31[c]
	Thickness	5.85 ± 0.12[a]	3.67 ± 0.29[b]	2.88 ± 0.23[c]
Aftertaste	Bitter	6.00 ± 0.00[a]	4.90 ± 0.22[b]	3.69 ± 0.30[c]
	Burnt	7.92 ± 0.08[a]	4.38 ± 0.31[b]	2.60 ± 0.23[c]
	Beefy	6.88 ± 0.09[a]	4.92 ± 0.32[b]	2.85 ± 0.24[c]
	Marmite	4.98 ± 0.04[a]	4.77 ± 0.37[a]	2.71 ± 0.29[b]
	Salty	3.98 ± 0.07[a]	5.58 ± 0.30[b]	5.54 ± 0.27[b]
	Overall	7.92 ± 0.08[a]	6.13 ± 0.23[b]	4.25 ± 0.24[c]

*Rows with different letters indicate a significant difference at the 95% level of confidence

Essential Cuisine was found to have a significantly darker colour, high transparency and a more particulate appearance than the other stocks. Signature Range had the lightest colour.

The flavour of Essential Cuisine stock had stronger burnt, beefy flavour and overall intensity than the other stocks. Signature Range had the weakest flavour in terms of beefy, burnt and

overall descriptors. Saltiness was highest in Campbell's, but was similar for Signature Range and Essential Cuisine.

The thickness and oiliness of Essential Cuisine stock was found to be higher than the other stocks. Signature Range had the lowest thickness and oiliness score of the stocks.

The aftertaste of Essential Cuisine had a stronger burnt beefy and overall intensity than the other stocks. Signature Range had the weakest aftertaste in terms of burnt beefy and overall intensity. Campbell's had the highest salty aftertaste.

It seems that the colour intensity, flavour intensity, thickness and aftertaste intensity reflect the solids content of the stock, all scoring higher for high solids. The stronger 'Burnt' flavours and aftertaste may be due to the roasting of the bones for EC although it is not known whether the other stocks use a roasting process. The higher saltiness for Campbell's may result from the addition of salt.

Clearly EC is a concentrated stock whilst the others are not. A useful comparison would be to test the different stocks at the same level of solids.

3.2.2 Documentation of the current Commercial Process

The current commercial process utilises beef bones supplied by various freezing works. These consist of leg, ribs, brisket, hip and shoulder bones as shown in Figure 3-6. The bones have had meat removed mechanically or manually but still contain significant coverage of red meat muscle, fat, tendons ligaments and collagen material. A typical 20 kg box was analysed and found to have 50 bones with a mean weight of 400 g and a standard deviation of 145 g. The average ± 1 standard deviation for the overall dimension from the longest to shortest were 110 ± 20, 80 ± 20 and 50 ± 17 mm

Bones are currently supplied in 25 kg corrugated cardboard cartons, chilled and stored at 5°C or less.

Tomato paste with a solids content of 20% is added to the stock and supplied in 5 kg plastic pouches.

Packaging for the product is 1 kg plastic pouches that are then placed into corrugated cartons. A key feature of the stock is that it is from 'Roasted' beef. The roasting is used as a strong marketing feature and is displayed on the packaging.

Figure 3-6 Bones used by Essential Cuisine Limited

The process flow diagram is given in Figure 3-7. Beef bones are manually cut to about 'fist' size or left uncut and then roasted in an oven for 20 minutes at a temperature of 220°C. For the bones described above no cutting is necessary. It would seem that if the bones were longer than 150 mm they would need cutting, but this is left to the judgement of the processing staff.

About 1,000 kg of roasted bones are placed into an extraction vessel of about 2,000 L. Water is added in a 1:1 ratio and the vessel heated to 92°C by electrical elements inside the vessel. The content in the vessel is held at 92°C for three days and then cooled to allow the fat to solidify, which is then scraped off the stock. The stock is then decanted from the bones and pumped through a 200 μm filter to remove suspended solids before being pumped to a clean tank where a prescribed amount of tomato paste, usually 1%, i.e. 10 kg per 1000 L, is added to the stock and the mixture is heated for a further 3 days at 92°C in which time there is about a reduction to 1/3 of the original volume. The final concentration is over 16°Brix. The stock is hot filled, at a temperature over 75°C, into 1 L plastic pouches. The pouches are sealed and chilled in a blast freezer to rapidly cool the product, placed in a cardboard outer and then stored in a chiller for distribution.

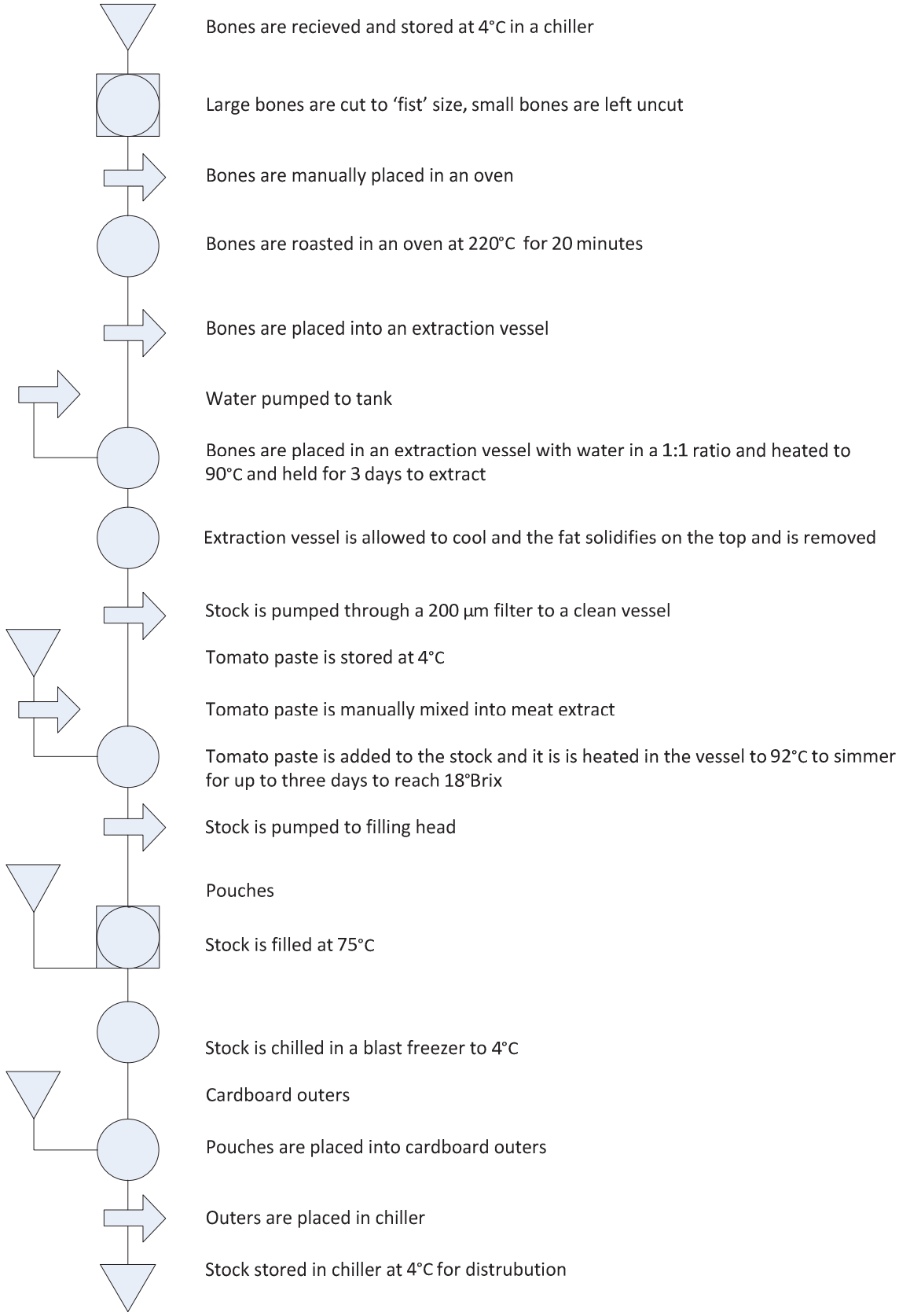

Figure 3-7 Process flow diagram for essential cuisine stock

3.2.3 Characterisation of stock

Physical properties and colour measurements for the different batches of stock are given in Table 3-4. There were significant differences between batches for both solids content and Brix with a range of 2.5% which indicates poor consistency and quality control. If the batches with the least solids (about 16%) are acceptable then economically it would make sense to dilute all batches to this level, or control the concentration process better.

Table 3-4 Physical properties of Essential Cuisine commercial stock[#]

Property	BB 22/9/07	BB 1/10/07	BB 5/10/07	BB 8/10/07	BB 10/10/07
Brix (± 0.1)	19.9[a]	20.1[a]	21.4[b]	22.1[c]	22.2[c]
Solids Content (± 0.1)	15.8[a]	16.1[b]	17.5[c]	18.2[d]	17.9[e]
pH (± 0.05)	6.00[a]	6.00[a]	6.27[b]	6.32[b]	6.32[b]
Density (kg m^3, ± 0.002)	1057[ab]	1054[c]	1060[bc]	1061[bc]	1062[c]
Colour L* (± 0.10)	30.50[a]	30.16[b]	30.46[a]	29.94[c]	30.14[bc]
Colour a* (± 0.05)	1.93[a]	1.59[b]	1.59[b]	0.94[c]	1.28[d]
Colour b* (± 0.05)	1.80[a]	1.47[b]	1.47[b]	0.94[c]	1.22[d]
a*/b* (± 0.10)	1.07[a]	1.08[a]	1.08[a]	1.00[a]	1.05[a]

[#]Numbers with different letters in each row are significantly different

A plot of solids concentration versus Brix was determined for the combined batch of stock at a variety of concentrations shows a linear relationship (Figure 3-8)

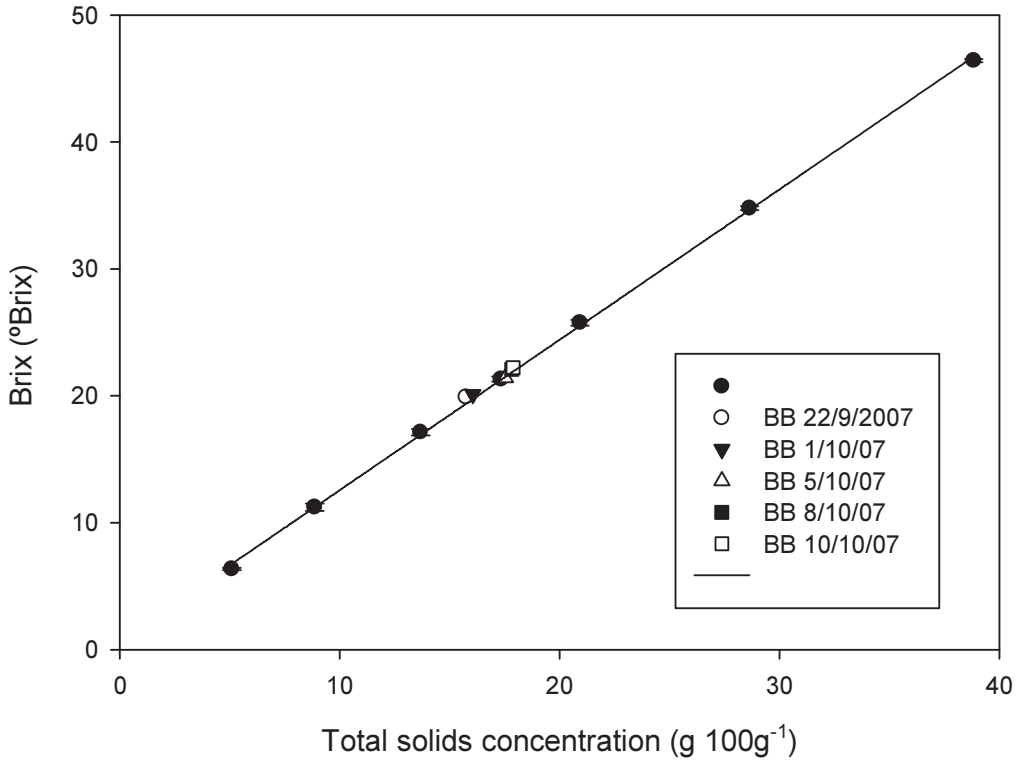

Figure 3-8 Solids versus Brix for one batch of essential Cuisine stock at different concentrations

A linear relationship was fitted to the combined batch with an R^2 of 1.00 and an equation re-arranged for the determination of total solids concentration from Brix is

$$Total\ solids\ concnetration = 0.844Brix - 0.7 \quad (3.2)$$

Equation 3.2 shows that the solids are lower than the Brix reading by about 15%. A similar relationship was found by Mikkelsen (1996) (Equation 3.3) for beef broth although this only covered the range of 0-3% total solids.

$$Total\ solids\ concentration = 0.89Brix + 0.127 \quad (3.3)$$

Because total solids is a labour intensive and time consuming measurement, soluble solids (°Brix) can provide a rapid measurement and the solids can be estimated from the Brix using equation 3.2.

A plot of density versus solids concentration shows a straight line relationship Figure 3-9. The equation (equation 3.4) was determined by regression to have a R^2 of 0.99

$$Density = 998.49 + 3.644 \times total\ solids\ concentration \quad (3.4)$$

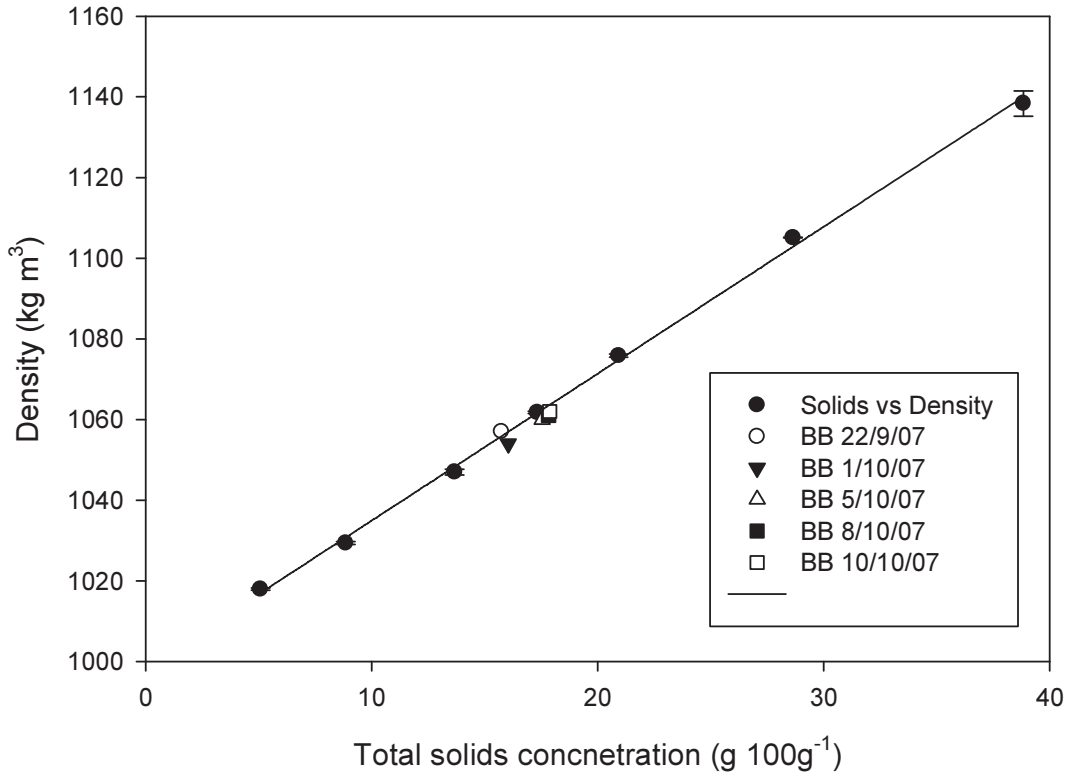

Figure 3-9 Density versus total solids concentration for Essential Cuisine stock at 20°C

The pH was 6.0 for two of the batches and around 6.3 for the other three. The low pH of the final stock is due to the presence of the tomato paste that is acidic in nature. The variation in pH may be due to variations in concentration of tomato paste present in the various batches of stock.

The density of the stocks was similar, around 1060 kg m^{-3}, and although statistically there were significant differences ($p>0.05$), the actual differences were very small.

Colour results are given Table 3-4 as the average of three replicates. The L* value represents the lightness to darkness scale with dark being 0 and 100 being light. The average value of L* was 30 for the stock and although statistically significant differences were found, the differences were very small.

Variation of a* and b* is significant with a twofold variation. However, the ratio of these values (a*/b*) was similar (a value between 1 and 1.08). Therefore the colour indicated by the ratio is constant, but the intensity or saturation of that colour varies between batches.

There does not appear to be any relationship between colour parameters and solids content, it is expected that a lower solids content would result in a lower darkness value (L*) and a lower values of red and yellow (a* and b*). This was not the case with batch BB 8/10/07 which has the lowest colour values despite being the second highest in terms of solids. Therefore, other factors are contributing to the differences in colour.

3.2.3.1 Rheology of Stock

Rheological flow curves at 20, 30, 40, 50 and 60°C for stock BB 5/10/2007 are shown in Figure 3-10. The curves are non-linear and show a small amount of hysteresis between the shear up and shear down legs. The shearing down legs are lower than the shearing up legs indicating thixotropic behaviour. The curves appear to pass close to the origin indicating a small or no yield stress. The gradient of the curves is higher for lower temperatures indicating lower viscosity at high temperatures. Higher viscosity at lower temperatures is very common in materials (Borne, 2002). The hysteresis is greater for lower temperatures indicating more non-Newtonian behaviour and a higher time dependency indicating the gelling property of the material is more apparent at low temperatures.

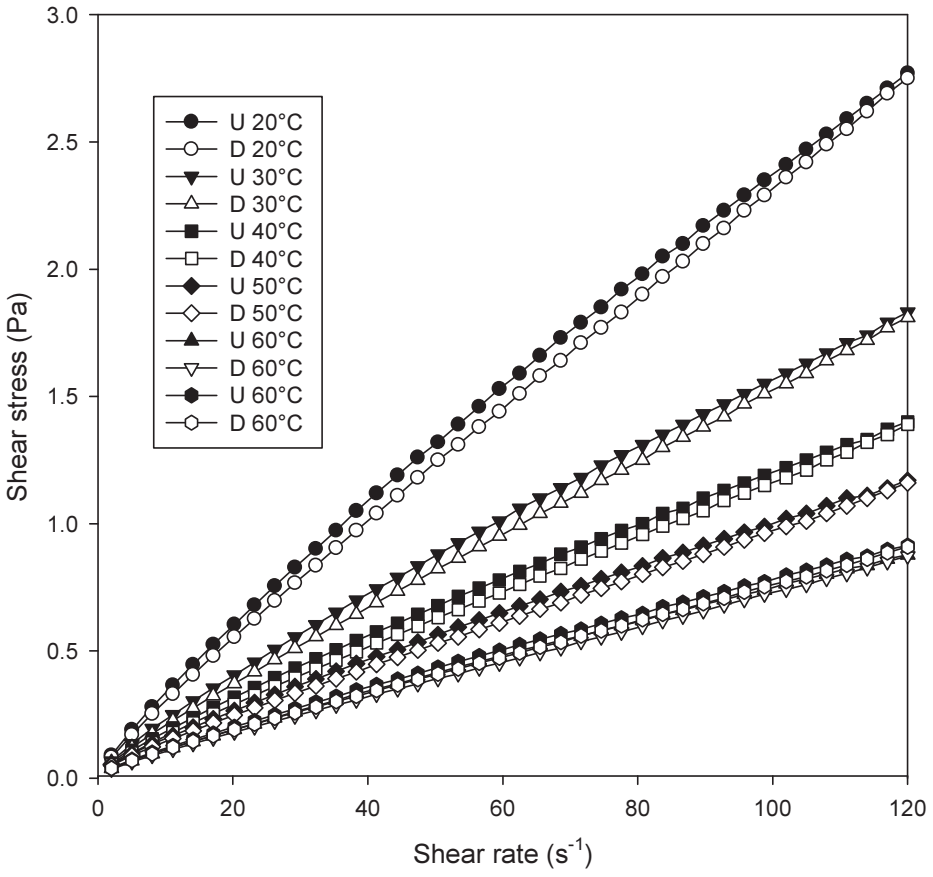

Figure 3-10 Flow curves shearing up (U) and down (D) for batch 5/10/07 measured at 20, 30, 40, 50 and 60°C

A closer look was taken at the time dependency of stock by shearing a sample up and down 5 times at 20°C. It was suspected that the time dependency could be due to the flocculating tendencies of the tomato paste added to the bone extract rather than the extract itself. Therefore the stock was centrifuged and centrate (the supernatant liquid) underwent shearing up and shearing down 5 times under the same conditions of temperature and shear rates as before. The results are shown in Figure 3-11.

The flow curves for the centrate are lower than those for the original stock, show no hysteresis and are identical for each successive shearing up and down. The curves for the original stock show some hysteresis and become lower after each shear cycle.

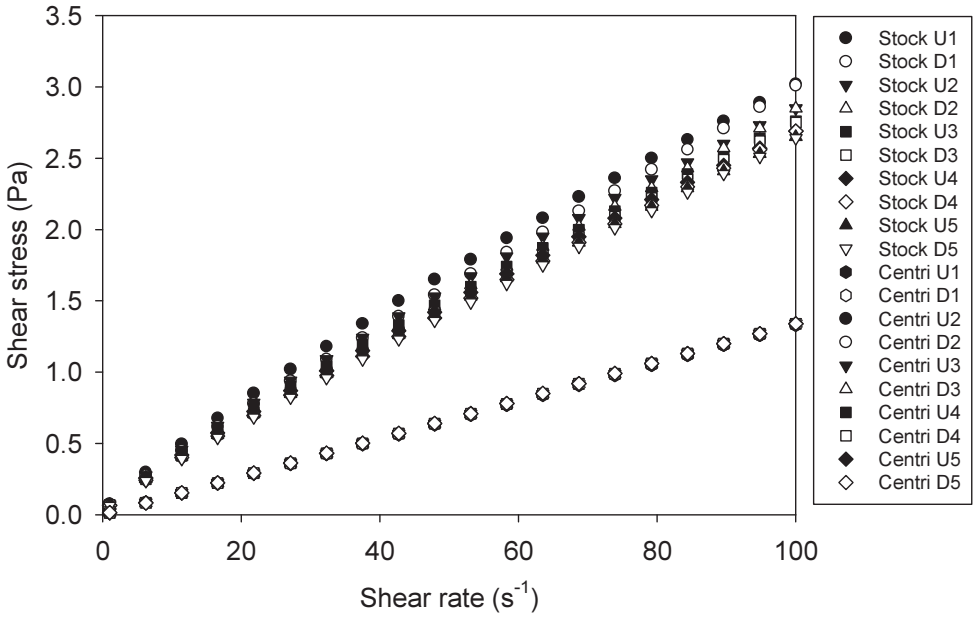

Figure 3-11 Flow curves shearing up and down five times for stock and centrate stock at 20°C

The results indicate that the presence of large particles significantly contributes to the final apparent viscosity of the solution and the large particles are responsible for the time and shear dependency. In addition it was observed that the solids centrifuged from the stock had a dark red colour similar to tomato paste. It must be recognised that the method is crude and it is not known if perfect separation of tomato paste particles was achieved without also separating out some of the collagen material. It is concluded that tomato paste contributes significantly to the final apparent viscosity and time and shear dependency of the Essential Cuisine stock.

For each of the curves in Figure 3-10 Hershel-Bulkley equations were fitted using SIGMA PLOT that uses the Marquardt-Levenberg algorithm (Marquardt, 1963) to estimate the parameters y_0, K and n by minimising the sum of the squared differences between the estimated and experimental values. An example of the equation fitted to a typical shear up leg is shown in Figure 3-12 which shows a very good fit ($R^2 > 0.99$).

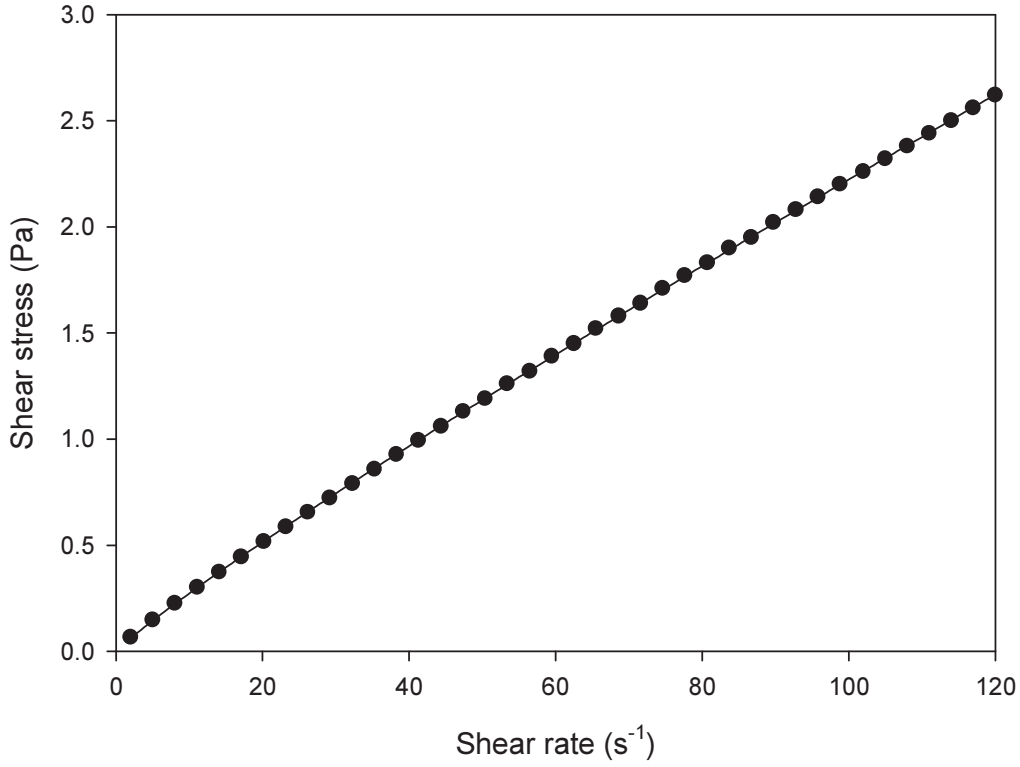

Figure 3-12 Hershel Bulkley model fitted to shear up leg at 20°C for BB 8/10/07

R-squared values for the Hershel-Bulkley model were greater than 0.999 and the typical standard error of estimate was less than 0.001 Pa indicating good fit. Replicates for BB 5/10/2007 at 60°C and BB 1/10/2007 showed uncertainty at the 95% level of confidence for the calculated Hershel-Bulkley parameters were less than 12% for K and less than 4% for n but in one cases for y_0 it was greater than 15%. The yield stress value y_o was very small in magnitude less than 0.06 Pa and therefore can be considered insignificant.

Values for K which provides an indication of thickness are plotted against temperature in Figure 3-13 and Figure 3-14 and follow similar trends but the curves do not coincide, indicating very poor consistency of quality between batches. Generally the consistency coefficient K decreases with temperature. Overall the value of K drops by 80% as the temperature is increased from 20 to 60°C.

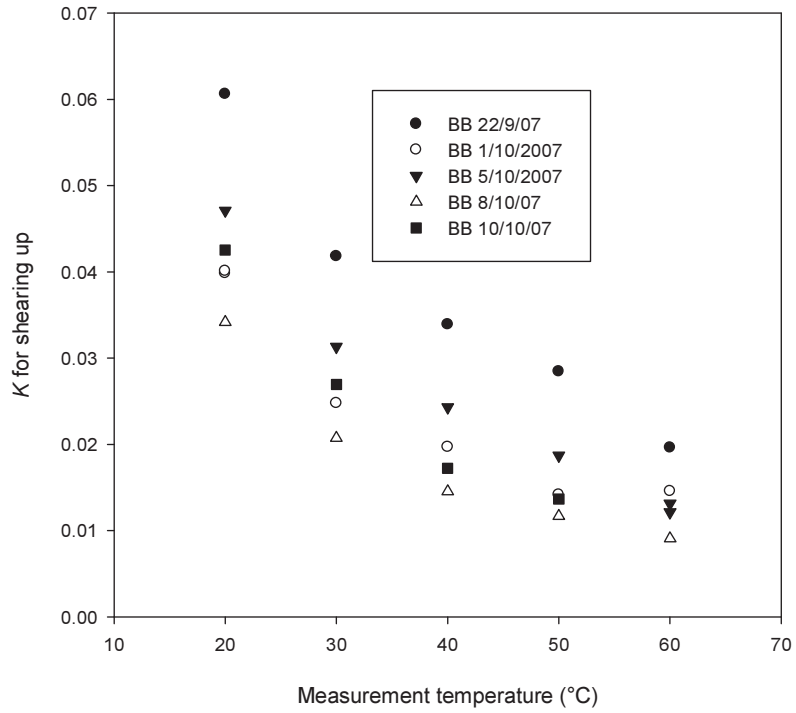

Figure 3-13 Consistency index, *K*, for fitted Hershel Bulkley models to shearing up leg. The legend indicates the sample designation

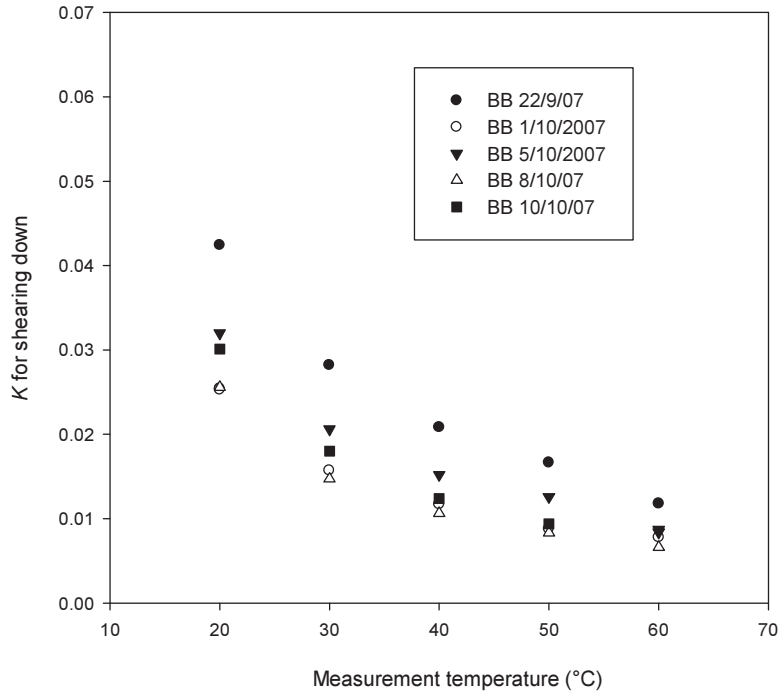

Figure 3-14 Consistency index, *K*, for fitted Hershel Bulkley models to shearing down leg. The legend indicates the sample designation

The *K* values for the shear down leg are shown in Figure 3-14 and the curves are lower than those for the shear up curves as would be expected for a thixotropic material. Variation between batches is significant, with the stock with the highest value of *K* being twice as high as that with the lowest value.

Plots of the flow behaviour index *n* against temperature for the shear up leg are shown in Figure 3-15 and the shear down leg is given in Figure 3-16. The numerical value is between 0.8 and 0.9 for the shear up leg and between 0.9 and 1.0 for the shear down leg. This is typical of very weakly shear thinning fluids since *n* = 1 is the value of the flow behaviour index for Newtonian fluids. In general the value of *n* increases slightly with temperature which reflects a decrease in gelling tendencies with increased temperature.

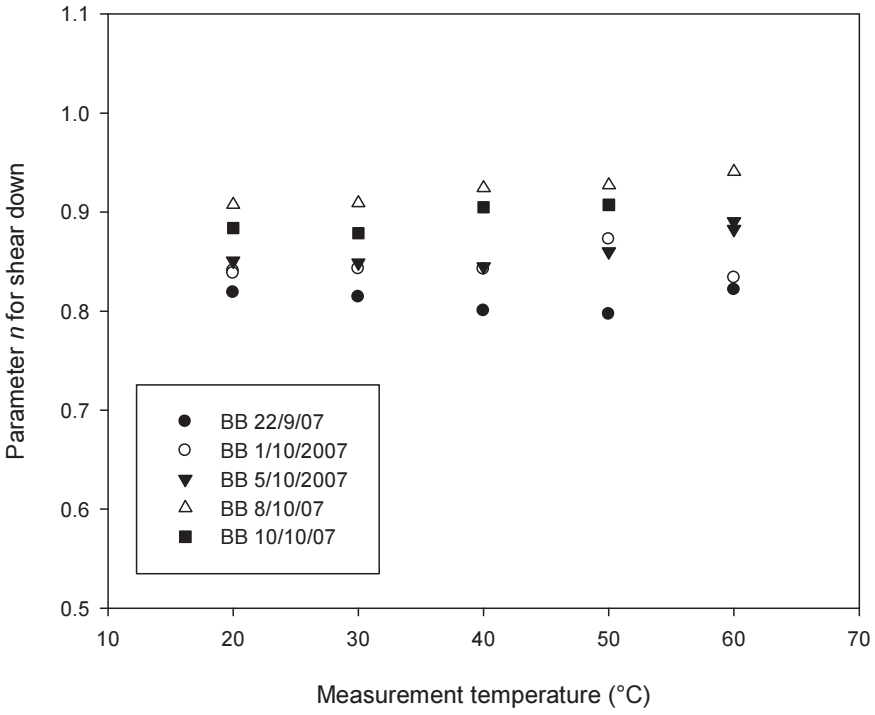

Figure 3-15 Flow index, *n*, for fitted Hershel Bulkley models to shearing up leg.

Hysteresis loop area (HLA) is plotted against temperature (Figure 3-17) and shows very similar trends to those of *K*. The HLA in general decreases with temperature in a non-linear fashion and shows significant variation between batches. The trend indicates that the time dependency of the material decreases with increasing temperature.

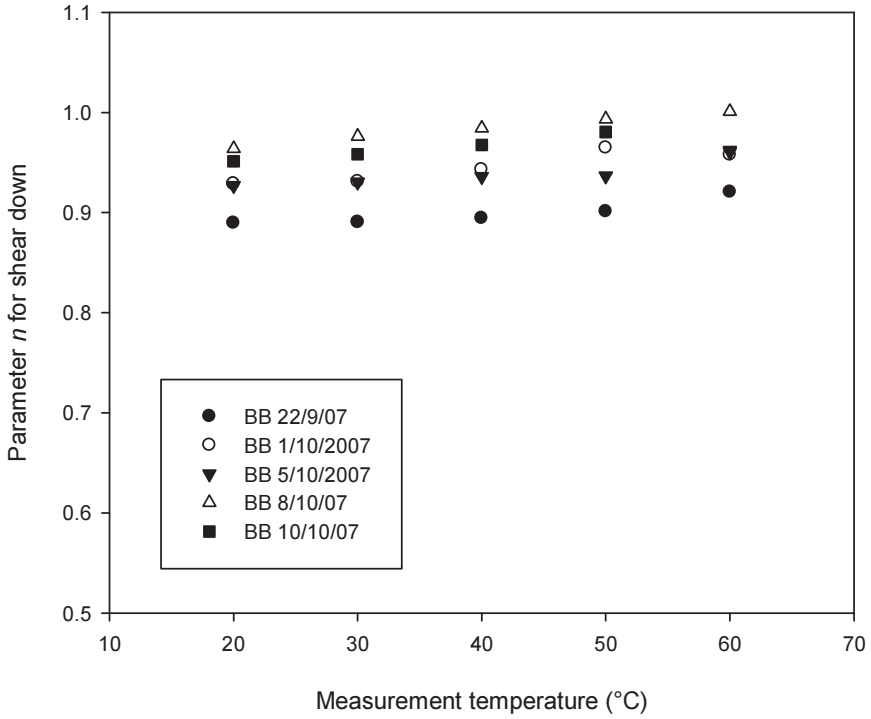

Figure 3-16 Flow index, *n*, for fitted Hershel Bulkley models to shearing shearing down leg

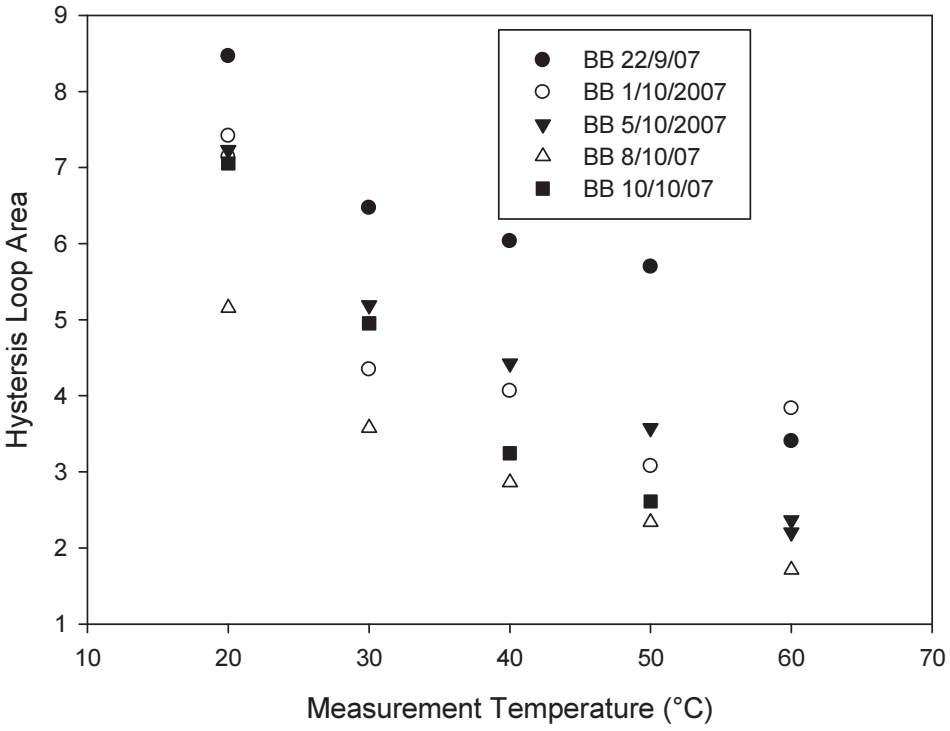

Figure 3-17 Calculated hysteresis loop area (HLA) at 20, 30, 40, 50 and 60°C

The rheological results show that the current EC product is a non-Newtonian fluid that thins with increased shear rate, time and temperature. Temperature has the most marked effect. The measures for the consistency coefficient, *K*, and non-Newtonian behaviour (HLA and *n*) seem to be correlated. Thus, the mechanisms or structures producing thickness, probably also cause the non-Newtonian behaviour.

It also must be noted that the method used does not completely separate time dependency from shear dependency as the shear rate is increased as a function of time. However, the method is simple and quick and provides a basis for comparing batches of stock. The results show there is variation of texture between commercial batches. The data can be used for the design of processes and equipment for the manufacture of stock.

3.2.3.2 Particle Size analysis

Particle size distributions of the stocks tested are shown in Figure 3-18. Triplicate measures on sample BB 22/9/07 found that maximum residual was 5%, indicating good repeatability. All of the stocks showed a peak in the particle size distribution between 220 and 300 µm. All of the distributions were cut off at 600 µm, indicating a significant presence of particles greater than 600 µm. Three of the five batches showed a small peak between 10 and 20 µm.

The centrate sample showed proportionally higher volume of particles in the less than 100 µm size range. The proportion at the peak of 200 µm has decreased showing the removal of some of the particles in this range. There is still a cutting off at 600 µm indicating there are particles greater than 600 µm left. Therefore the centrifuging has changed the particle size distribution but has not achieved a complete removal of particles greater than 600 µm.

In general solutions with larger particles have a higher viscosity. Particle size analysis reflects the rheological results in Figure 3-11 where the centrifuged stocks have a lower apparent viscosity due to the removal of some of the larger particles.

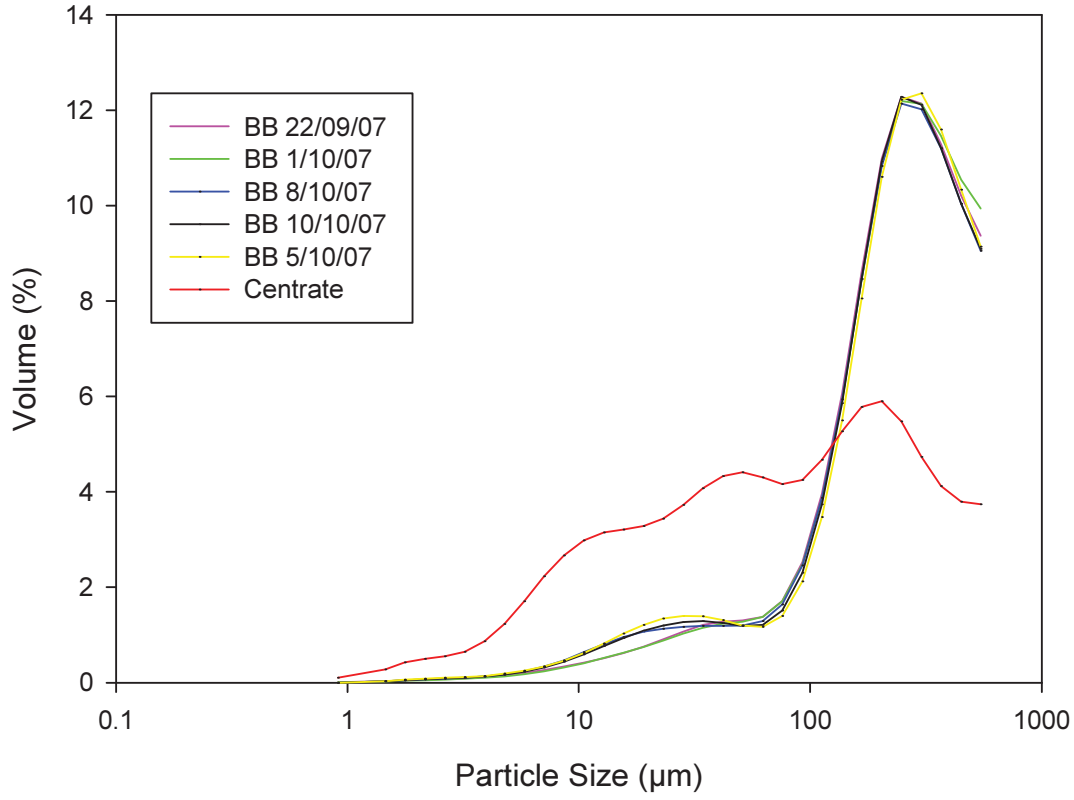

Figure 3-18 Particle size distributions for different batches of stock and the centrate of the centrifuged stock.

3.2.4 Conclusions

EC stock is more concentrated than other stocks on current retail market. Because of this it was found to have stronger flavour and aroma characteristics and is thicker.

EC stocks showed large variation between batches in terms of solids content and rheological properties. This indicates poor quality control.

Addition of tomato paste significantly alters the viscosity and likely affects mouth feel. At lower temperatures the stock is time dependant due to the presence of tomato paste and gelling properties of the gelatine present. At higher temperatures the stock is practically Newtonian.

3.3 Studies of the Current Procedure of Extraction

The current extraction process uses hot water at 90-95°C in a (1:1) ratio and takes up to 3 days to yield a 5 to 6% solution. Prior to processing, the bones were cut into the size of a fist and then roasted in order to develop flavour. It is not known if the roasting process affects the yield.

The aim of the experiments here were to gather mass balance data from the process and identify the effect of roasting and bone size on the final yield. The data is necessary for a formal design process.

3.3.1 Materials and methods

3.3.1.1 Extraction

Bones used were from beef deboning operations and include some meat and connective tissue. Bones used were a 50:50 ratio by weight of sternum/ rib cage to leg bones. The solvent was water.

The extraction vessel was a stainless steel jacketed vessel of 445 mm internal diameter and 400 mm internal height. The vessel was covered with a lid. The water jacket was heated with a heating element inside. The temperature of the jacket was controlled with a thermostat. Two thermocouples were placed inside the vessel, T1 was placed 10 cm from the bottom and T2 was placed 10 cm from the top of the liquid level. The thermocouples were linked to a squirrel data logger and the temperature of each thermocouple was recorded every 60 seconds.

The effect of roasting was investigated. The roasting treatment involved placing bones in stainless steel trays and roasting in a pre-heated hot air oven at 220°C for 20 minutes. The bones were weighed before and after roasting. A treatment using smaller sizes of bones was also conducted. The extraction treatments are summarised in Table 3-5.

For the extraction process a 1:1 ratio of bones to water was added to the vessel. Following the extraction and while still at 60°C the stock and fat was drained through a 2 mm screen into a vessel and weighed. The remaining bones were collected and weighed. The fat was then separated from the stock and each was weighed.

Table 3-5 Experimental design for experiments on the current extraction process

Treatment	Replicates	Batch size	Bone size	Water/bones ratio	Roasting conditions	Extraction conditions
Non Roasted	2	20 kg	< 750 cm^3	1:1	-	92°C, 3 days
Non Roasted Small Bones	2	20 kg	< 160 cm^3	1:1	-	92°C, 3 days
Roasted	2	20 kg	< 750 cm^3	1:1 (for roasted bone)	220°C for 20 minutes	92°C, 3 days

3.3.1.2 Analysis

For the bone extract brix and solids were measured as outlined in sections 3.1.3.1 and 3.1.3.2 respectively. In addition the following analysis were made.

3.3.1.2.1 Crude Nitrogen

Total Nitrogen was determined using the Kjedahl method AOAC 980.20. About 1 g was weighed exactly into a digestion tube. Two (2) Kjeltabs (each containing 3.5 g K_2SO_4 and 0.0035 g Se) and then 15 mL concentrated H_2SO_4 were added to the tube. A blank digestion was carried out at the same time (i.e. no sample but all other reagents).

The tubes were placed in a block digestion unit and digested at 420°C for 45 to 60 minutes until clear. On cooling about 75 mL of warm water was added to the tubes.

Tubes were placed in to a Keltec (Foss) steam distillation unit. NaOH was added automatically and 100 mL was distilled into a conical flask with 25 mL boric acid solution with bromocresol green and methyl red indicators.

The flask was then titrated with 0.1 M HCl until a grey mauve end point.

The analysis was carried out in triplicate with one blank.

3.3.1.2.2 Non-Protein Nitrogen

Non-protein nitrogen was determined using a method based on AOAC 991.21. In this method the protein was precipitated out by using a trichloroacetic acid (TCA) solution.

About 45 g of liquid extract was mixed with 5 g of trichloroacetic acid (50%), in a glass centrifuge tube and centrifuged for 10 minutes at 2000 rpm. 10 g of the supernatant were placed directly in the Kjedahl distillation and total nitrogen was determined.

3.3.1.2.3 Ash

Ash was determined using a furnace at 550°C in following the method AOAC 942.05.

3.3.2 Results and Discussion

A typical time temperature profile for the extraction in the vessel is shown in Figure 3-19 for the Roasted Bones Run 2. There was excellent agreement between the two thermocouples T1 and T2. The difference between the two thermocouples was on average less than 1°C for all 6 runs reported in Table 3-5. The temperature overshot the automatic temperature setting of 92°C by 2°C and then came back to a constant 92°C and remained stable for the remainder of the 72 hours. This extraction temperature profile applied to all the 6 runs.

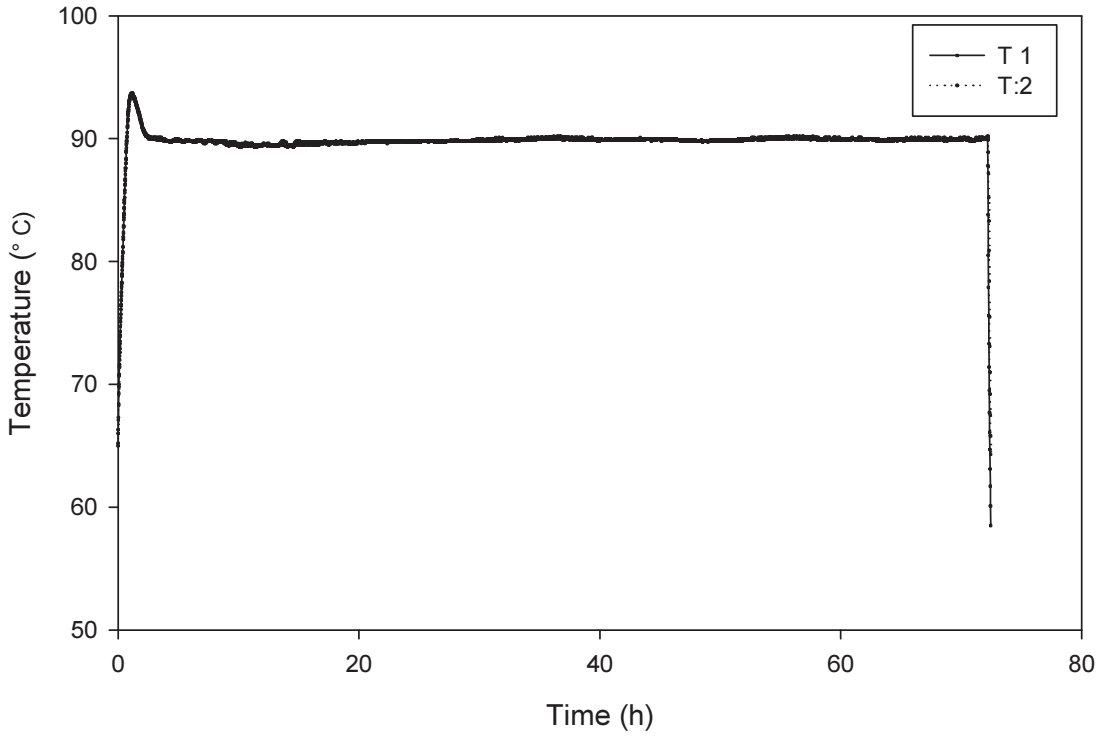

Figure 3-19 Temperature time profile of extraction vessel with two thermo couples T1 placed 10 cm from the top and T2 10 cm from the bottom.

3.3.2.1 Mass Balance of the processes

3.3.2.1.1 Roasting

There was a 10-12% of weight lost from bones in the roasting process. Therefore 111.5 ± 1.3 of fresh bones are required to provide 100kg roasted bones.

3.3.2.1.2 Extraction

The yields of each component are given in Table 3-6. The yields are presented as percentages of the weight going into the vessel based on the average of the two replicates with the uncertainty based on a 95% confidence interval of the means. The replicates are in good agreement as indicated by the small uncertainties at the 95% level of confidence.

Table 3-6 Yields from extraction processes on a wet weight basis.

Treatment	Stock	Waste	Fat	Loss
Non Roasted	50.8 ± 0.4%	40.0 ± 0.9%	5.8 ± 0.4%	3.0 ± 0.3%
Small Bones	52.0 ± 1.0%	39.7 ± 1.0%	5.3 ± 0.3%	3.2 ± 0.9%
Roasted	47.8 ± 0.9%	42.2 ± 1.7%	5.7± 0.3%	3.0 ± 1.1%

The loss represents material remaining in the tank after the bones have been removed, any evaporation that may have occurred in the experiment (which should be minimal as the extraction vessel was covered with a lid), and other losses from the separation and filtering process. The total loss for all treatments was around 3%. Some material adhered to the tank and some liquid remained in the bottom. The amount lost due to evaporation is not known. A very small component of the loss was observed in the separation of the fat and the stock.

Table 3-6 shows that the size of the bones (<760 cm^3 and, <160 cm^3) had little difference in yield. Roasting made a small difference decreasing the yield of stock by about 3%. Since a 1:1 ratio of water to bones was used in both cases and there had been a moisture loss during roasting this difference can be interpreted mainly to the changing basis for the yield estimate.

Of most interest in terms of yield is the amount of solids non-fat (SNF) of the stock as presented in Table 3-7. It was found that the amount of SNF was in the range of 5.6-6.0 kg per 100 kg of bones and there were no significant differences between the different treatments. The solids concentration of the resultant stocks varied from 5.5 to 6.5 g 100 g^{-1}, the roasted treatment producing the higher concentration.

The fat yield per 100 kg bones is typically 10-12 kg. Roasting of the bones yielded significantly less fat than the non-roasted bones. This was possibly due to losses in the roasting process which liquefies and separates some of the fat from the bones. This separated fat remains in the trays and is not transferred into the extraction process. Raw material variation could also cause some of the differences in the fat yield.

Table 3-7 Solids yield for the extraction process

Treatment	SNF concentration (g 100g^{-1})	Stock yield per 100 kg of bones (kg 100 kg^{-1})	SNF yield per 100 kg of bones (kg 100 kg^{-1})	Fat yield per 100 kg of bones (kg 100 kg^{-1})
Non-roasted	5.5 ± 0.2^{a}	101.5 ± 0.7^{a}	5.6 ± 0.2^{a}	11.6 ± 0.7^{a}
Small Bones	5.8 ± 0.2^{a}	103.9 ± 0.2^{b}	6.0 ± 0.2^{a}	10.5 ± 0.6^{ab}
Roasted Bones	6.5 ± 0.5^{a}	95.5 ± 1.7^{c}	5.6 ± 0.4^{a}	10.2 ± 0.4^{b}

Next of interest is the makeup of the extracted solids and this is presented in Table 3-8. The Nitrogen content was similar for all treatments at around 16%. The mineral content indicated by the Ash content is between 5.5 to 5.8% of the total solids. The non- protein nitrogen (NPN) was found to be significant up to about 60% of the total nitrogen, although there is large uncertainty in these measurements.

Table 3-8 Nitrogen and Ash components in extracted Solids*

	Total Nitrogen (%)	% Ash	NPN as % of Total Nitrogen
Non –roasted	16.0 ± 1.2^{a}	5.8 ± 0.3^{a}	65 ± 15^{a}
Small Bones	16.0 ± 1.2^{a}	5.3 ± 0.5^{a}	57 ± 13^{a}
Roasted	15.8 ± 1.6^{a}	5.5 ± 0.7^{a}	57 ± 13^{a}

*Numbers with different letters are significantly different to those in the same column

Overall the results show the yield of solids for stock extracted at 92°C for three days is 5.6 kg for 100 kg of bones and this is unaffected by the roasting process. The solids are composed mainly of nitrogenous material that is a mixture of protein and non-proteins.

3.4 Extraction kinetics of the current process

An extraction experiment was set up where samples were taken at regular intervals during an extraction in order to establish the rate.

3.4.1 Materials and Methods

The raw materials and extraction method was the same as in section 3.3.1.1. The bones were roasted and the roasted bones were placed into the extraction vessel along with water in a 1:1 ratio. The temperature of extraction was 92 ± 1°C. Samples were taken at the following times after the contents of the vessel had reached 92°C; 1, 2, 4, 8, 16, 24, 33, 42.5, 49, 56, 67 hours.

A 100 mL was taken for each analysis. The soluble solids was determined. Samples were then sent to the Nutrition Lab, IFNHH Massey University, where total solids was determined by convection oven 105°C (AOAC 930.15, 925.10), fat by Soxtec extraction (AOAC 991.36), nitrogen by Leco total combustion method (AOAC 968.06), ash by furnace at 550°C (AOAC 942.05) and amino acid analysis by hydrochloric acid hydrolysis followed by HPLC separation (AOAC 994.12).

Solids non-fat (SNF) was determined by the total solids minus the fat content. Crude protein was determined as Nitrogen x 6.25 (Duerr & Earle, 1974).

3.4.2 Results

The data collected for the rate of extraction in terms of SNF concentration is given in Figure 3-20 (Full data for the analysis is given in Table 11-1 of the Appendix). There is a rapid rise in solids concentration in the first day with a declining rate for the rise in solids concentration over days two and three. There seems to be a discrepancy in the data at 1.75 days, this is likely due to a sampling error as all the SNF, nitrogen and ash values seem lower than expected. It is observed that after three days the extraction has not reached equilibrium however after three days the rate of solids increase is very low. From a practical point of view, extraction over a single day will achieve over 66% of the solids concentration when compared to a three day process. Extraction over a two day period will achieve 95% of the solids concentration compared with a three day process.

The material consists mainly of nitrogen based material as estimated as crude protein, and a small amount of ash. The minerals (ash) are extracted rapidly at the beginning of extraction appear to reach equilibrium within a day. These are most likely free minerals present in the materials and hence rapidly extracted.

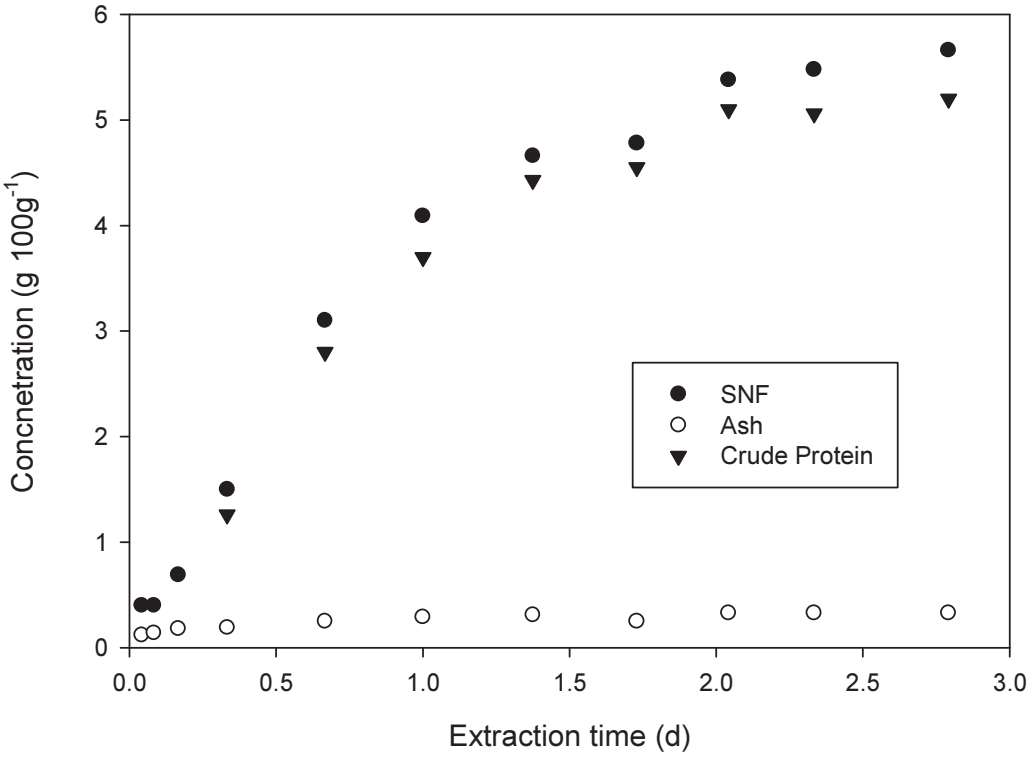

Figure 3-20 Extraction with time for SNF, ash, and crude protein concentrations at 92°C

The nitrogenous material is expected to come from both collagen and muscle proteins. Hydroxyproline is unique to collagen material and methionine is not present in collagen but is present in muscle proteins. The concentration of hydroxyproline and methionine were determined for selected samples and these were plotted along with total nitrogen as concentrations relative to the concentration achieved at the end of the extraction (after 67 hours) in Figure 3-21. Methionine is rapidly extracted in the first day of extraction while the collagen is slower. This provides evidence that collagen is extracted at a slower rate than the material extracted from the muscle proteins.

The methods used to measure amino acids such as hydroxyproline are expensive and time consuming as they involve the hydrolysis using concentrated acid. An alternative low cost method using alkaline hydrolysis was considered but this too proved time consuming. The results show the kinetics of hydroxyproline extraction are similar to the kinetics of nitrogen extraction, and the kinetics of nitrogen extraction strongly correlate with the kinetics of the solid non-fat extraction. In other words following the solids non-fat concentration with time during an extraction provides a low cost and simple method of measuring extraction kinetics.

This avoids the time consuming and expensive methods of following individual amino acids for a more detailed analysis.

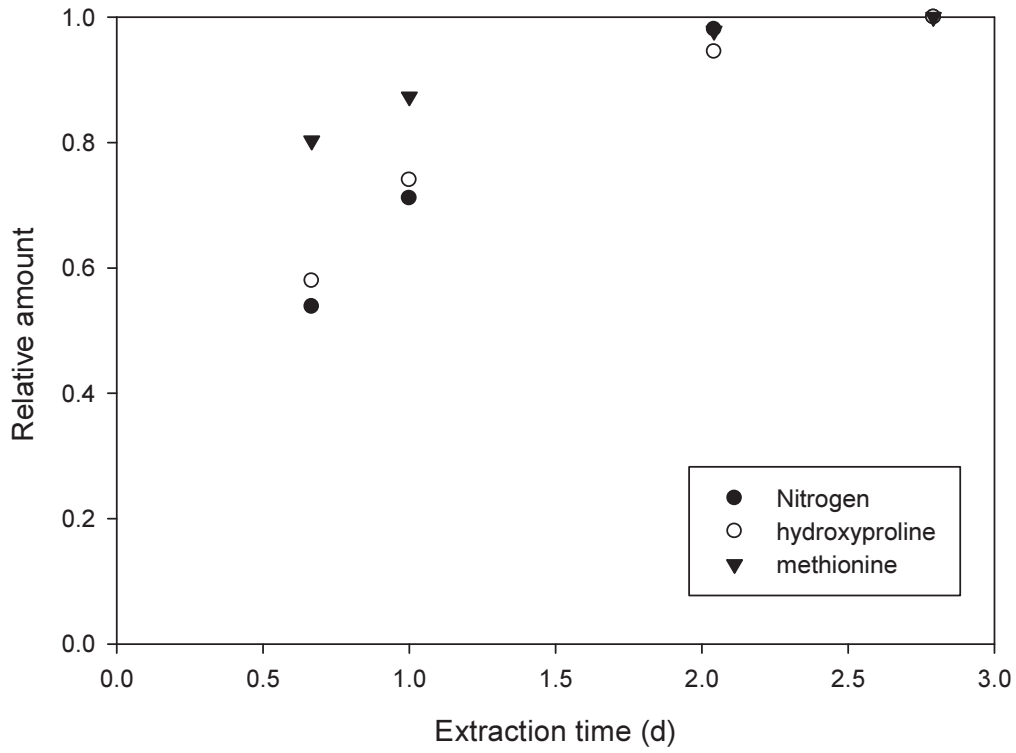

Figure 3-21 Extraction profiles of nitrogen, hydroxyproline and methionine at 92°C

3.4.3 Conclusion

The extraction process results largely in nitrogen containing material, much of which is derived from collagen, along with a small amount of minerals. The roasting process and size of the bones within the range tested did not affect the overall yield of solids-non-fat from the bones. The rate of extraction decreases with time and relative to the amount that is extracted in the current 3 day process about 67% of the material is extracted after 1 day and 95% of the material is extracted after 2 days. Minerals have the fastest rate, and collagen material is slowest. Overall a reasonable measure of the extraction kinetics can be determined by measuring the change of concentration of solids non-fat.

3.5 Concentration studies of current stock

The current stock produced by EC has a solids concentration between 15-18% which is produced by atmospheric pan evaporation. Samples of EC's original stock extracts from EC were vacuum concentrated in a series of studies to look at the potential of increasing the solids concentration and the effect of the process on the product flavour and taste.

3.5.1 Materials and methods

EC provided extract from bones at approximately 6.8°Brix. The stock was stored overnight at 5°C.

The extract was then pre-heated in a stainless steel bucket placed in a vessel of hot water as the stock had set in a gel during refrigeration. The stock was heated sufficiently to melt the gel.

Evaporation was carried out in a rising film vacuum evaporator (Anhydro Laboratory Vacuum Evaporator (Anhyrdro, Denmark)) at the Massey University pilot plant. The vacuum was controlled by setting the flowrate of the cooling water through a liquid seal pump. The main calandria comprised of a shell (tube of 165 mm internal diameter 1000 mm high) with 18 tubes (22 mm internal diameter and 800 mm high). The separator was a cylinder of (500 mm internal diameter and 480 mm high) with a tube to draw vapours (100 mm diameter 400 mm high). The concentrate was recovered and fresh feed added by opening the feed valve. Vapours were condensed by the cooling water that doubled as a vacuum generator. The concentrated solution that came out at the top of the tube bundle was returned to the bottom of the tubes via the down tube of 1400 mm length and 100 mm diameter.

3.5.1.1 Operation of the evaporator

This evaporator was run in batch mode. The vacuum pressure was kept at 0.7 bar vacuum. The evaporator was first run with water on the product side in order to warm the surface of the evaporator before stock was introduced as cold surfaces could cause gelling of the extract. The water was drained from the evaporator before the raw extract was added.

When the vacuum was applied the stock extract was automatically sucked in from the feed tank and controlled by the feed valve. Twenty litres of feed where sucked in for each cycle and left to re-circulate until the right concentration was reached.

The initial stock concentration was 6.8°Brix. Operating conditions for the evaporator settled at the following within 10 minutes of start up:

- Steam temperature 80 ± 4°C.
- Steam pressure 0.6 bar vacuum
- Product Temperature 58 ± 2°C
- Vacuum pressure 0.7 bar vacuum

The total solids were determined from the Brix using the method given in Section 3.1.3. Samples were taken periodically using a syringe through a septum that was located at the bottom of the tube bank.

3.5.2 Results and Discussion

It was observed that the product flow through the tubes was very turbulent and caused the stock to foam. At times the foam rose sufficiently high in the product tank to flow through the vacuum pump. When this happens a proper mass balance cannot be made between the feed and the final product.

The stock was successfully reduced to 40°Brix in the first trial and 22.5°Brix in the second trial. Samples were taken for sensory testing by the client.

From the data recorded during the runs it was estimated that an evaporation of 50 L per hour was achieved. The evaporator overall heat transfer coefficient is estimated at 2.0 kW $m^{-2} K^{-1}$ which is a typical value for evaporators.

The feedback from the client was that the stocks had a good flavour but where thicker than the current stocks even at the same concentration.

Therefore it is concluded that vacuum evaporation even in a batch evaporator with a relatively long residence time gives a better texture than pan evaporation at atmospheric pressure. Possibly even better results could be made if a falling film evaporator with a much shorter residence time was used.

3.6 UHT treatment of stock

The objective was to determine the effects that UHT processing has on Essential Cuisine beef stock in terms of flavour, texture and colour.

3.6.1 Materials and Methods

3.6.1.1 Materials

Processed commercial stock at 18.6 g 100 g^{-1} solids concentration was provided by Essential Cuisine Limited. The stock was received and stored at 4°C before used for processing.

3.6.1.2 Equipment

The UHT processing plant (Alfa-Laval) in the Massey University Food Pilot plant was used.

3.6.1.3 Method

The plant was sterilised by running hot water through the product side. The water was heated in the main heat-exchanger to 150°C and the temperature in the pre-heater and cooling tube was maintained above 120°C. Water was circulated at these temperatures for 30 minutes, sterilising all of the product contact surfaces from the pre-heater onwards.

The processing conditions used were 145°C with a holding time of 5 s. The pre-heater was not used, the main heater was set to a temperature of 145°C and this was automatically controlled with a thermal couple feeding back to the boiler. Cooling water was circulated in the cooling section. The plant was run on water in order to establish stable temperature and correct product flow rate conditions. The heating temperature established at 145 ± 1°C and the temperature on the product side exiting the plant was 22 ± 1°C.

The flowrate was set to 1.00 ± 0.03 L s^{-1} in order to achieve a holding time of 5 s by adjusting the speed of the pump and measuring the flow exiting the plant with a stop watch and 1 L measuring cylinder.

Once the temperatures were stabilised and the flow was correct, stock was placed into the second holding tank and the valve was opened in order to pump the stock into the plant. Three litres of stock was used. Product was taken once it was observed to have flowed through the plant.

Product was collected and then placed into foil laminate pouches and heat sealed.

Sensory analysis was conducted by pouring 60 mL of stock into porcelain dishes. The dishes were heated in a microwave for 20 s. Odour was observed by sniffing and flavour and texture

by tasting. Colour was also compared visually. Samples were also sent to EC and analysed by a chef and a waitress.

Rheological measurements were made as described in section 3.1.3.6. and colour was determined as in section 3.1.3.5

3.6.2 Results

The sensory analysis conducted at Massey University is presented in Table 3-9 with the comments by a chef and a waitress discussed below.

Table 3-9 Sensory results observed by author at Massey University

Stock	Fresh, Non UHT treated	UHT treated
Texture	Has a week like gel texture that breaks down in the mouth to leave an astringent feel.	Thinner texture in the mouth. Breaks down to an astringent feel.
Odour	A fresh sweet fatty flavour and odour.	The odour is meaty but with a stronger caramel, burnt type smell rather than sweet fatty.
Flavour	The flavour is bland but meaty, sweet and fatty with a strong bitter/metallic after taste.	Flavour has a stronger roasted flavour rather than fresh fatty with a bitter/metallic after taste.
Colour	Dark red/brown	Dark/red brown

The UHT stock appeared to be thinner in the mouth its odour and flavour changed because the UHT sample had a stronger roasted flavour. No difference was seen in the colour.

The fresh sample and UHT samples were tasted by a chef. The chef commented that the fresh sample compared to the UHT sample "was gutsier, tasted stronger, more body." The UHT however was "not too bad, if you had nothing to compare it with." It was concluded that a chef would be able to tell the difference between a UHT and non-UHT sample and preferred the non-UHT sample.

A waitress was also presented with the fresh and UHT samples and commented that the fresh sample was "stronger in terms of flavour" but preferred the "smoother flavour of the UHT sample.

There is a difference between the fresh and UHT in terms of taste and texture. The difference is small but is expected to be noticed by chefs and would be distinguished by a trained taste panel.

The results for solids, Brix, pH and density are presented in Table 3-10. The results show that the UHT process does not change Brix or density. The solids content decreases slightly with UHT, although this is minimal and may be due to diluting of the sample. The pH decreased slightly with UHT treatment indicating the UHT resulted in some chemical changes in the stock.

Table 3-10 Physical and chemical analysis of Fresh and UHT stock samples

	Fresh Stock	UHT treated
Solids concentration (g $100g^{-1}$)	18.42 ± 0.01	18.26 ± 0.04
°Brix	22.6 ± 0.1	22.6 ± 0.1
pH	6.34 ± 0.02	6.15 ± 0.01
Density (kg m^{-3})	1063 ± 1	1064 ± 1

The measured colour differences (Table 3-11) show that no significant difference between fresh and UHT treated stock for any of the colour parameters indicating that there is no change in colour due to the UHT process. This is consistent to what was observed in sensory analysis.

Table 3-11 Colour measurements of Fresh and UHT treated samples

Parameter	Fresh Stock	UHT treated
L*	29.818 ± 0.008	29.823 ± 0.024
a*	1.45 ± 0.09	1.50 ± 0.04
b*	1.07 ± 0.04	1.09 ± 0.03

The particle size distribution for all of the samples (Figure 3-22) shows a typical particle distribution curve that has previously been observed. There is some evidence that the UHT

process has resulted in a higher proportion of particles at 300µm at the expense of particles between 10 and 80 µm.

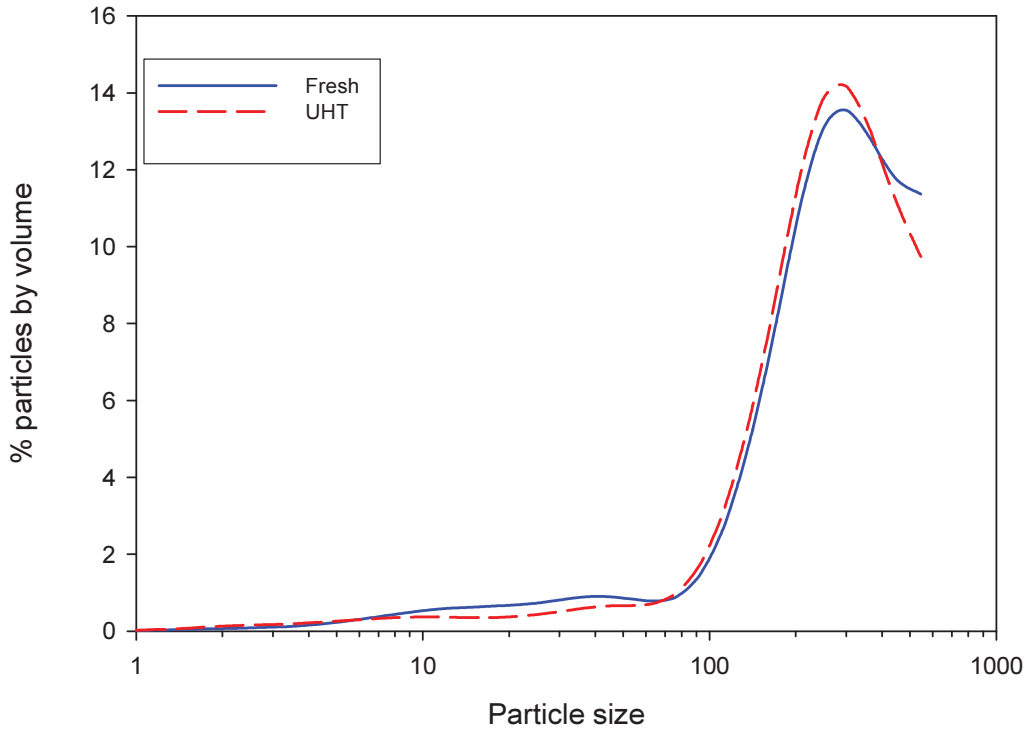

Figure 3-22 Particle size distributions for for Fresh and UHT treated stock samples

Flow curves at 20°C with shearing up and down legs for both Fresh stock and UHT stock are given in Figure 3-23. The curves for UHT and Fresh stock show similar behaviour to each other and to previous measurements on stock in section 3.2.3.1. Slight shear and time dependency is observed.

Comparing the shear sweeps for fresh and UHT treated stocks shows slightly lower values of shear stress for UHT treated stock. Therefore UHT treated stock has a slightly lower apparent viscosity for a given shear rate. The observation is consistent with the sensory analysis which reported a lower thickness for the UHT treated stock. The slight change in the apparent viscosity could be due to the slight dilution or that the high UHT temperature has degraded the gelatine.

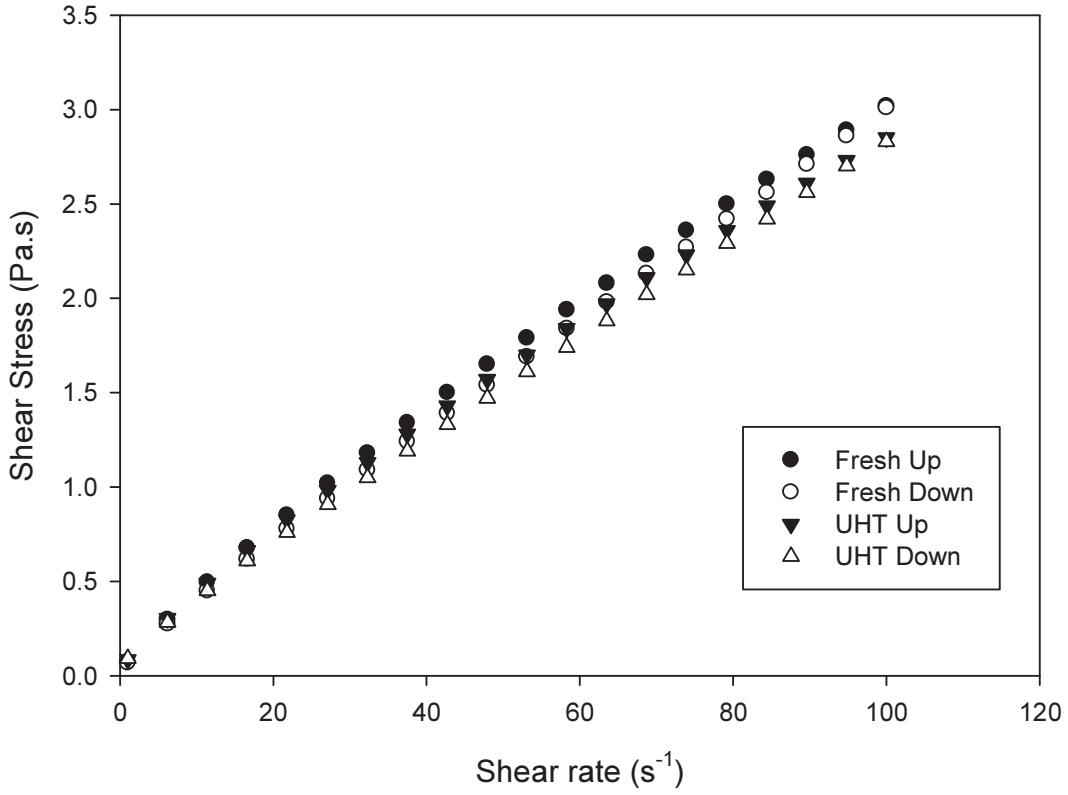

Figure 3-23 Flow curves (shearing up and down legs) for Fresh and UHT Stock

3.6.3 Conclusions

It was concluded that UHT treatment did cause changes to the texture and flavour but not colour. The changes were detectable but relatively small. It was concluded that UHT processing could be used, but the resulting product would be of a lower quality.

4 Research Objectives

After consideration of the current process and product, the following objectives were set for the experimental work in this project to complement the data which is not available anywhere in the open literature or by examining current processes.

1. Determine the kinetics of textural changes with temperature and time of the bone extract.
2. Determine the extraction kinetics of solids-non-fat (SNF) from bones using hot water.
3. Measure the extractable SNF content of the bones. This is different from the content of collagen in the bones.
4. Determine the equilibrium distribution of the extractable SNF between the solid phase (bones) and the liquid phase (water).

5 Kinetics of textural and viscosity changes with temperature and time for bone extract

The aim of this Chapter was to characterise the texture of the bone extract and how it was affected by concentration and exposure to temperature and time. The apparent viscosity was used as an indication of texture.

5.1 Materials and Methods

5.1.1 Preparation of bone extract

Bone extracts were prepared using thawed bones that had some attached meat and connective tissue that were obtained from Silver Fern Farm's Pacific beef plant. The bones were placed in stainless steel trays and roasted in a hot air oven at 220°C for 20 minutes in order to simulate the EC manufacturing process.

About 20 kg of the roasted bones were placed into a water jacketed tank maintained at 91 ± 2°C. Cold water was added to the roasted bones in a 1:1 ratio. The water reached a temperature of 91 ± 2°C within 2 hours and was maintained at this temperature for 72 hours after which the bones were removed. Cold water (10^{o}C) was run through the jacket for 2 hours to cool the extract. The layer of fat on top of the solution hardened and was skimmed from the tank. The remaining solution was filtered through a 200 µm mesh and stored in 20 L buckets. Typical yields for the process was 17 L of extract at 7°Brix. Stock was frozen and stored at -30°C.

Three batches of extract were thawed at 40°C, mixed, and then concentrated. Concentration was performed using the rising film vacuum evaporator described in section 3.5. Concentration from 7 to 20°Brix was completed within 20 minutes and then diluted to the appropriate concentrations with water. Samples of 150 mL were filled into retort pouches, frozen and stored at -30°C.

5.1.2 Heat Treatments

Pouches of the product were thawed to room temperature (~20^{o}C) and placed in a water bath at temperatures of 60, 70, 80, 90°C. For 100°C, 120°C treatments the samples were placed into Kimax test tubes that were sealed with a screw cap lid and soya bean oil was used as the heating medium in the bath. Table 5-1 provides a summary of the heat treatments. The temperature of the heating medium was controlled within ± 1°C. Samples were taken at regular intervals over a period of three days and placed in ice water for immediate cooling. Samples were then stored at -30°C until required for rheological measurements.

5.1.3 Rheological Determination

Frozen samples (150 mL) were thawed by placing the pouches into a 40°C water bath. Then 20 mL aliquots were drawn from the pouches and filled into the rheometer. The rheometer used is described in Section 3.1.3.6.1. A 10 minute equilibration time was used prior to shearing to ensure the sample was at the correct temperature. The rheometer was used in control shear rate mode and a shear sweep was performed for shear rates between 2 and 120 s^{-1}, by shearing up over a time of 200 s, holding at 120 s^{-1} for a time of 15 s and then shearing down to 2 s^{-1} over a time of 200 s. Measurements were recorded at 5 s intervals. Measurements were performed at 20, 30, 40, 50 and 60°C for runs H1-H5 and at 40°C for runs H6-H12. A summary of the experimental runs is given in Table 5-1.

Table 5-1 Summary of experimental runs for heat treatments

Run	Temperature (^{o}C)	Solids Concentrations (^{o}Brix)	Sampling Times (h)
H1	60	20	0, 0.5, 8, 24, 48, 72
H2	70	20	0, 0.5, 8, 24, 48, 72
H3	80	20	0, 0.5, 8, 24, 48, 72
H4	90	20	0, 0.5, 2, 4, 8, 24, 48, 72
H5	100	20	0, 0.5, 24, 48
H6	60	5, 10, 15, 20	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.4, 4.0
H7	70	5, 10, 15, 20	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.4, 4.0
H8	80	5, 10, 15, 20	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.4, 4.0
H9	90	5, 10, 15, 20	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.4, 4.0
H10	100	5, 10, 15, 20	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.4, 4.0
H11	120	5, 10, 15, 20	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.4, 4.0

5.2 Results and Discussion

5.2.1 Replication of measurements

Three replicate flow curves with shear up and shear down legs are plotted for 20°Brix bone extract measured at 40°C are given in Figure 5-1. The shear up and shear down legs coincide indicating that this material is rheologically time-independent. The replicates show good

agreement and the uncertainty in the slopes of the three replicates is 1.63% based on a 95% confidence interval.

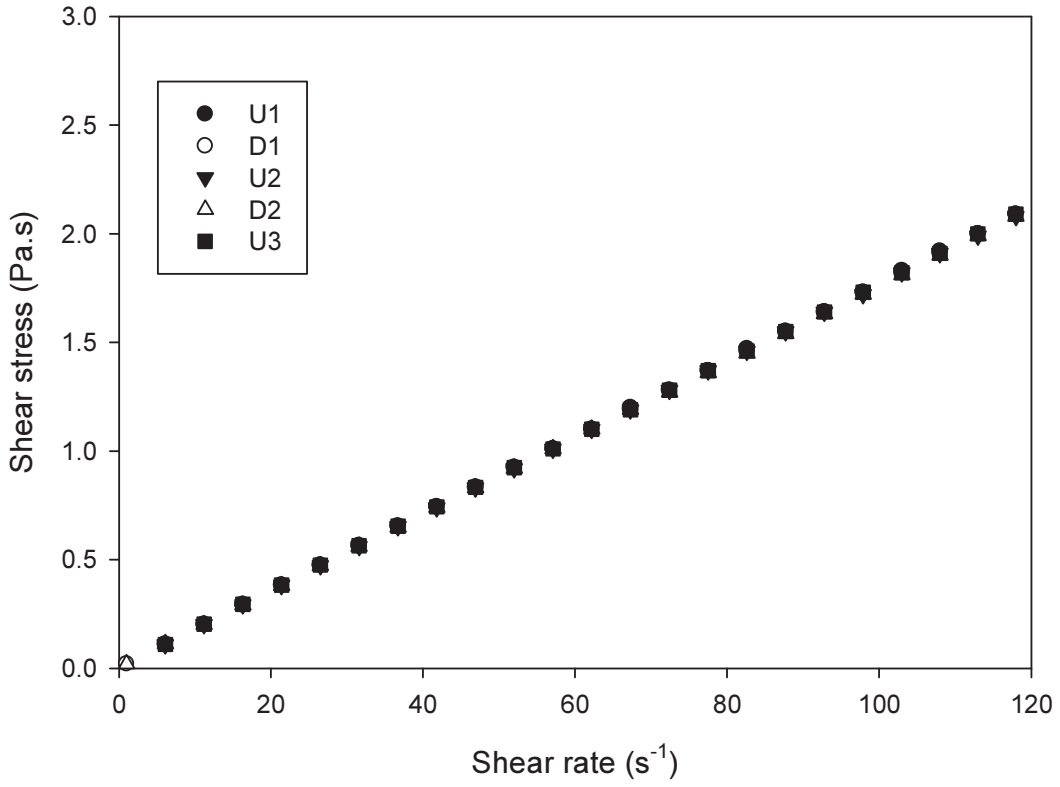

Figure 5-1 Flow curves with shear up (U) and down (D) legs for replicates (1), (2) and (3) for 20°Brix bone extract measured at 40°C.

5.2.2 Modelling of rheological curves

Linear equations were fitted to all the curves. An example is given in Figure 5-2 which shows the fitted line passes through the centre of all the data points. Fitted lines for all the experimental runs gave R^2 values greater than 0.9998 and low standard error of fit, less than 0.02 Pa. It was found that some of the intercepts were statistically significant. However, the maximum intercept was 0.014 Pa which was still smaller than the minimum stress of 0.015 Pa that the rheometer could detect within the reliable range as shown by the assessment in 3.1.3.6.2. The fitted lines were forced through the origin (i.e. the samples were considered Newtonian) firstly because the intercepts were considered non-significant on physical grounds and secondly because the procedure did not alter the value of the slope of the regression line significantly from the Bingham plastic model; the largest error was 1%. The slope's regression coefficient for each measurement is show in Table 5-2.

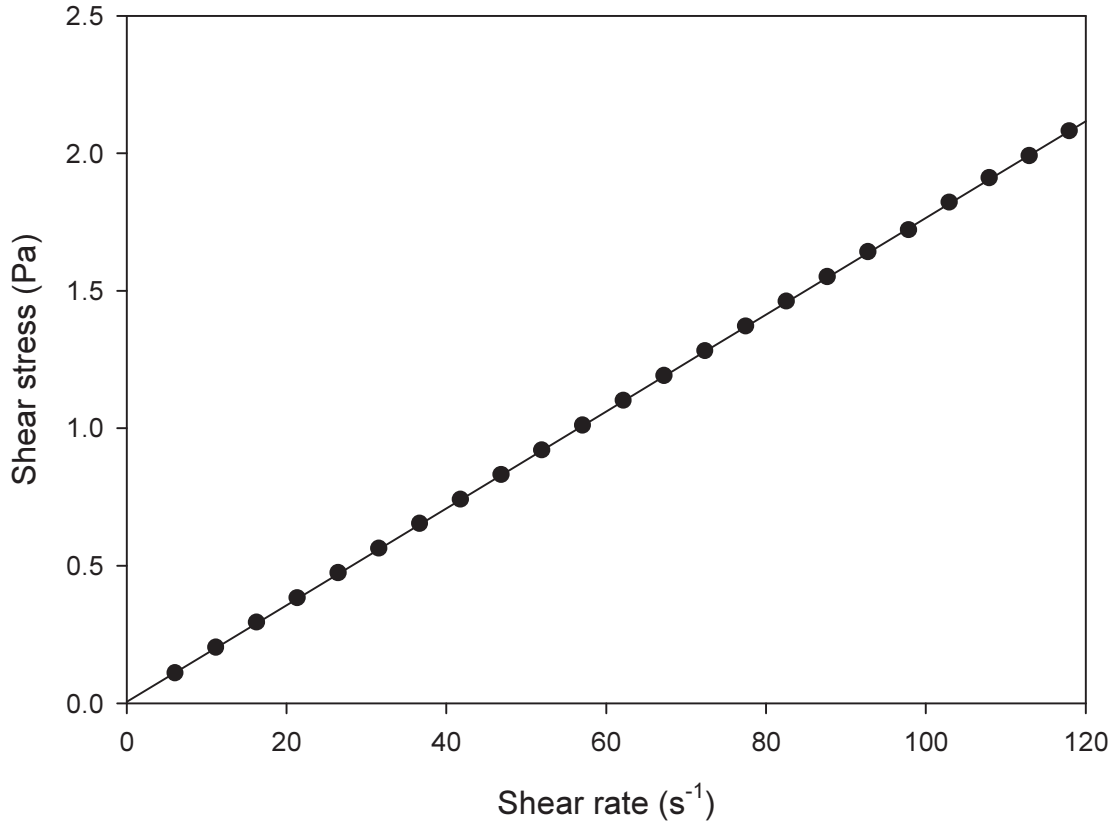

Figure 5-2 Linear curve fit for shearing up leg of extract measured at 40°C

Table 5-2 Data for fitted Newtonian fit for flow curve data for 20°Brix extract

Measurement temperature	Replicate	Shear Up leg				Shear Down leg			
		Slope	SE of slope	R^2	SE of fit	Slope	SE of slope	R^2	SE of fit (Pa)
20	R1	0.04970	0.00005	1.0000	0.0086	0.05010	0.00008	0.9999	0.0102
20	R2	0.04760	0.00003	1.0000	0.0059	0.04770	0.00009	0.9999	0.0206
20	R3	0.04770	0.00002	1.0000	0.0052	0.04780	0.00010	0.9998	0.0225
30	R1	0.02640	0.00003	1.0000	0.0057	0.02630	0.00002	1.0000	0.0035
30	R2	0.02540	0.00003	1.0000	0.0057	0.02540	0.00002	1.0000	0.0053
30	R3	0.025	0.00002	1.0000	0.0052	0.025	0.00002	1.0000	0.0051
40	R1	0.01767	0.00002	1.0000	0.0036	0.01763	0.00002	1.0000	0.0033
40	R2	0.01760	0.00001	1.0000	0.0025	0.01760	0.00001	1.0000	0.0025
40	R3	0.01756	0.00002	1.0000	0.0033	0.01766	0.00001	1.0000	0.0018
50	R1	0.01390	0.00002	1.0000	0.0028	0.01390	0.00002	1.0000	0.0026
50	R2	0.01320	0.00001	1.0000	0.0023	0.01320	0.00001	1.0000	0.0025
50	R3	0.01380	0.00001	1.0000	0.0029	0.01390	0.00001	1.0000	0.0033
60	R1	0.01160	0.00002	1.0000	0.0025	0.01160	0.00002	1.0000	0.0027
60	R2	0.01190	0.00002	0.9999	0.0035	0.01190	0.00002	1.0000	0.0026
60	R3	0.01120	0.00001	1.0000	0.0024	0.01120	0.00001	1.0000	0.0024

The mean viscosity and its standard deviation for triplicate measurements of bone extracts at 20, 30, 40, 50 and 60°C are reported in Table 5-3.

Table 5-3 Mean viscosity of 20°Brix extract calculated from flow curves

Temperature	Viscosity (Pa s)	% uncertainty (95% level of confidence)
20	0.0485 ± 0.0016	3.27%
30	0.0256 ± 0.0018	6.99%
40	0.0177 ± 0.0003	1.53%
50	0.0136 ± 0.0009	6.89%
60	0.0115 ± 0.0005	4.37%

An Arrhenius plot was constructed for viscosity (Figure 5-3) as it is observed that the relationship between viscosity and the temperature of measurement follows the Arrhenius relationship (Croome, 1953; Marcotte, 2001). But it failed to fit a straight line (fitting of line is not shown). Therefore the interactions induced between the components in the sample upon heating are likely to be complex and numerous.

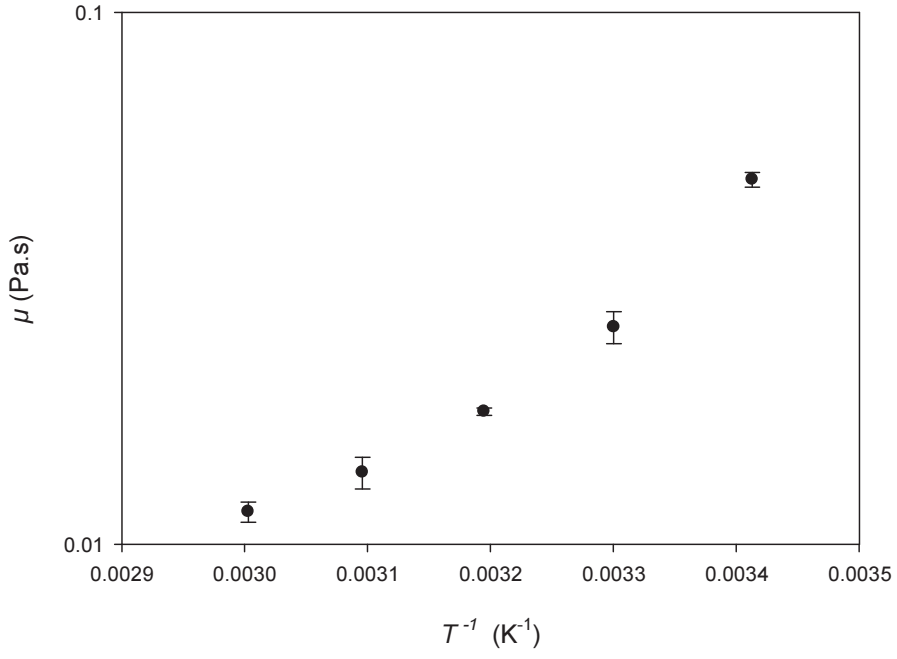

Figure 5-3 Arrhenius plot for viscosity for given measurement temperatures

However, the bone extract is characterised as a Newtonian fluid above 20°C. This means that above this temperature, measurement of the Newtonian viscosity provides a measure for the texture of the product.

5.2.3 Repeatability of the heat treatment test

Three replicate heat treatments were performed at 90°C for four hours. Straight line relationships through the origin were fitted with the slope giving the viscosity of the aliquots taken at the end of the four hour treatment is shown in Table 5-4. The three replicates show reasonable agreement and the 95% uncertainty calculated from the replicates was found to be less than 5% for all measurement temperatures. Therefore there is good repeatability for the heat treatment and measurement of viscosity.

Table 5-4 Mean viscosity and uncertainty for triplicate heat treatments

Measurement Temperature	Viscosity (Pa.s) R1	Viscosity (Pa.s) R2	Viscosity (Pa.s) R3	Viscosity (Pa.s)	% uncertainty for 95% confidence interval
20°C	0.0411	0.0434	0.0427	0.0424 ± 0.0013	3.12%
30°C	0.0247	0.0230	0.0230	0.0236 ± 0.0011	4.73%
40°C	0.0169	0.0165	0.0166	0.0166 ± 0.0002	1.39%
50°C	0.0129	0.0132	0.0131	0.0131 ± 0.0002	1.23%
60°C	0.0106	0.0109	0.0107	0.0107 ± 0.0002	1.74%

5.2.4 Effect of temperature and time

As discussed in section 5.1.2 the effect of temperature on the viscosity of the different samples were made with single non-replicated tests.

The viscosity for all of the heat treatments was calculated as the slope of a straight line passing through the origin. This viscosity was then expressed as a fraction of the initial viscosity for zero time treatment. The error bars are based on the 5% uncertainty established in 5.2.3.

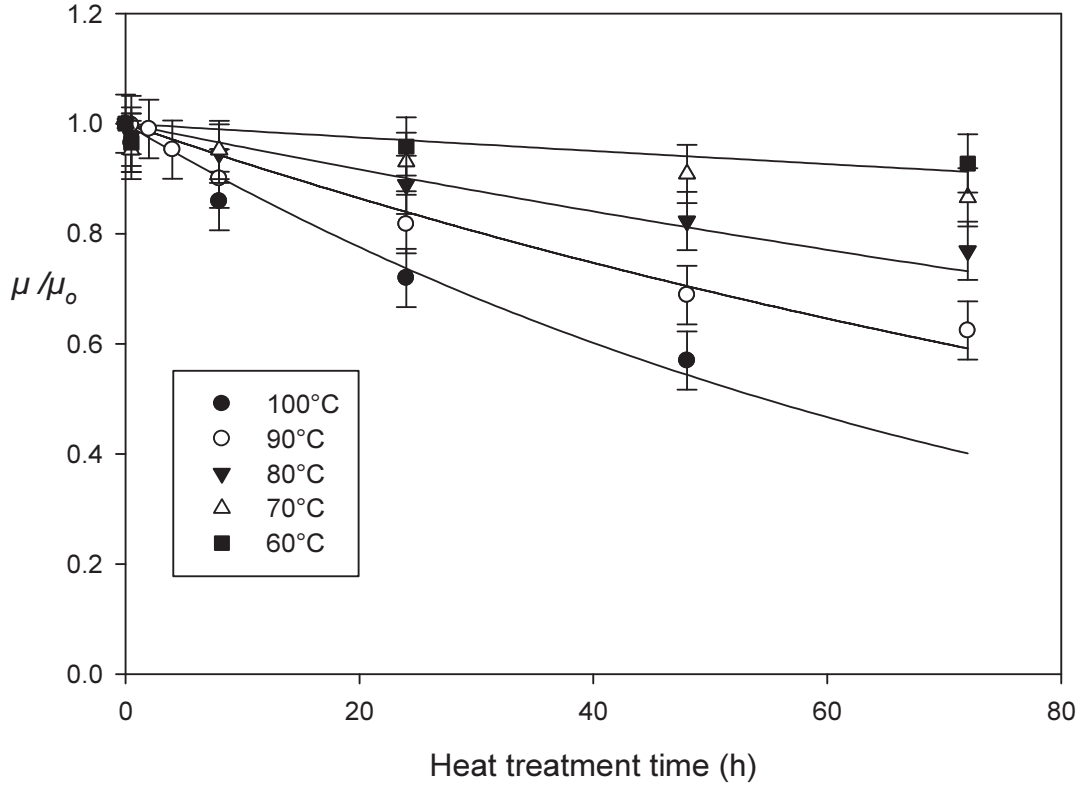

Figure 5-4 Decay in relative viscosity with time for 20°Brix extract heat treated at 60, 70, 80, 90 and 100°C when the viscosity of the extract was measured at 40°C

As shown in Figure 5-4, a heat treatment of 100°C over 2 days resulted in a 40% reduction of viscosity. The data also shows that the current EC concentration process, which is equivalent to heating at 90°C for 3 days, must result in a 25% loss of viscosity. Heating at 60°C for three days only resulted in a 5% loss of viscosity which is less than the uncertainly of measurement.

The observation of decline in viscosity for gelatine with exposure to temperatures for a period of time is reported by others (Ames, 1947; Croome, 1953; Johnstone-Banks, 1990). Ames (1947) found the rate of decline was increased with exposure to higher temperatures and longer exposure times. An acid or alkaline pH was also found to increase the rate of degradation. The cause of the decline is said to be due to hydrolytic cleavage of the gelatine chains resulting in a weaker gel strength and lower viscosity. Croome (1953) states that the rate of degradation for a given temperature and pH follows first order kinetics.

Later extraction experiments were conducted at 120°C for 4 hours. Therefore, for design purposes samples were heat treated for a range of higher temperatures and much shorter times (Runs H6-H11).

5.2.4.1 Effect of concentration

The effect of extract concentration on the viscosity before and after heat treatments (H6 to H11) was investigated. The measured Brix and viscosity is plotted in Figure 5-5, where the error bars represent the 95% confidence interval for Brix and viscosity based on the 6 replicates.

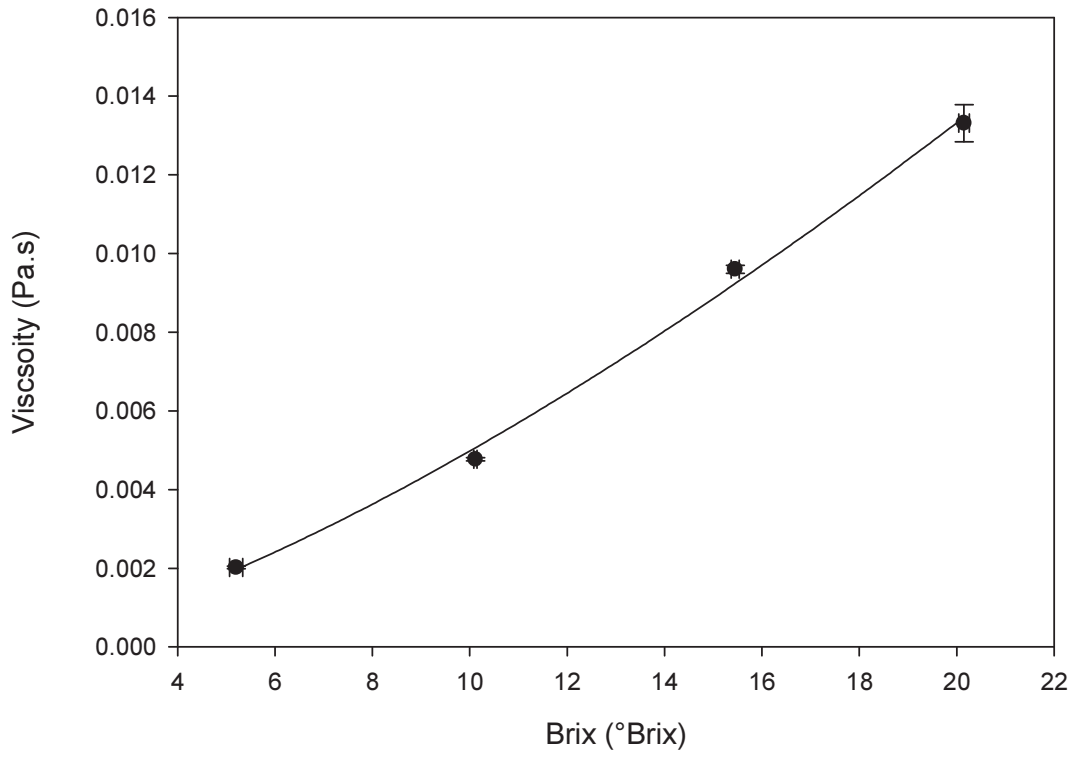

Figure 5-5 Relationship of viscosity measured at 40°C with soluble solids for samples H6-H11 prior to heat treatments.

It was found that as the concentration increased from 5°Brix to 20°Brix the viscosity increased 6.5 times. The relationship is not linear and a power law fits the data well with an R^2 of 0.9968 and the standard error of estimate is 0.0004Pa.s. The equation for the relationship is described by

$$\mu = 0.00020(brix)^{1.42} \qquad (5.1)$$

The relationship needs correction as the stock extract used was already subjected to heat during the extraction process which is an additional exposure on top of the heat treatment described in section 5.1.2. Therefore the viscosity correlated in equation 5.1 does not represent the virgin viscosity of material not yet exposed to heat. Using a method in Chapter 7

it is estimated that the process would reduce the viscosity at 20°Brix by 9.0%. Therefore μ_0 the theoretical viscosity without any heat exposure is given by

$$\frac{\mu_0}{\mu} = 1.11 \qquad (5.2)$$

It is assumed that the exponent 1.42 remains the same for the corrected equation, then only the constant multiplier in equation 5.1 (0.00018) which is defined as (*A*) will change. The new constant A_o can be determined from

$$\frac{A_0}{A} = \frac{\mu_0}{\mu} = 1.11 \qquad (5.3)$$

$$A_0 = 1.11 \times 0.00020 = 0.00022 \qquad (5.4)$$

Thus the equation to describe μ_0 is

$$\mu_o = 0.00022(brix)^{1.42} \qquad (5.5)$$

This relationship described by equation 5.5 is empirical so no attempt has been made to explain it in terms of a fundamental mechanism. The equation only applies to stock measurements made at 40°C. While the data is available to model both the viscosity as a function of solids concentration and measuring temperature, it was decided that a measurement temperature of 40°C was practical and determining the viscosity at other temperatures was not necessary.

The viscosity of the 20°Brix solution for H1-H5 was found to be 0.0166 Pa.s (when measured at 40°C) which is 20% higher than the value of 0.0133 Pa.s for the solution used for H6-H11. This significant difference is due to the different raw materials and extraction processes used. Therefore equation (5.5) is unique to the batch of extract used for the study, the extract used for Runs H6-H11, although the proportional changes with concentration would be similar.

Because the viscosity is expressed as a fraction of the initial viscosity i.e. μ/μ_0, then it is possible to compare the results obtained from different batches of stock that have been given the same temperature/time treatments.

A comparison for the data for heat treatments at different temperatures (H6-H11) at 20.2°Brix is shown in Figure 5-6. The decline in viscosity at 120°C was greater than the other treatments and viscosity dropped to about 65% of the original viscosity when heated for 4 hours. The decline for the other temperatures was minimal over 4 hours.

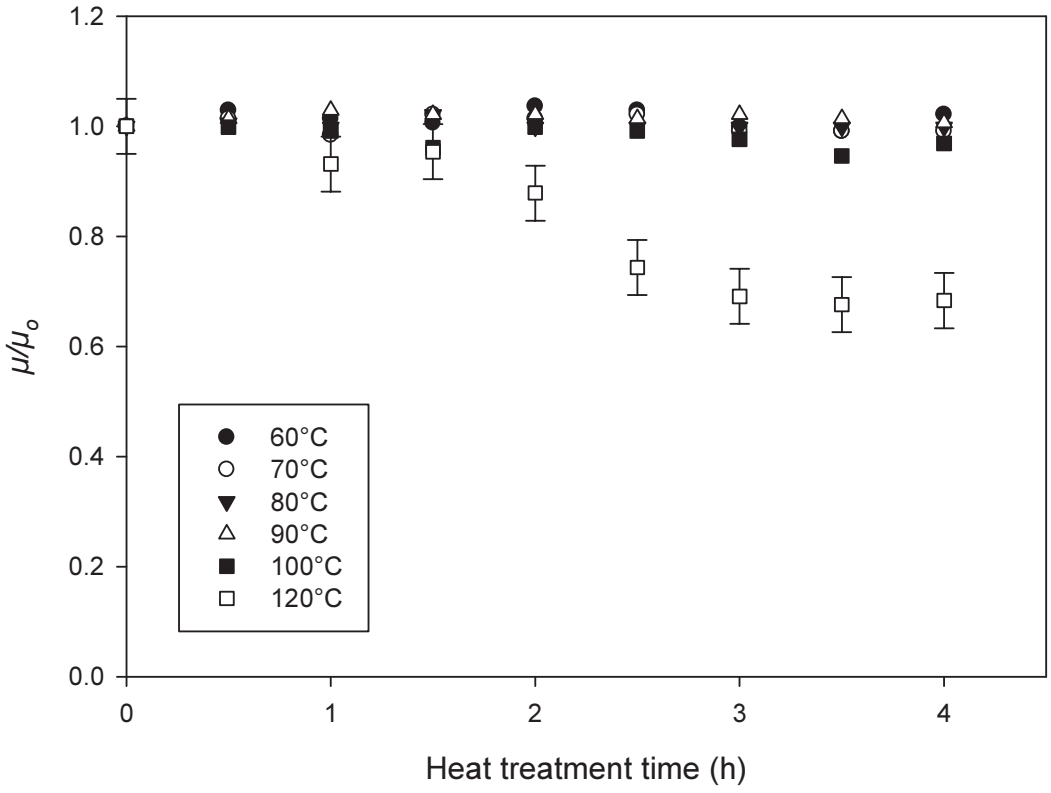

Figure 5-6 Effect of time on the relative viscosity for different heat treatment temperatures for 20.2°Brix extract. Error bars are shown on the 120°C treatment.

The effect of concentration on the change in viscosity with heat treatment at 120°C is shown in Figure 5-7. The error bars are of similar magnitude for all concentrations. Only the error bars for the 20.2°Brix concentration is shown in Figure 5-7 and they are based on the uncertainty of the viscosity measurement and the uncertainty calculated in the replications of heat treatment. Figure 5-7 shows similar trends for all of the concentrations and all results are within the experimental uncertainty. Therefore the decline in viscosity is independent of concentration.

At heat treatment temperatures less than 120°C the decrease in viscosity is less than the uncertainty of measurement for the four hour period, so these data are not useful in determining the effect of concentration.

Therefore it is concluded that concentration does not affect the rate of breakdown of relative viscosity due to temperature treatments between 60 and 120°C.

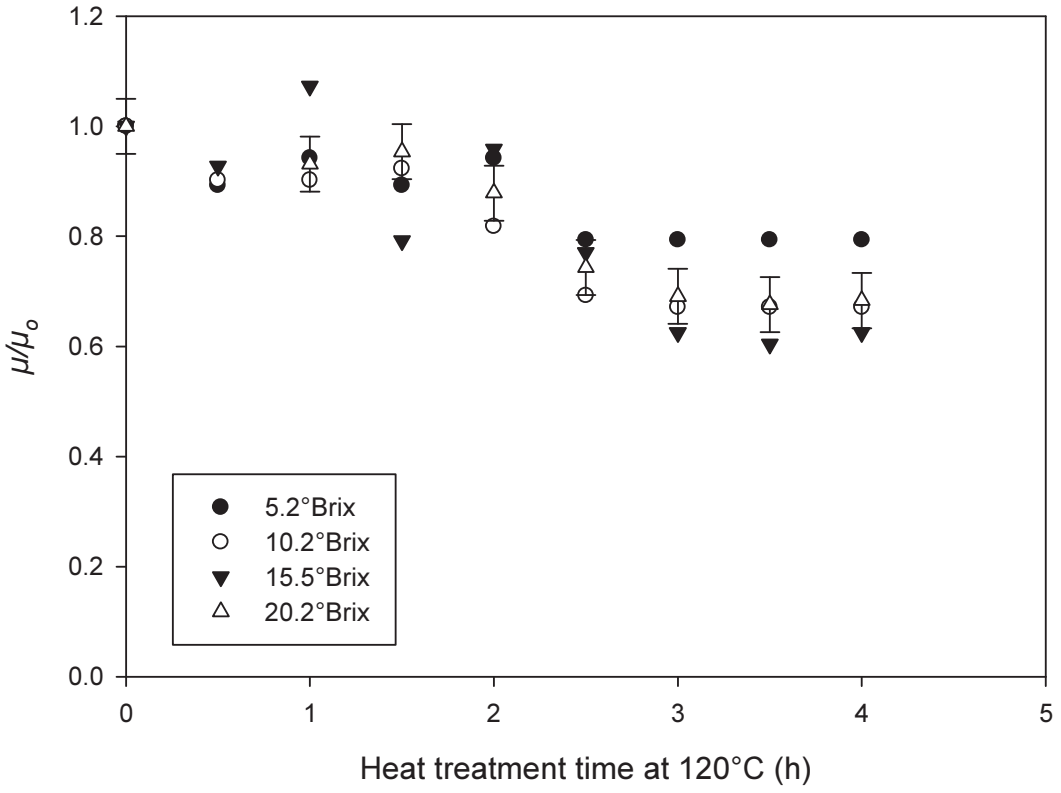

Figure 5-7 Effect of concentration on the relative change of viscosity (measured at 40°C) for a heat treatment of 120°C with error bars on the 20.2°Brix data.

5.2.5 Modelling of the kinetics of viscosity change with exposure to heat

In order to model the decay of viscosity as a function of time and temperature the data from the first experiment was used as this provided a greater extent of reaction due to the longer time. As it was found that concentration did not matter this was not considered in the modelling.

The decay in time of the fractional viscosity in Figure 5-4 appears to follow an exponential decline. Therefore a plot of $\log(\mu/\mu_o)$ versus time is given in Figure 5-8 and demonstrates a straight line relationship indicating that the decline was exponential.

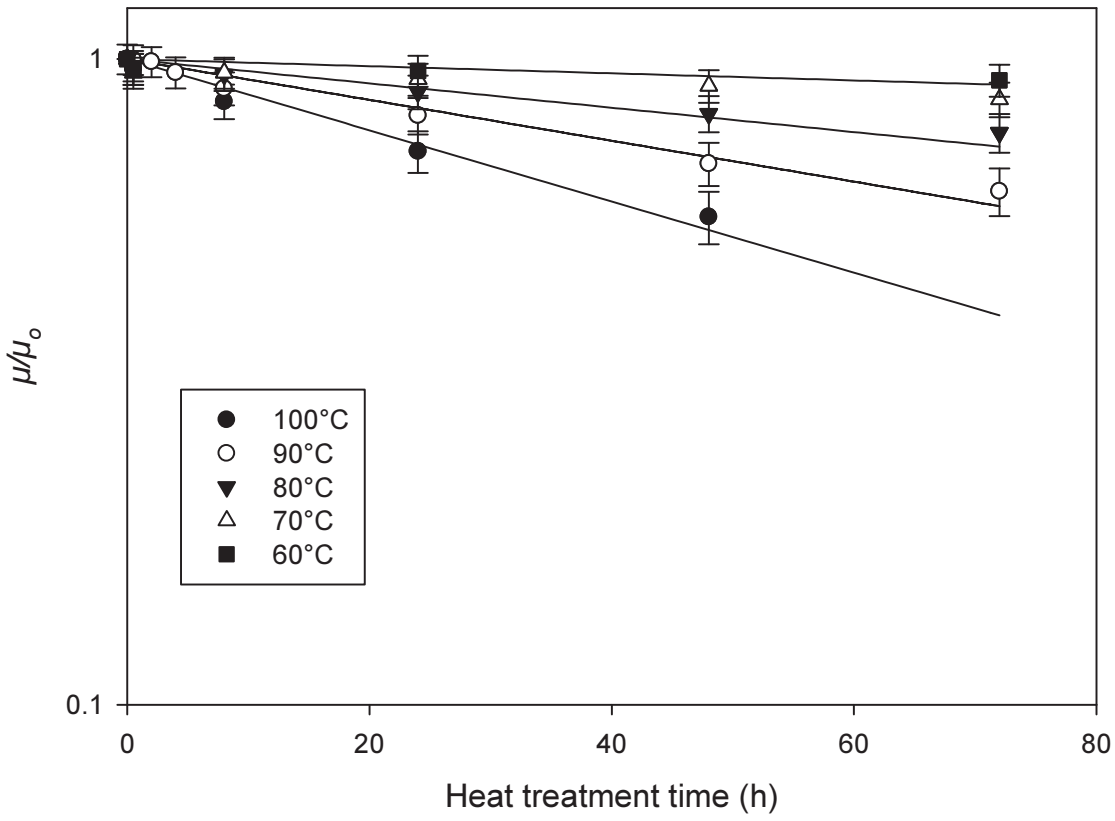

Figure 5-8 Decline in relative viscosity on a log scale with fitted first order kinetics

Therefore first order kinetics was fitted using SIGMA PLOT (least squares method) to describe the decay of fractional viscosity (Equation 5.6).

$$\frac{\mu}{\mu_0} = e^{-kt} \qquad (5.6)$$

where μ/μ_0 = viscosity expressed as a fraction of the original viscosity and k is the rate constant (h^{-1}) and t is time in hours.

The fitted exponential line is within the uncertainty of the data for all data points. As an example the treatment at 90°C has an R^2 value of 0.917 and a standard error of estimate of 0.02 indicating a good fit. Measures of fit for other temperatures had similar values.

To test the model the predictions were fitted to the four hour data at 20°Brix and this is shown in Figure 5-9 for the heat treatment of 100 and 120°C. For the heat treatment of 100°C the data fits the model, although the change in the four hour period is less than the uncertainty of measurement. This trend was also observed for heat treatment temperatures of 60, 70, 80

and 90°C. For the 120°C heat treatment some of the data points do not fit the curve within the calculated uncertainty, indicating there was additional errors.

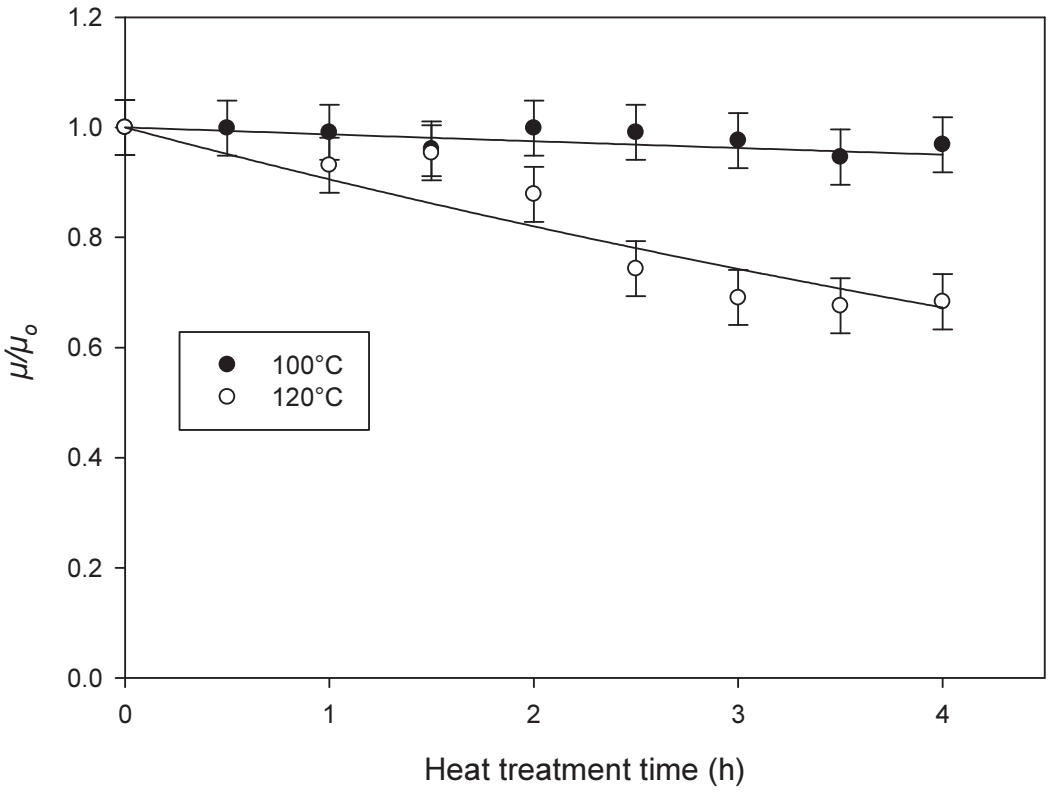

Figure 5-9 Fitted exponential models with experimental data for extract at 20.2°Brix for 100°C and 120°C heat treatments

It was observed that the heat treatment at 120°C was found to have poor control with fluctuations in temperature of up to 10°C. The 120°C heat treatment samples were placed in Kimax tubes, some of which were found to have poor seals which probably allowed some moisture to evaporate. This was confirmed with some tubes having soluble solid values as high as 1°Brix above their 20.2°Brix starting values which could explain the additional errors seen in the data. To gather more precise data the temperature control and the tubes used for the heat treatment need to be improved.

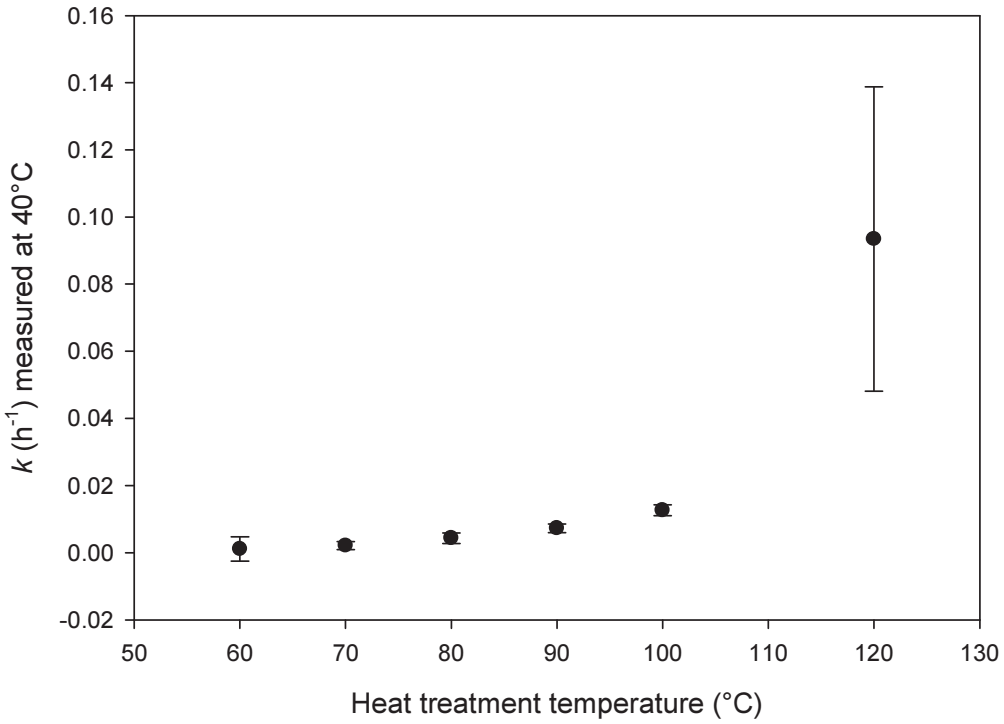

Figure 5-10 The characteristic rate constant (*k*) for viscosity decay (measured at 40°C) plotted as a function of heat treatment temperature for bone extract at 20°Brix

The characteristic rate constant was plotted as a function of heat treatment temperature for each of the measurement temperatures (Figure 5-10). The uncertainties were calculated using the 95% confidence intervals for the fitted coefficient *k*. The calculated uncertainties for the lower treatment temperatures are relatively large due to the small number of points used for the regression. At heat treatment temperatures of 60 and 70°C, *k*, is very low and the uncertainties indicate that it is not significantly different to zero indicating very little loss of viscosity at these temperatures. The heat treatment at 120°C shows a rapid rise in *k* and a large uncertainty, due to the errors previously mentioned. Because of the big change in *k* going from 100 to 120°C it is recommended that more data be collected above 100°C and up to and including 120°C.

The Arrhenius plot constructed for *k* at the different heat treatment temperatures is given in Figure 5-11. In general the data shows a straight line, but there is some deviation at the high temperature (120°C) which is known to have some unaccounted for errors.

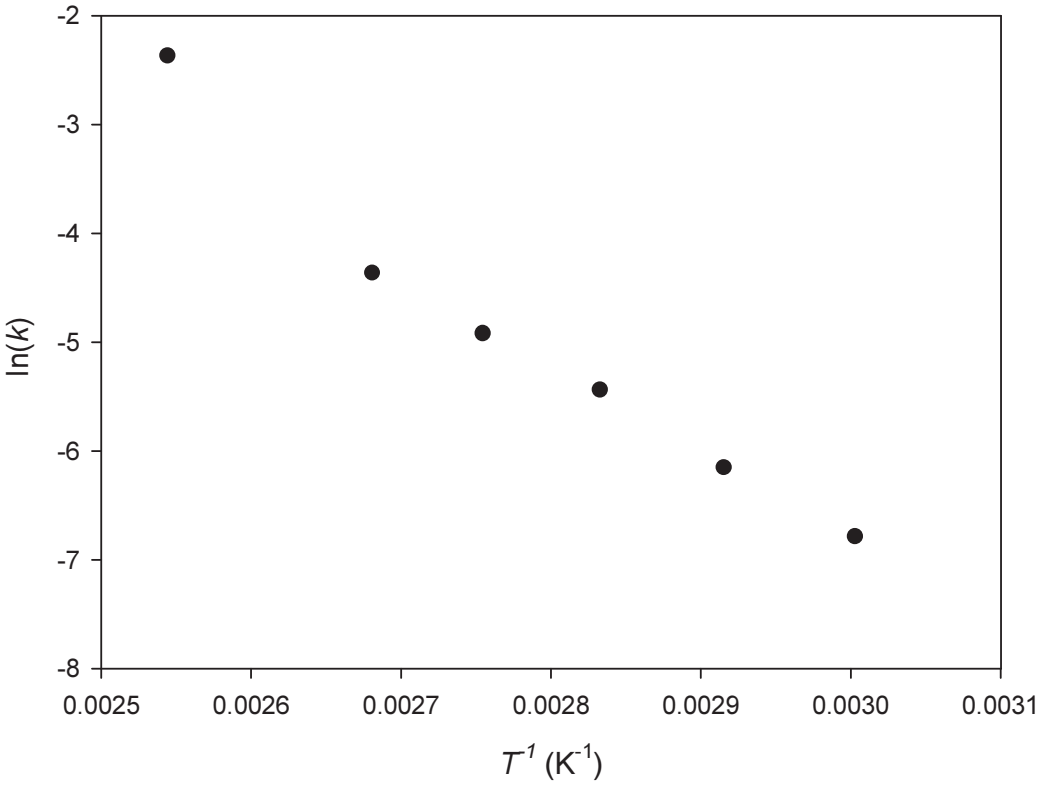

Figure 5-11 Arrhenius plot for rate constant *k* as measured at 40°C

A straight line could be fitted to Figure 5-11 and the activation energy and a pre-exponential term could be calculated from the slope and intercept in order to describe the Arrhenius relationship between the rate constant and the temperature. However, there are only 5 points to fit a line to and these are estimates involving some error. The intercept requires significant extrapolation. A better approach is to fit a model using all of the raw data and use a reference temperature rather than the intercept, as described by (Van Boekel, 1996). An Arrhenius relationship was simultaneously fitted to all temperatures from 60°C to 120°C as described by (Van Boekel, 1996) using equations 5.6 and 5.7

$$k = k_{ref} e^{\frac{-E_a}{R}\left(\frac{1}{T+273} - \frac{1}{T_{ref}+273}\right)} \quad (5.7)$$

where E_a is the activation energy; k_{ref} is the rate at a reference temperature (T_{ref}). T_{ref} was selected as 90°C as this was the midpoint of the temperature range.

The Solver feature in Excel was used for the curve fitting. The initial guesses for k_{ref} and E_a were given the value 1. For each data point the time and temperature were used to calculate k and then (μ/μ_0). A residual was calculated as the difference between the experimentally

measured (μ/μ_0) and the calculated (μ/μ_0). The residuals were summed and Solver was used to minimise the summed residuals by changing k_{ref} and E_a. The fitted parameters for k_{ref} and E_a were found to be 0.00704 hr^{-1} and 98,260 J mol^{-1} respectively (data is given in Table 11-2 of the Appendix). The standard error of estimate is 0.03, therefore the model predicts the data change in relative viscosity (μ/μ_0) of 0.06 at the 95% level of confidence which is 20% of the maximum drop in viscosity shown in Figure 5-9.

Therefore equations 5.6 and 5.8 can be used to determine the loss of viscosity measured at 40°C for a heat treatment in the range of 60 to 120°C, for any concentration.

$$\frac{\mu}{\mu_0} = e^{-kt} \qquad (5.6)$$

$$k = 0.00704e^{\frac{-98,260}{8.314}\left(\frac{1}{T+273}-\frac{1}{90+273}\right)} \qquad (5.8)$$

5.3 Conclusions and recommendations

It was found that bone extracts were Newtonian when measured at temperatures between 30 and 60°C. There was some time dependency observed at 20°C, probably due to flocculation of collagen material. However, with rapid measurements this time dependency was negligible. Therefore the Newtonian viscosity can be used as a measure of texture.

The viscosity of the material decreased with exposure to high temperatures for long periods of time. Loss of viscosity was minimal at 60°C, but significant at temperatures above 70°C and highly significant at 120°C.

The loss of viscosity could be modelled by a first order kinetic model and the effect of temperature on heat treatment was found to obey the Arrhenius law.

6 Extraction Studies

In order to design an extraction process data is needed on the yield and the rate of extraction under various conditions. This data was not available in the literature.

Work presented in Chapter 3 looked at the rate of extraction in the current EC process at 92°C. In order to get a kinetic equation for the extraction rate as a function of temperature work was completed at 80, 100, 110 and 120°C. The higher temperatures were seen as having potential to reduce the processing time and possibly increase the yield. Specifically, the new extraction work was carried out for periods of up to 5 hours and designed to give a time series of yield over this period. The data also allowed the determination of extraction time to reach equilibrium at 120°C, the likely temperature of a new process design. A distribution curve of non-fat extractable solids between the liquid and solids phase at equilibrium time for the temperature of 120°C was also established.

6.1 Effect of temperature on extraction rate and extent

6.1.1 Materials and Methods

The bones used in this study were rib and sternum bones from Silver Fern Farms beef plant in Hastings. The bones were cut into pieces less than 160 cm^3. This cut size is smaller than is used in the current EC process because the batch size for each experimental run was less than 2 kg of bones.

In order to process at temperatures of 100°C and above the sample had to be in an enclosed container. Therefore samples cannot be taken at fixed time intervals to provide a time series, rather a separate container has to be used for each time interval, making the gathering of data time consuming.

In similar studies Wilkinson and Glasgow (2009) and Wilkinson (2009) placed bones with water in a 1:1 ratio in a stainless steel container covered with tin foil that was then placed in a retort. The retort was filled with steam to achieve 121°C. There was no guarantee that bone material or the bone extract were not lost from the container, particularly if the contents boiled at any time, which is possible during the initial temperature rise or cooling of the retort.

For this work food processing cans (A10) were used to provide sealed containers. About 1.5 kg of bones was placed into 3 litre A10 cans (internal diameter 154 mm and 172 mm in height). Water or bone extract was added in a 1:1 ratio. The cans were vacuum sealed by flushing the headspace with steam and then seaming using a Dixie Double Seamer, model number

UVGMD-ALCC serial number 09274. The gain in weight from the steam was found to be less than 2 grams and was therefore negligible.

The cans were placed into a retort on a perforated steel tray. The retort was filled with sufficient water to cover the top of the cans by 5 cm. Steam was introduced into the retort from the bottom in order to heat the water to the desired temperature. When the water temperature approached extraction temperature the pressure above the water was increased to at least 20 kPa above the boiling point for the set temperature. The extraction time was started once the retort reached the desired extraction temperature. The come up time was 20, 15 and 10 minutes for the 120, 110, 100°C treatments, respectively.

At the end of the processing time the steam supply was stopped and cold water was introduced to cool the retort. The drain was partially opened to release the water and manually controlled in order to maintain a constant water level. Compressed air was introduced from the bottom of the retort to achieve mixing and ensure uniform temperature. The 20 kPa over-pressure inside the retort was maintained until the internal temperature reached 80°C. The pressure inside the retort was decreased slowly in steps so that atmospheric pressure was reached after the retort temperature was below 45°C. Once the internal temperature decreased to 30°C the retort was drained and opened.

The cans were removed and allowed to cool to room temperature. The cans were weighed and then opened. The fat was skimmed off and weighed. The bone extract was drained through a 1 mm and then a 180 µm mesh screen into a bucket. The resulting extract was weighed, its soluble solids content was taken, and it was placed in a pouch that was then heat sealed and frozen. The spent bones were also weighed, placed in a flexible pouch then heat sealed and frozen.

Table 6-1 Details of experimental runs for extraction kinetics

Run	Extraction Temperature (°C)	Sample times (h)	Liquid	bones:liquid ratio	Heating	Geometry
E1	120	1, 2, 3, 4, 5, 3, 4	Water	1:1	Water immersion	A10 can
E2	110	1, 2, 3, 4	Water	1:1	Water heated retort	A10 can
E3	100	1, 2, 3, 4	Water	1:1	Water heated retort	A10 can
E4	80	1, 2, 3 4, 5, 6, 7, 24, 48	Water	1:1	Water jacket	Jacketed vessel

The relationship between Brix and total solids concentration was determined by taking several samples in the range of 0.2 to 20°Brix and measuring the total solids. With this relationship the easily measured Brix could be used to calculate the total solids content. Table 6-1 gives details of the runs conducted.

6.1.2 Results and Discussion

A plot of total SNF concentration versus soluble solids concentration for bone extract solutions is given in Figure 6-1. A straight line was fitted having an R^2 of 0.9990 and a standard error of estimate of 0.14 g 100 g^{-1} (Equation 6.1).

$$Total\ solids\ concentration = 0.807 brix \qquad (6.1)$$

Equation 6.1 applies to bone extract and is similar but not the same as Equation 3.3 that described the relationship between total solids concentration and Brix for EC's commercial stock which has tomato paste added to the extract.

The uncertainty in using Equation (6.1) was calculated to be 0.3 g 100 g^{-1} solids concentration at the 95% level of confidence based on the standard error of estimate.

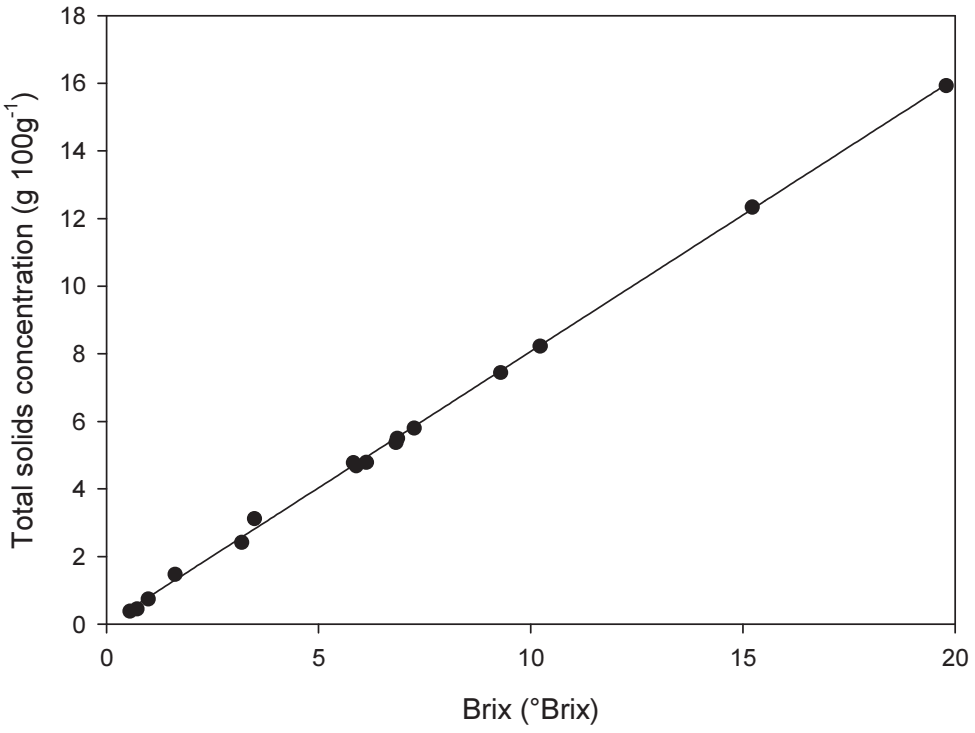

Figure 6-1 Solids content Brix relationship for bone extract

The extraction kinetic data is presented in Figure 6-2. The extraction data for 110°C and 120°C does not follow a straight line, but rises approaching a maximum value at a declining rate. It appears that the extraction reaches an equilibrium concentration. The extraction data for temperatures 80, 92 and 100°C, temperatures follow a straight line, however the extent of reaction is is very low after 4 hours. The data shows that increasing the extraction temperature increases the rate of extraction and greatly reduces the time to reach equilibrium. Extracting at 120°C results in 6 fold increase in the solids content of the liquid extract solution after 4 hours compared with extraction at 92°C. At the same time the extraction at 120°C had reached equilibrium maximum value, whereas at 92°C the extraction had not reached equilibrium conditions. As shown in chapter 3 the extraction process for EC at 92°C had not reached a maximum value even after three 3 days.

Replicate measurements for 120°C at 3 and 4 hours of extraction show some variation of about 0.5 g 100 g^{-1} SNF concentration. The difference between the replicate runs may be the results of many factors most importantly raw material variation.

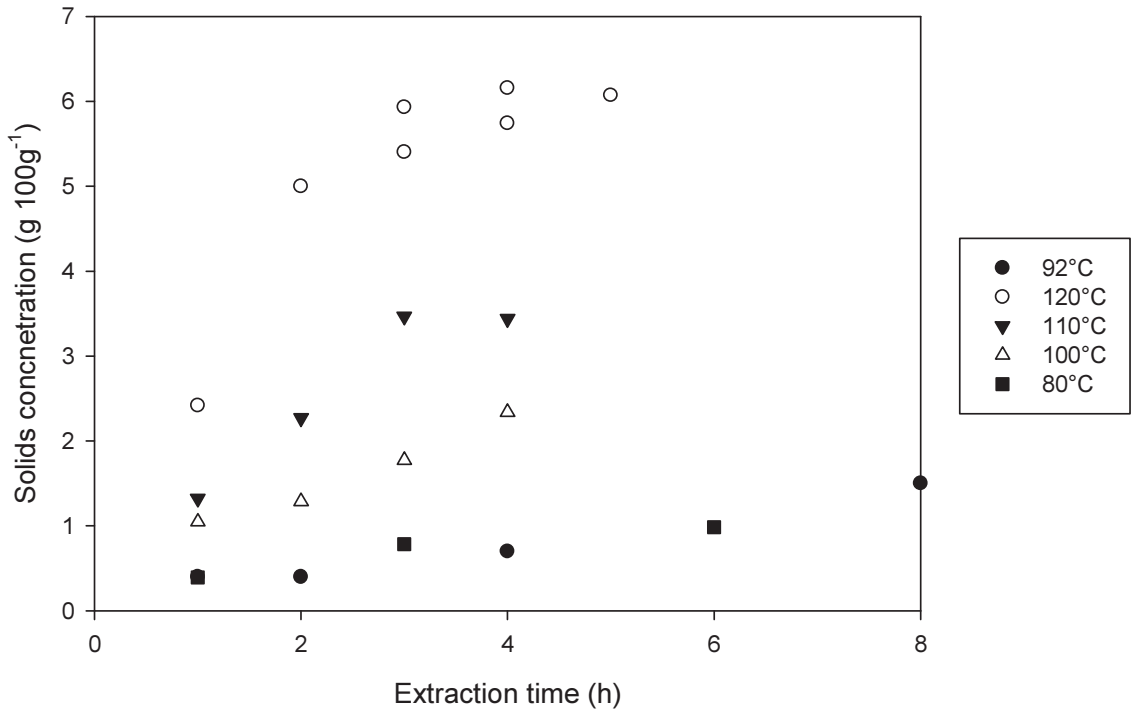

Figure 6-2 Extraction data for different temperatures.

The observed rise in SNF concentration to a maximum with a declining rate is consistent with first order kinetics. Nicolas-Simonnot et al. (1997) found that acid extraction process for de-mineralised bone powder was best represented by a first order kinetic model. Therefore a first order exponential model (Equation 6.2) was applied to the extraction data at each temperature using SIGMA PLOT.

$$E_s = E_{se}(1 - e^{-bt}) \qquad (6.2)$$

E_s is the extracted SNF concentration (g 100 g^{-1}), E_{se} is the extractable SNF concentration at equilibrium (g 100 g^{-1}) and *b* is a kinetic rate constant. The fitted parameters are given in Table 6-2.

Table 6-2 Fitted parameters for first order extraction kinetics

Extraction temperature (°C)	E_{se} (g 100g^{-1})	*b* (h^{-1})	R^2	Standard Error of estimate (g 100 g^{-1})
80	5.7 ± 1.9	0.035± 0.022	0.9928	0.18
92	6.1± 0.4	0.04± 0.01	0.9969	0.18
100	3.3± 3.9	0.28 ± 0.19	0.9004	0.22
110	4.9 ± 5.4	0.3± 0.5	0.9434	0.30
120	6.6 ± 1.1	0.6± 0.3	0.9240	0.39

The rate constant *b* is shown to significantly increase with temperature while E_{se} is not significantly different at different temperatures. The uncertainty of the parameters is high due to the small number of data points for each temperature.

The rate controlling reaction for the extraction experiments is not known. It could be external diffusion, internal diffusion or the chemical reaction to convert collagen into soluble gelatine. Nicolas-Simonnot et al. (1997) demonstrated that the rate controlling reaction was the chemical reaction and not diffusion for extraction on gelatine. However, they used smaller particles and were extracting under acid conditions. But the data in Table 6-2 shows that temperature has a large effect on the reaction rate constant, *b*. This is observed in the cases when the controlling reaction is a chemical reaction, but not when the controlling reaction is diffusion. Thus there is reason to believe that the chemical reaction is the rate limiting step in agreement with Nicolas-Simonnot et al. (1997).

If the chemical reaction is the rate limiting step, *b* will be a lumped parameter involving the true reaction rate constant and the surface area of the core at which the reaction takes place. This area will change as the reaction proceeds and is difficult to quantify from the geometry of the bones as they are irregular in shape and are non-homogenous in composition.

It was concluded that resolving the extraction rate constant *b* to greater detail was not practical. A limitation of this is that the kinetics can only be applied to bones of the same type and range of dimensions. Earlier experiments showed little difference in the final extraction yields for bones of the same size and the larger sizes used commercially at 92°C for three days. This suggests the effect of bone size has little effect on the extraction in the range of sizes tested which cover the range of size that is commercially practical. Going to sizes many times smaller is likely to result in different extraction kinetics, but such was considered impractical for the commercial process studied.

The parameter E_{se} represents the maximum SNF concentration for the extraction. This is likely to be an equilibrium phenomenon between the SNF in the liquid and the extractable SNF in the bones. It is expected that this relationship will change with temperature with higher temperatures allowing more collagen to solubilise. However, this is not reflected in the data obtained due to the large uncertainties in the values fitted; the extent of extrapolation required to estimate the parameter for the lower temperatures is just too large. Due to the limitations of the data a constant average value of E_{se} was selected for all of the temperatures.

An Arrhenius plot for the rate constant, *b* is plotted in Figure 6-3. The Arrhenius plot shows a straight line for four of the points while the fifth point measured at 80°C shows some deviation. The reason for this is not known. It may be that the dominant reaction or component at 80°C is different from those at the higher temperatures.

Given the design for the extraction step is unlikely to use temperatures lower than the current commercial practice of extracting at 92°C because this will result in a slower rate of extraction it was decided to fit an Arrhenius relationship to data from 92°C to 120°C as described by Equation 6.3

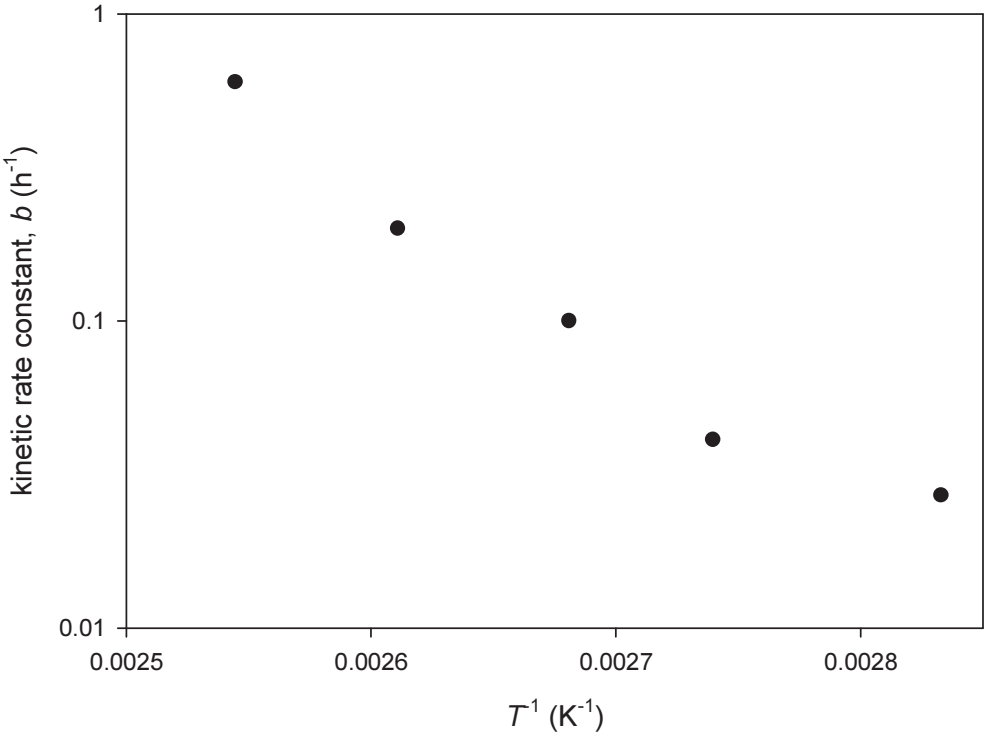

Figure 6-3 Arrhenius plot for the rate constant *b*

$$b = b_{ref} e^{\frac{-E_{ae}}{R}\left(\frac{1}{T+273} - \frac{1}{T_{ref}+273}\right)} \quad (6.3)$$

E_{ae} is the activation energy; b_{ref} is the rate at a reference temperature (T_{ref}). T_{ref} was selected as 120°C as this was the temperature of most interest. E_{se} was assumed to be constant for all temperatures and the Solver feature in Excel was used for the curve fitting of the whole data set at different temperatures and times using equations 6.2 and 6.3 simultaneously using the method of Van Boekel (1996) and described in section 5.2.5. The initial guesses for b_{ref}, E_a and E_{se} were given the value 1. For each data point the time and temperature were used to calculate b and then E_s. A residual was calculated as the difference between the experimentally measured solids concentration and E_s generated by the model. The residuals were summed and Solver was used to minimise the summed residuals by changing b_{ref}, E_a and E_{se}. A summary of the fitted parameters are given in Table 6-3 and the spreadsheet is given in Table 11-3.

Table 6-3 Fitted parameters for extraction kinetics

Fitted parameter	Value
E_{se} (g 100 g^{-1})	6.35
b_{ref} (120°C)	0.65
E_a (J mol^{-1})	119,483

The fitted model is plotted along with the experimental data in Figure 6-4. The model follows the general trend of the data but is not exact.

An indication of the reliability of prediction was estimated by calculating the 95% confidence interval based on the standard error of estimate. This was calculated and found to be 0.64 g 100 g^{-1} or an uncertainty of 11% for a bone extract with a SNF concentration of 6 g 100 g^{-1}. This uncertainty is of similar magnitude as the difference between measured replicates. The final equations with fitted parameters are

$$E_s = 6.35(1 - e^{-bt}) \quad (6.4)$$

$$b = 0.65e^{\frac{-119{,}500}{R}\left(\frac{1}{T+273} - \frac{1}{120+273}\right)} \quad (6.5)$$

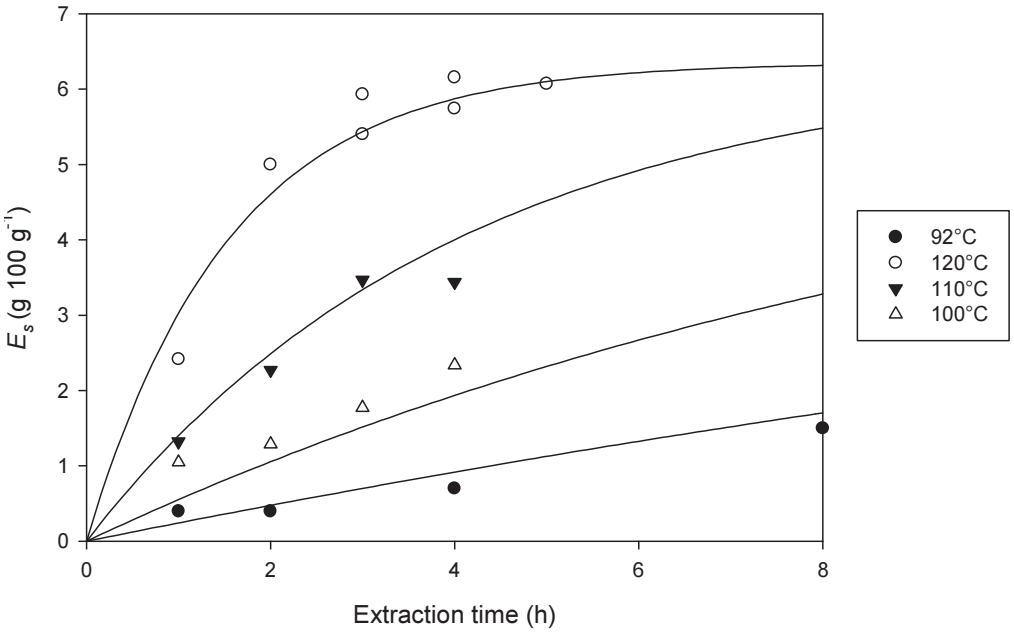

Figure 6-4 Fitted model for extraction kinetics

6.2 Extractable Components in Fresh Bones

The aim of the work here was to establish the maximum amount of non-fat extractable material in raw bones. The procedure involved performing a series of extractions of the bones until a last extraction resulted in no solids. The amount of extractable solids was determined based on the volume and (Solid Non-Fat) SNF concentration of all the solutions resulting from the extraction. The extraction experiments were accelerated by cutting the bones to a small size (3-10 mm) and using a high temperature and a high water to bones ratio. A simple soluble solid content determination was made to calculate the total solids using equation 6.1.

6.2.1 Materials and Methods

Cut raw bones were separated into fat, meat and bones with a scalpel to quantify the proportion of each. The separation was based on visual judgment. Three replicates were performed (BC1-BC3).

Two sets of runs were performed. In the first set of runs a band saw was used to cut frozen brisket and rib bones into small pieces so the largest dimension was about 20-40 mm and a the smallest dimension was about 3-10 mm.

About 400 to 500 g of the cut raw bones were weighed and placed into a 7 L pressure cooker (210 mm internal diameter and 205 mm internal height). Two litres of water was placed into the pressure cooker. The pressure cooker was sealed and placed on an electric element and heated. The pressure cooker was fitted with a 15 psi weight, thus achieving an internal pressure of 103.4 kPa above atmosphere and a temperature of 121°C nominally.

The material was extracted for 1 hour, allowed to cool and the water lost through the pressure release valve was replaced. The 1 hour extraction cycle was repeated 4 times for a total extraction time of 4 hours then the liquid was poured off and weighed.

The bones from the 4 hours of extraction were crushed using a pestle and 1 L of water was used to cover the crushed material. The pestle was washed with that water to ensure that all the solids remained in the pressure vessel. The vessel was then sealed, heated and another 1 hour of extraction was conducted after which the liquid was cooled, poured off and weighed. This 1 hour extraction was repeated using fresh water until a 0°Brix solution was obtained. The liquids resulting from the extraction cycles were allowed to cool and the fat manually skimmed off. Each of the skimmed liquids were weighed and soluble solids was determined.

The entire process for measuring the maximum extractable solids from fresh bones was repeated six times (Y1-Y6).

A second set of data was made using the bones left from the extraction conducted during runs E5 to E9. The spent bones were taken through a series of 1 hour extractions as described above. This second determination of maximum extractable solids was made on four samples (Y7-Y10).

6.2.2 Results and Discussion

6.2.2.1 Physical make-up of bones

The proportion of fat, meat and bones for the raw bones is given in Table 6-4. The bones comprised of 55-60% while fat and meat made up 27 and 17% respectively. It is recognised that this is a crude separation, but provides some idea of the makeup of the bones.

Table 6-4 Separated components of the brisket and rib bones on a weight basis

Component	BC1	BC2	BC3	AVERAGE
Fat	23%	31%	25%	27 ± 5%
Meat	23%	14%	13%	17 ± 6%
Bones	55%	55%	61%	57 ± 6%

6.2.2.2 Extractable Solids

The extractable solids per 100 kg of raw bones determined in the first set of experiments (runs Y1-Y6) are given in Table 6-5. The data shows large variation in fat and SNF. A low yield of SNF for Y3 was matched by a large amount of fat. Y5 and Y6 appear to have a very high yield of SNF based on fat free bones.

Table 6-5 Yields of extractable components for the first set of data (Runs Y1 - Y6)

Run	Yield of SNF in raw bones (kg 100 kg^{-1})	Yield of fat in raw bones (kg 100 kg^{-1})	Yield of SNF in raw fat free bones (kg 100 kg^{-1})
Y1	11.5	20.6	14.4
Y2	9.7	30.8	14.0
Y3	7.7	43.4	13.6
Y4	9.4	34.1	14.2
Y5	10.1	41.3	17.2
Y6	12.9	32.1	19.0
Mean	**10.2 ± 1.4**	**34 ± 7**	**15.4 ± 1.7**

Data from the second set is presented in Table 6-6 and show higher values for yield of SNF on both a raw bone and fat free bone basis although the differences in the means are not statistically different ($p>0.05$) due to the large variation in the yield for both methods.

Table 6-6 Extractable solids from bones for the second set of data (Y7 – Y10)

Run	Yield of SNF in raw bones (kg 100 kg^{-1})	Yield of fat in raw bones (kg 100 kg^{-1})	Yield of SNF in raw fat free bones (kg 100 kg^{-1})
Y7	11.69	33.97	18.11
Y8	12.02	25.44	16.13
Y9	11.63	41.17	17.33
Y10	12.15	35.34	17.04
Mean	**11.9 ± 0.25**	**31 ± 4**	**17.2 ± 0.8**

Pooling the data together gives an average SNF yield of 10.9 ± 1.0 kg 100 kg^{-1} and a fat yield 34 ± 4 kg 100 kg^{-1}. Calculated on a fat free bone basis the SNF yield is 16.1 ± 1.1 kg 100 kg^{-1}.

The large variation in yield is due to variations in raw material, but may also be due to experimental errors. The pressure cooker used is not a perfectly sealed container and some steam is lost during the process. Attempts were made to include a thermo-couple in the pressure cooker vessel but this interfered with the seal and resulted in a lower temperature due to steam escaping. Other errors in the process are the imperfect fat separation and possible loss of material when each liquid extraction is removed. While efforts were made to minimise these it is felt that further improvements can be made. Ideally the extractions would be best made in a sealed container, in which the temperature could be monitored.

Ockerman and Pellegrino (1988) stated that gelatine yields for wet bones are 10-16% and the data are within this range. Field et al. (1974) determined the composition of beef bones but removed the tendons and surface fat manually. They found that such bones yielded 8.8% fat, 5.8% nitrogen and 58.9% ash. The reported yield of hydroxyproline was 3.88% indicating a collagen content of 27.5% based on a factor of 7.1 to calculate collagen from hydroxyproline (Nicolas-Simonnot, et al., 1997). Therefore, if all of the collagen was extractable, a yield in the order of 37.5 kg 100 kg^{-1} of fat free bones would be expected plus a small amount of minerals and material derived from metabolites and muscle proteins. The yields are well below these values, indicating that the process does not release all of the material available, but is in agreement with the observations of Ockerman and Pellegrino (1988).

Not all of the collagen can be extracted by hot water due to its interaction with calcium phosphate. In the processing of gelatine bones are treated with acid or alkali in order to allow the release of collagen which can then be extracted rapidly even at low temperatures (Nicolas-Simonnot, et al., 1997). Therefore in order to test this for one of the samples the spent bones were treated with acid for 1 hour at 70°C after which the bones were washed three times with water. Further extractions were performed with hot water, but no solids were yielded. A second experiment was repeated but this time the wash from the acid was tested and found to yield 7.4% solids. The composition of the solids was not determined, but it is likely that it was calcium phosphate. The observation shows there is potential for further processing of the bones following extraction to increase the yield, but further work is needed to identify and quantify exactly what can be extracted.

It can be concluded that the variation in the data could be due to a number of factors. Raw material variation no doubt plays a part, but the technique used needs further work in terms of temperature control and monitoring.

While the two sets of data for the maximum yield are not statistically different, it is felt that the second set of data should be used as a measure of the total extractable solids. This is due to the fact that the techniques used were improved after the first practice resulting in a smaller scatter about the mean. Therefore the maximum yield of SNF is taken as 11.9 ± 0.3 kg 100 kg^{-1} on a raw bone basis or 17.2 ± 0.8 kg 100 kg^{-1} on a fat free bone basis.

The results show that the current commercial process that yields SNF of 6 kg 100 kg^{-1} of bones is achieving only about 60% of the total possible yield, indicating further room for improvement.

The yield of fat from the raw bones is 31 ± 4 kg 100kg^{-1} of raw bones, significantly higher than the yield of SNF. It would therefore make sense to utilise this stream as a product rather than simply consider it as waste.

6.3 Equilibrium distribution between solid and liquid phases at high extraction temperature

The aim of the work here was to establish the relationship between the extractable solids content in the spent bones and the bone extract when the extraction had been completed to equilibrium. The data collected would also provide an idea of the time required to achieve equilibrium for the extraction. The data was collected using an extraction temperature of 120°C as this was likely to be the temperature used for the process design given the increase in rate of extraction.

6.3.1 Methods and Materials

Extractions were performed using the methods outlined in section 6.1.1 using A10 cans inside a retort. The results from run E1 were used for extraction equilibrium data and other runs were completed using the same method, but water was replaced with solutions at 3, 6, and 9°Brix. For these different solutions the solids content was determined (Section 3.1.3.2) and the result used to define the initial solids concentration of the extract (E_i). Extractions were completed for 3-5 hours to identify the when the extraction had reached equilibrium. A summary of the runs are presented in Table 6-7.

Table 6-7 Experimental runs for equilibrium data

Runs	Extraction Temperature (°C)	Sample times (h)	Liquid	E_i (g 100g^{-1})	bones:liquid ratio	Heating	Geometry
E5	120	3,4,5	3°Brix bone extract	2.41	1:1	Water heated retort	A10 can
E6	120	3,4,5	6°Brix bone extract	4.84	1:1	Water heated retort	A10 can
E7	120	2,3,4	9°Brix bone extract	7.25	1:1	Water heated retort	A10 can

The solids content in the solution Y_o at equilibrium was determined by measuring the total solids, rather than relying on the soluble solids reading. The extractable solids content left in the bones (X_o) was determined by two methods. Firstly by calculation based on the average

determined maximum extractable content minus the amount of solids gained by the liquid and secondly by direct measurement through repeated extractions on the resulting bones.

6.3.2 Results and discussion

A plot of the solid non-fat versus extraction time for the four different solutions is given in Figure 6-5. The data shows a rapid increase in the SNF concentration ($E_s - E_i$) followed by a reduction in rate until eventually a constant value is reached. The time to achieve equilibrium for all treatment appears to be four to five hours, although much of the SNF is gained after 3 hours of extraction.

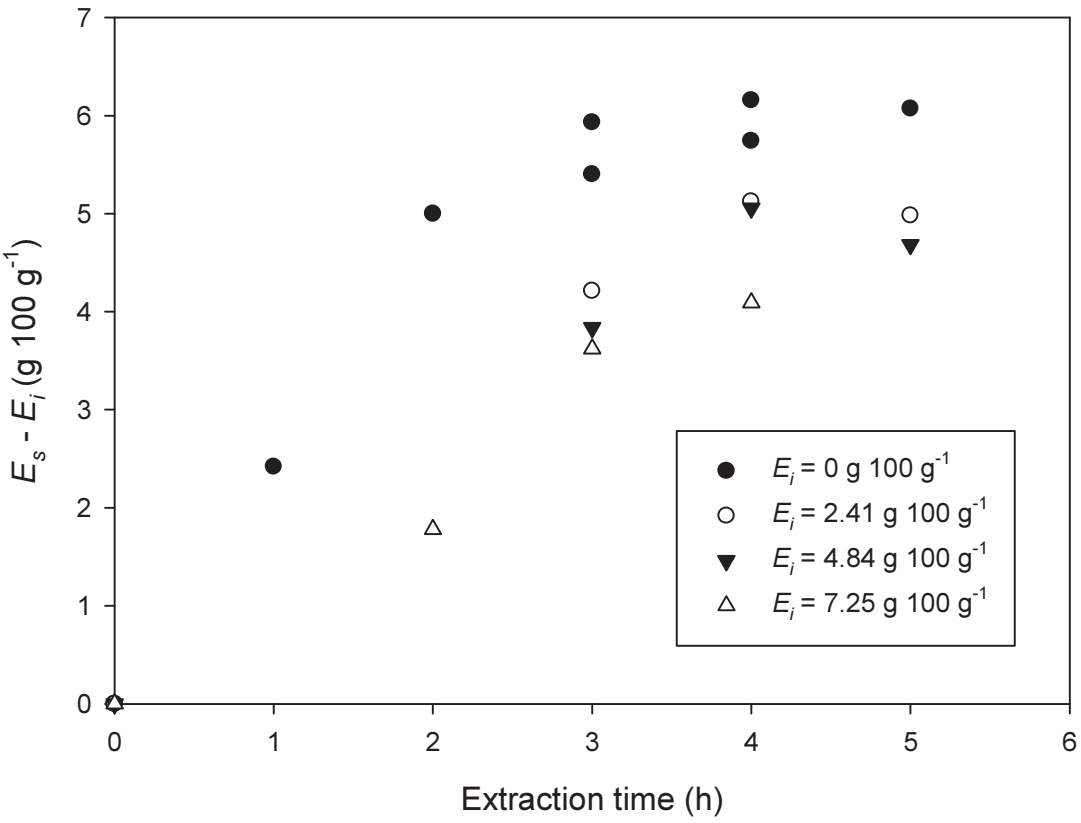

Figure 6-5 Extraction curves using fresh bones with solutions of different concentrations initial concentrations

The data also shows the higher solids content that is achieved by adding fresh bones to bone extract of different concentrations. Even with an E_i of 7.25 g 100 g^{-1} a significant increase of 4 g 100 g^{-1} was achieved. The rate of extraction over the first three hours is higher for the solutions with a lower E_i. However the data demonstrates that multiple stage extractions can achieve significantly higher concentrations than single stage extractions.

Using the data for each of the runs at the longest time the solids content in the bones and the solution were determined to construct an equilibrium curve. The equilibrium content in the solution (Y_o) and the bones (X_o) are plotted in Figure 6-6 as a traditional equilibrium curve where Y_o and X_o are expressed as mass fractions. Two sets of data are plotted for X_o for the two methods of determination; (1) calculated and (2) measured.

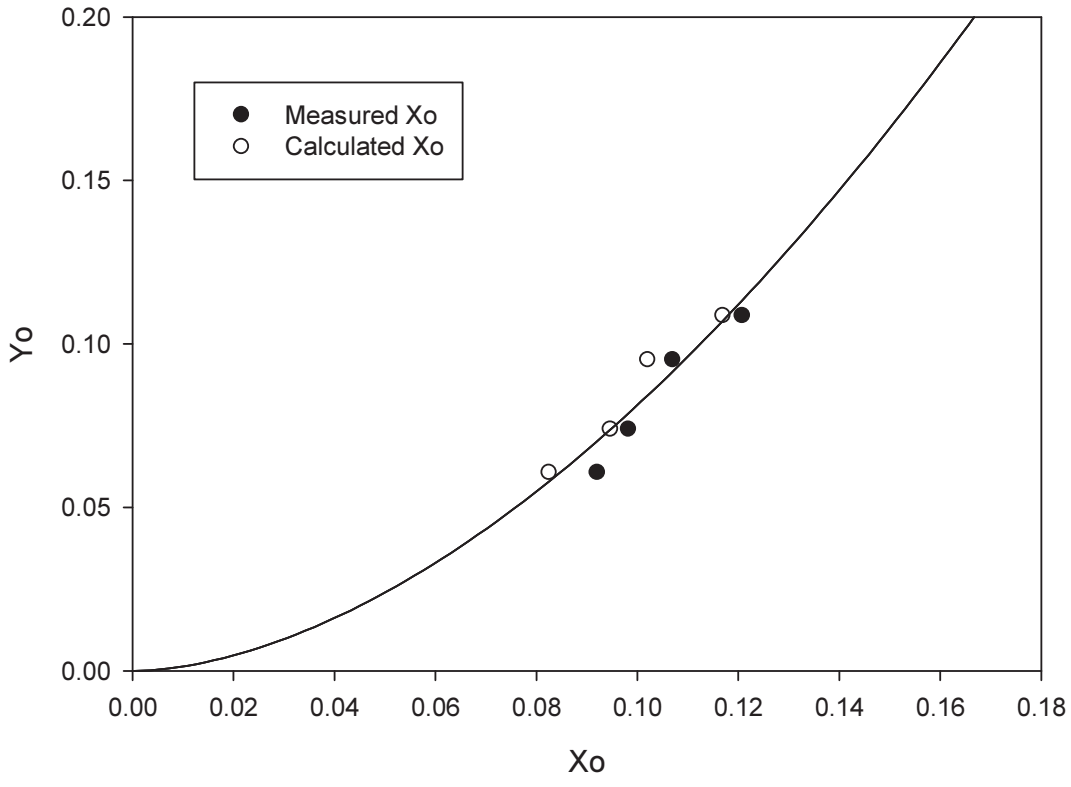

Figure 6-6 Equilibrium curve for bone extract at 120°C.

The measured and calculated values for X_o are similar with the calculated values tending to be lower. This may be due to an error in the estimation of the maximal extractable content in section 6.2 or the uncertainty of the repeated extractions to measure the actual remaining solids.

In order to represent the data curves where fitted to the data with both the measured and calculated values of X_o. It was found that the data can be represented by a power law curve (Equation 6.6) which had a R^2 of 0.8991 and standard error of estimate of 0.0068.

$$Yo = 4.68{X_o}^{1.76} \qquad (6.6)$$

Equation (6.6) is plotted in Figure 6-6 against the data that only goes down to X_0 = 0.08. There is always a danger in extrapolating an equilibrium curve beyond its experimental range and it is recommended that data be gathered to cover the gap in the range (X_0 less than 0.08).

6.4 Conclusions

The extraction studies presented in this chapter have given experimental results for the extraction kinetics, extraction times, maximum extractable solids and equilibrium distribution curve at 120°C for the rib bones used in this study.

These results were not available in the searched open literature. While the scatter in the data is still larger than ideal, especially for the equilibrium curve (Figure 6-6), the new trends observed allow better and rational decisions in process and equipment design. Since time in a PhD is limited the improved collection of data is left as suggestions to the next workers in the field.

7 Process design

7.1 Guiding principles

There were two overall guiding principles for the design of the process. The first goal was to preserve the texture of the stock as far as possible, the second was to maximise the yield from the bones.

In addition EC's request to increase the production volume to 15,000kg per week, roughly 10 times the current capacity was taken into consideration.

7.2 Process modelling and considerations

7.2.1 Prediction of total solids

7.2.1.1 Extraction step

The concentration of Solids Non-Fat (SNF) extracted at any point in time in an extraction process considered can be predicted from a re-arrangement of equation 6.4 as

$$E_{s(j+1)} = E_{sj} + \left(E_{se} - E_{sj}\right)\left[\ 1 - e^{-b(t_{j+1}-t_j)}\right] \quad (7.1)$$

E_{se} is 6.35 g 100 g^{-1} for the bones studied in this work and the coefficient b is the rate of extraction that is dependent on temperature as given by equation 6.5.

7.2.1.2 Evaporation step

The evolution of the SNF in the solution (E_s) during the concentration process were determined for an original concentration coming out of the extraction step (E_{Si}), a residence time in the evaporator (t_v) and a final concentration of SNF coming out of the evaporator. The rate of water removal V_r is given by

$$V_r = \frac{W_v}{t_v} \qquad (7.2)$$

where W_v is the amount of water removed at time t_v

$$W_v = W_i - W_o \qquad (7.3)$$

W_i is the amount of water coming into the evaporator and W_o is the amount coming out of the evaporator therefore using a 100 g feed to the evaporator:

$$W_i = 100 - E_{si} \quad (7.4)$$

$$W_o = E_{si}\frac{(100-E_{so})}{E_{so}} \qquad (7.5)$$

where E_{so} is the concentration of SNF coming out of the evaporator. Therefore

$$W_v = (100 - E_{si}) - E_{si} \times \left(\frac{100-E_{so}}{E_{so}}\right) \quad (7.6)$$

V_r is assumed to be constant throughout the evaporation process.

The solids for the j+1 time step was given by

$$E_{s(j+1)} = \frac{E_{s(j)}}{E_{s(j)}+(W_i - V_r(t_{(j+1)}-t_{v0}))} \quad (7.7)$$

where t_{vo} is the starting time of the evaporation process.

7.2.2 Prediction of viscosity

The viscosity of the extract solutions was a function of both total solids and thermal exposure. It was observed from results in chapter 5 that the texture kinetics (change in viscosity with time at each temperature) was independent of concentration. In that sense the process can be considered linear and the effects are additive, not interactive. Therefore the change in viscosity ($\Delta\mu$) for a time step (*(j+1)-j*) is given by

$$\Delta\mu_{((j+1)-j)} = (\Delta\mu_{((j+1)-j)})_c + (\Delta\mu_{((j+1)-j)})_T \quad (7.8)$$

where $(\Delta\mu)_c$ is the change due to concentration and $(\Delta\mu)_T$ is the change due to exposure at high temperature.

The change of viscosity due to concentration for a time step is given by equation 5.5 which can be rearranged for the change in viscosity

$$(\Delta\mu_{(j+1-j)})_c = \left\{0.00022\left[\frac{E_{s(j+1)}}{0.806}\right]^{1.42} - 0.00022\left[\frac{E_{s(j)}}{0.806}\right]^{1.42}\right\} \quad (7.9)$$

where *K* is a constant and was found to be 0.00022 Pa.s in section 5.4.2.1.

The change of viscosity due to thermal exposure was determined using

$$(\Delta\mu_{(j+1-j)})_T = \mu_j\left[\ 1 - e^{-k(t_{j+1-j})}\right] \quad (7.10)$$

where *k* is a rate constant dependent on temperature as described by equation 5.7

$$k = k_{ref}e^{\frac{-Ea}{R}\left(\frac{1}{T+273} - \frac{1}{T_{ref}+273}\right)} \quad (5.7)$$

where k_{ref} is the rate constant which was found to be 0.007 at the reference temperature (90°C), E_a is the activation energy which was found to be 98,260 kJ mol^{-1} (section 5.2.5). Then

$$\mu_{j+1} = \mu_j - \mu_j\left[\ 1 - e^{-k(t_{j+1-j})}\right] + \left\{0.00022\left[\frac{E_{s(j+1)}}{0.806}\right]^{1.42} - 0.00022\left[\frac{E_{s(j)}}{0.806}\right]^{1.42}\right\} \qquad (7.11)$$

An Excel spreadsheet was set-up in order to generate the evolution of viscosity for given extraction and evaporation conditions. A time step of 1 minute was used hence,

$$t_{j+1} - t_j = \frac{1}{60} = 0.01667\ h \qquad (7.12)$$

An example spreadsheet of the model is given in Table 11-4 of the Appendix.

7.2.3 Model validation

The model was tested by predicting the viscosity of the extract for a 72 hour extraction at 92°C followed by 20 minutes evaporation at 60°C and comparing with a sample produced under these conditions. The model predicts 0.0138 Pa.s at 16 g 100 g^{-1} SNF concentration compared with a measured value of 0.0133 Pa.s and 16.1 g 100 g^{-1} SNF concentration.

The effect of the time step was tested by running the model with a time step of 30 s, half the time step normally used. This did not change the evolution of E_s or μ. Therefore it is concluded that the time step of 1 minute is adequate.

Thus the model performs adequately and can now be used to analyse and compare different process options.

7.2.4 Process Modelling

7.2.4.1 Viscosity concentration profiles

The procedure was used to analyse the viscosity/concentration profile of several alternative processes:

1) Current EC process (Extraction at 92°C and pan evaporation at 92°C for 3 days).
2) Keep the EC extraction process at 92°C but vacuum evaporation at 60°C for 20 minutes.
3) High temperature short time extraction (HSTE) 120°C for 4 hours with evaporation at 60°C for 20 minutes.

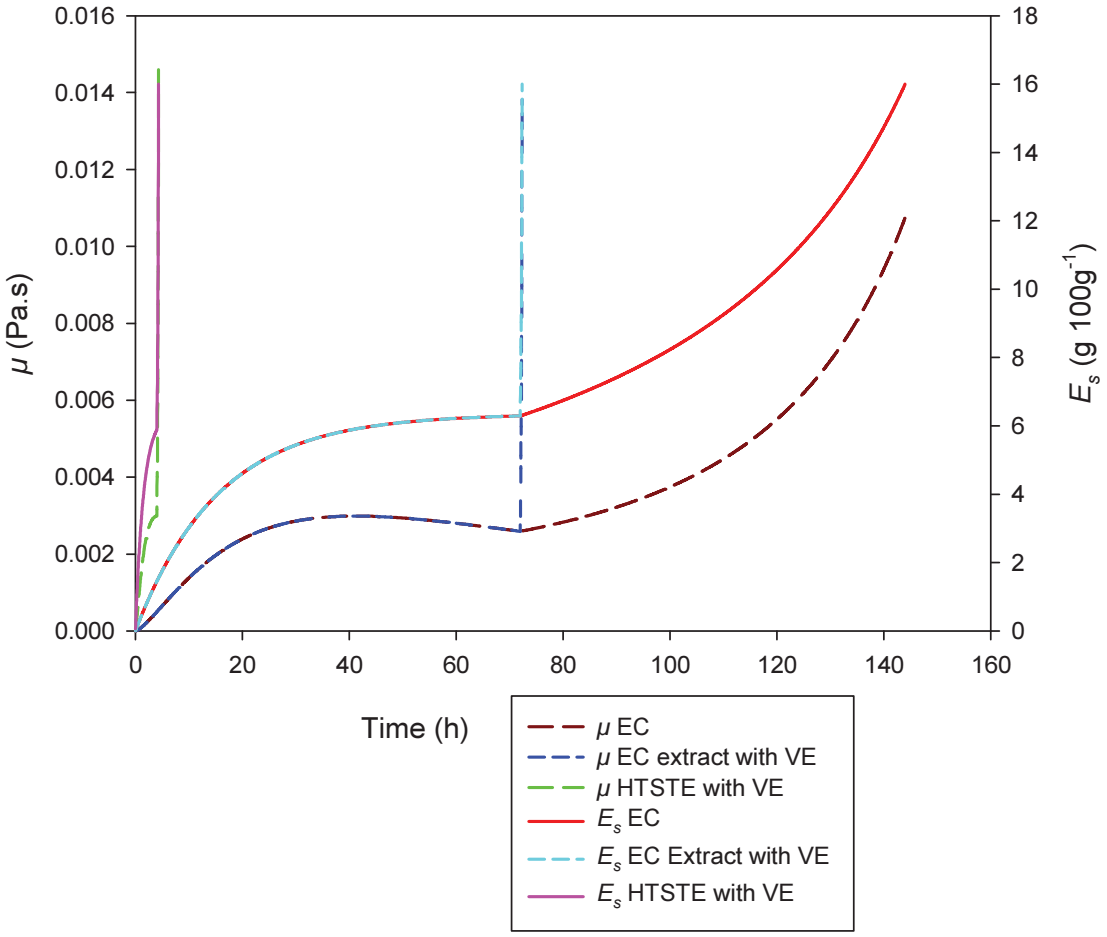

Figure 7-1 Comparison of E_s and μ evolution for the current EC process, EC extraction with vacuum evaporation (VE) and high temperature short time extraction (HTSTE) (120°C for 4 hours) with VE.

The results are shown in Figure 7-1. In the present EC process the solids content (shown by the red line) increases over the 72 hour extraction to 6.29 g 100 g^{-1} but increases more sharply during the 72 hour evaporation process to 16 g 100 g^{-1}. In that process, the viscosity (shown by brown line) passes through a maximum viscosity of 0.0030 Pa.s at 41.6 hours of extraction and then decreases slightly to 0.0026 Pa.s at 72 hours of extraction even though the solids content kept increasing. After 3 days of pan evaporation to 16 g 100 g^{-1} SNF the viscosity was 0.0108 Pa.s. When vacuum evaporation over 20 minutes was introduced the viscosity (shown by the dark blue line) of the 16 g 100 g^{-1} solution became 0.0138 Pa.s.

This simple analysis suggests improvements to the current process:

1) Vacuum evaporation significantly improves (shortens) the run time

2) A higher final viscosity can be achieved by decreasing the extraction time
3) EC can take advantage of these improvements in two ways
    a. Keep the same final total solids and market the thicker solution as a better product
    b. Reduce the final total solids obtained by vacuum evaporation to 13 g 100 g^{-1} to match the present viscosity of 0.00108 Pa.s

The High Temperature Short Time (HTST) process (shown by the green and pink lines) gives a slightly lower final concentration after extraction of 5.87 g 100 g^{-1} but an increased viscosity after concentration of 0.0146 Pa.s for a total process length of only 4 hours and 20 minutes. This would mean that the production throughput per day would increase over 30 times. In addition the viscosity after concentration shows a substantial increase over the current process.

7.2.4.2 Extraction temperature and time

Figure 7-2 plots the change in solids and viscosity for a single stage extraction at temperatures between 92 and 120°C. While the total solids content of the extract solution increased over time up to an equilibrium concentration, the viscosity peaks earlier than the equilibrium time for extraction of solids at each temperature. This time to peak viscosity is approximately 12% of the time to equilibrium concentration during which 93% of the equilibrium concentration is achieved. Interestingly, the peak viscosity, according to the model, is fairly independent of the temperature of extraction but the time to reach that peak drops dramatically as the extraction temperature rises. Therefore, there is clear advantage to work at the highest temperature practical, since a short run time can be identified with a substantial increase in revenue for the same size of plant.

The argument of using higher temperatures has to be balanced with considerations of cost and safety in equipment design, since higher temperature (above 100°C) equates to higher pressures in the extraction vessels.

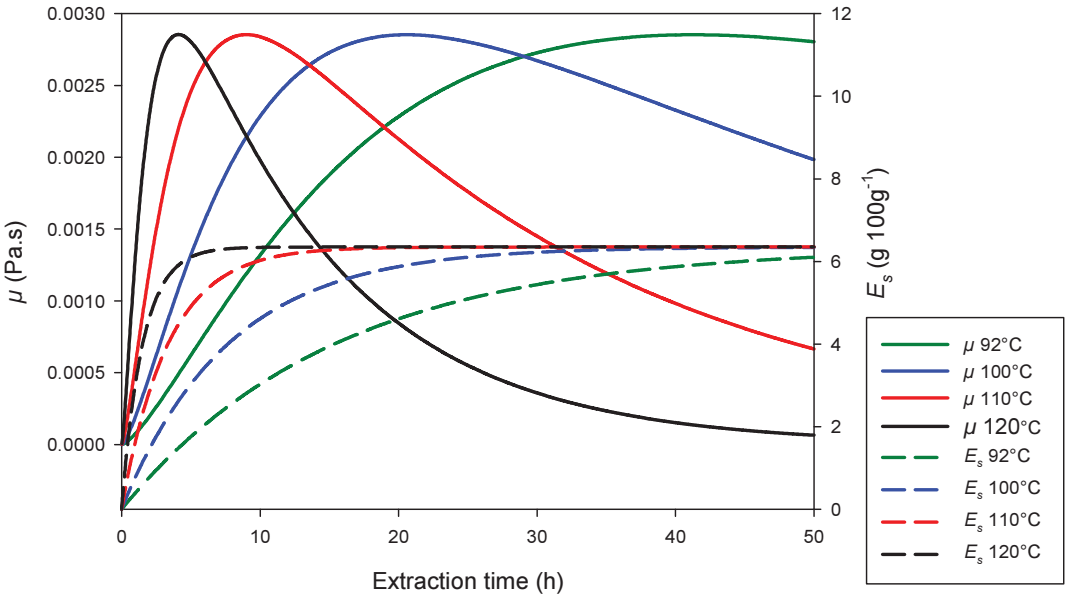

Figure 7-2 Effect of extraction temperature on E_s and μ evolution

7.2.4.3 Single stage versus multi-stage extraction

The extraction studies in Chapter 6 indicated that there was a substantial amount of extractable SNF left in the bones after a single extraction. It makes sense to see whether multiple extractions would have a substantial effect on the yield from the bones. In one method of producing gelatine from bones, the extraction of gelatine (ossein) is achieved by a six stage counter-current 1 N HCl acid treatment Ockerman & Hansen (2000). The gelatine is then extracted from the ossein by heating the ossein in up to six successive hot water extraction stages where the repeated extractions were always done with fresh water on the spent ossein. The first stage was performed for only 1 hour at 60°C to preserve the gelling properties. The temperature of extraction is then increased by 5°C for each successive stage and the time of extraction for each subsequent stage is usually one hour. Clearly, the temperature-time for each stage also plays a role.

The goal in stock extraction is not only to get the best yield from the bones, with the best preservation of original viscosity but also to get the most concentrated solution to minimise the size of the evaporator which is likely to be the most expensive piece of equipment in the process. For this purpose an analysis for a semi-counter current process was performed. The term "semi" means here that only one of the phases moves (the aqueous phase), the other phase (the spent bones) is left standing in the extraction vessels and the counter-current process is run by redirecting the aqueous stream through a system of appropriate flow

controllers. In that sense the analysis presented here is not exactly the counter current extraction process found in classical process engineering text books (Earle, 1966; McCabe, et al., 2005). In addition this food process is made more complex by the presence of fat which also comes out during the extraction process but is present in different samples of bones at varying levels of concentration. Since, as discussed in Chapter 6, each point in the extraction curve at 120°C required different samples of bones in different sealed cans, the effect of varying fat composition between cuts from the same batch of bones can be substantial. To deal with this problem fat was taken out of the problem and only dealt with the extraction curve in terms of the extractable solids non-fat left to total solids non-fat (SNF) left in the bones. A similar approach has been taken by people who model the thermal properties of foods that contain fat. Essentially they look at the contribution of the fat enthalpy as simply additive to the contribution of the rest of the food which includes both water, ice and solids non-fat e.g. Miles et al, (1983). Essentially it means that a multiple extraction process (fat and solids non-fat from green bones) is turned to a simple one component extraction process. An example of multi-stage extraction is presented schematically in Figure 7-3.

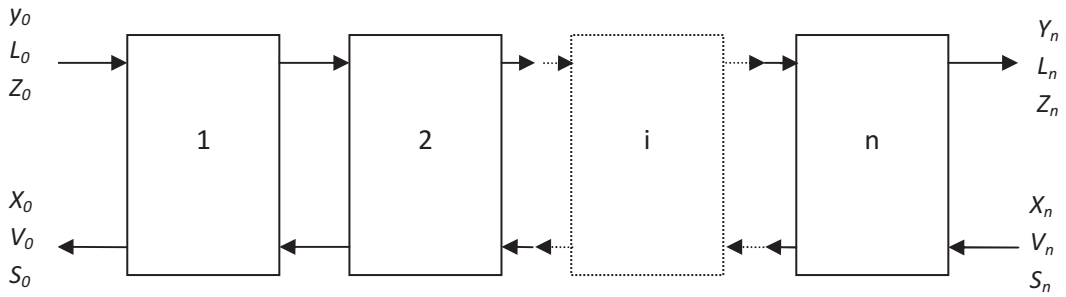

Figure 7-3 Theoretical multi stage extraction assuming equilibrium

x = the concentration of extractable solids in the bones (fraction)

y = the concentration of extractable solids in the liquid (fraction)

L = the total mass of the liquid stream (kg)

V = the mass of the bone stream (kg of SNF)

Z = the absolute extractable solids in the liquid stream (kg)

S = the absolute extractable solids in the solid stream (kg)

n = the number of theoretical stages

The non-extractable SNF, *N*, remains constant and can be defined by

$$N = V_n - S_n \quad (7.13)$$

It is also assumed that there is no moisture uptake into the liquid stream from the bones hence the mass of liquid in stream L remains constant. Experiments in Chapter 6 showed that the moisture loss from the bones was minimal.

Consider the i^{th} stage as shown in Figure 7-4

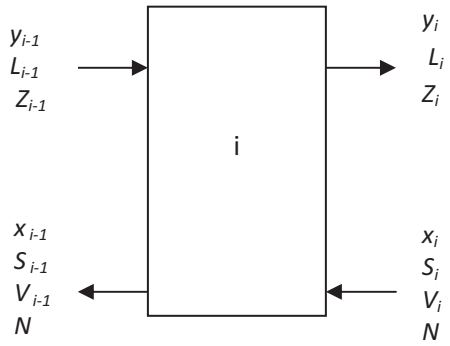

Figure 7-4 Definition of the stage *i*

The liquid stream coming in has a solids concentration y_{i-1} and the liquid stream going out with a solids concentration y_i. In the solids stream, the solids concentration coming into stage *i* is x_i and the solids concentration out of stage *i* will be x_{i-1}. The solids and liquid streams going out of stage *i* (x_{i-1} and y_i) are in equilibrium in the calculation of theoretical stages. Therefore using the equilibrium curve (equation 6.6)

$$y_i = 4.68\mathrm{x}_{\mathrm{i}-1}{}^{1.76} \qquad (7.14)$$

Z_i can is then determined by

$$Z_i = \frac{L_0 y_i}{(1-y_i)} \qquad (7.15)$$

and

$$L_i = Z_i + L_o \qquad (7.16)$$

S_i can then be determined by mass balance of the solids

$$S_i = Z_i + S_{i-1} - Z_{i-1} \qquad (7.17)$$

x_i can be determined by

$$x_i = \frac{S_i}{S_i+N} \qquad (7.18)$$

and

$$V_i = S_i + N \qquad (7.19)$$

These equations (7.13 to 7.19) allow an iterative calculation of stage *i* which can be repeated with subsequent stages until the final stream x_n is achieved and the process is terminated: *n= i.*

An example is shown here on a basis of 100kg water (L_0 = 100kg and x_0 = 0) and 100kg of green bones (Figure 7-5).

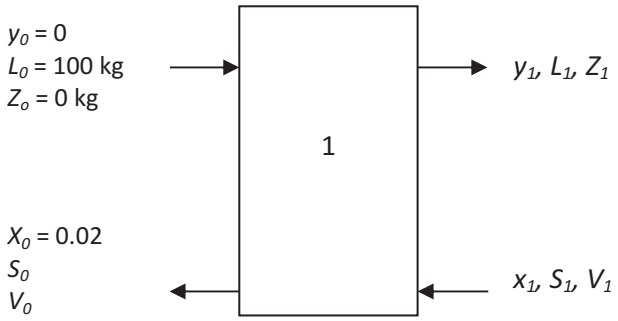

Figure 7-5 Schematic representation of Stage 1

The bones contain on average 31% fat (section 6.2.2.2) and therefore V_n = 69 kg. On average the maximum total extractable solid non-fat is x_n = 0.172 (section 6.2.2.2) and therefore

$$S_n = 0.172 \times 69 = 11.87\ kg \quad (7.20)$$

Equation 7.19 gives *N* = 57.13 kg

The analysis begins with stage 1: the compositions of the outlet streams y_1 and x_0 must fall on the equilibrium curve. To start the analysis a first guess is entered for the composition of x_0 which means that a desired yield for the extraction is set. If the first guess is very far from the true value Solver will take a long time (many iterations) to come to a solution. A value between 0.01 and 0.05 is suggested to ensure Solver finds a quick solution. Let us use as a first guess x_0 = 0.03.

$$S_o = \frac{N \times x_o}{1 - x_o} = \frac{57.13 \times 0.03}{1 - 0.03} = 1.77\ kg \qquad (7.21)$$

and

$$V_0 = S_0 + N = 1.77 + 57.13 = 58.9\ kg \qquad (7.22)$$

y_1 is determined from the equilibrium curve

$$y_1 = 4.68x_0^{1.76} = 4.68 \times 0.03^{1.76} = 0.0098 \qquad (7.23)$$

Equation 7.15 gives

$$Z_1 = \frac{L_o \times x_1}{1 - x_1} = \frac{100 \times 0.0098}{1 - 0.0098} = 0.9868\ kg \qquad (7.24)$$

Equation 7.16 gives.

$$L_1 = Z_1 + L_0 = 0.9868 + 100 = 100.99\ kg \qquad (7.25)$$

Equation 7.17 gives

$$S_1 = Z_1 + S_0 - Z_0 = 0.9868 + 1.77 - 0 = 2.75\ kg \qquad (7.26)$$

Equation 7.18 gives

$$x_{i+1} = \frac{S_1}{S_1 + N} = \frac{2.75}{2.75 + 57.13} = 0.046 \qquad (7.27)$$

Equation 7.19 gives

$$V_1 = S_1 + N = 2.75 + 57.13 = 59.88kg \qquad (7.28)$$

The resulting analysis of stage 1 is presented in Figure 7-6

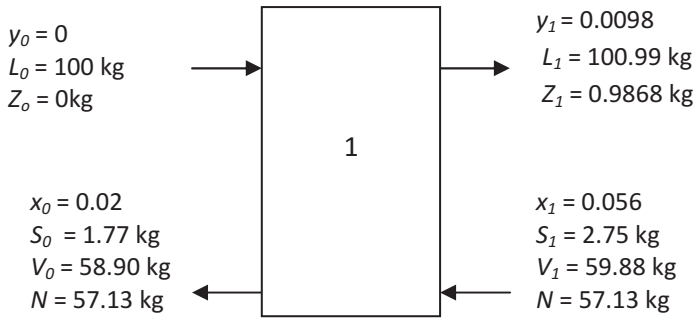

Figure 7-6 Results of analysis of stage 1

The analysis now progresses to stage 2 and this iteration continues for *n* number of stages.

The reason for taking this stage by stage approach, instead of a classical multi-stage counter-current analysis such as that of McCabe-Thiele, is simple. In solid-liquid extraction some of the solvent is always held-up in the solids and forms part of the solid stream. Without an accurate value for this hold up, which must be determined experimentally, it is not possible to construct an operating line with confidence. In the design under consideration, the solids (bones) are not moved and it is possible to drain the extraction vessel at the end of each stage; in other words the hold-up is zero. For counter-current extraction at 120°C, the conveyor belt moving the bones in a true counter-current process would have to be located in a pressurised environment, which presents obvious problems in mechanical design and cost. In addition, for systems with three stages and more, the stage-wise procedure introduced here can analyse mixed co- and counter-current processes as well as variable contact times. This method, that is now defined as "stage-wise iterative analysis" of multi-stage extraction, also offers much greater flexibility than the traditional McCabe-Thiele technique. An example is shown later on for application to situations when each extraction stage starts with fresh bones, the experiment shown in Figure 6-5, Section 6.3. The stage-wise iterative analysis allows us to construct a different operating line for each stage instead of an operating line for the whole system based on an overall mass balance. This means that if hold up data is measured for each stage it can be incorporated in the mass balances to create new operating lines. This hold up may vary between stages since the porosity of the spent bones will change substantially as fat and SNF are removed, resulting in an operating curve, not a straight line for the whole process. The stage-wise approach deals with these issues much more successfully.

There is another constraint to this analysis because the real process has started with not only water, $y_0 = 0$, but also fresh green bones which have an extractable fraction of 0.172 as stated earlier. This sets the value of x_n coming out of the last stage. The analysis can be conducted in one of two ways, either continue with an original targeted yield until the final stage reaches or exceeds the value of x_n or set the number of stages in the process design and perform a goal seek on an Excel spreadsheet to readjust for a value of x_0 and yield achieved with that set number of stages. The latter approach and a graphical representation for three stages is shown in Figure 7-7.

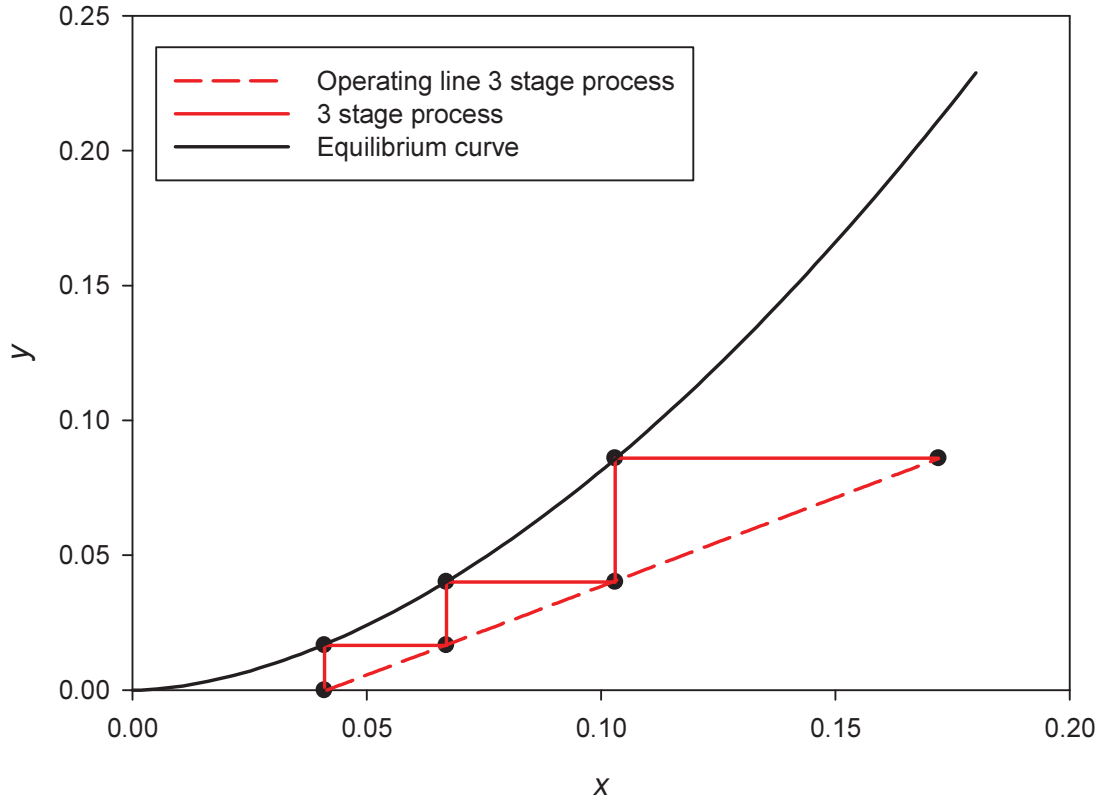

Figure 7-7 Extraction plot for a 3 stage process with each stage going to equilibrium at 120°C.

Next consider the time taken to reach equilibrium and the resulting viscosity profile of the process. Because the concentration of the aqueous extract reaches a constant value asymptotically, the equilibrium time was defined as the time required for the total solids to reach 99% of its final value. The SNF concentration and viscosity evolution for equilibrium extraction is shown in Figure 7-8. The equilibrium times are 6.8, 6.3 and 6.1 hours for stages 1, 2 and 3 respectively, giving a total processing time of 19.2 hours. This provides a shorter processing time than the current EC extraction process of 72 hours and therefore would increase production capacity by over 3.5 times. The process also provides a higher yield and higher solids content compared to the current EC process.

However, there is a peak and then a decline in viscosity for each stage due to long exposure at high temperature for little gain in solids. The peak appears at 4.1, 3.4 and 2.7 in stages 1, 2 and 3 respectively. In the final stage there is a peak viscosity of over 0.004 Pa.s, but this declines to about 0.0035 Pa.s or by 12.5% when equilibrium is reached.

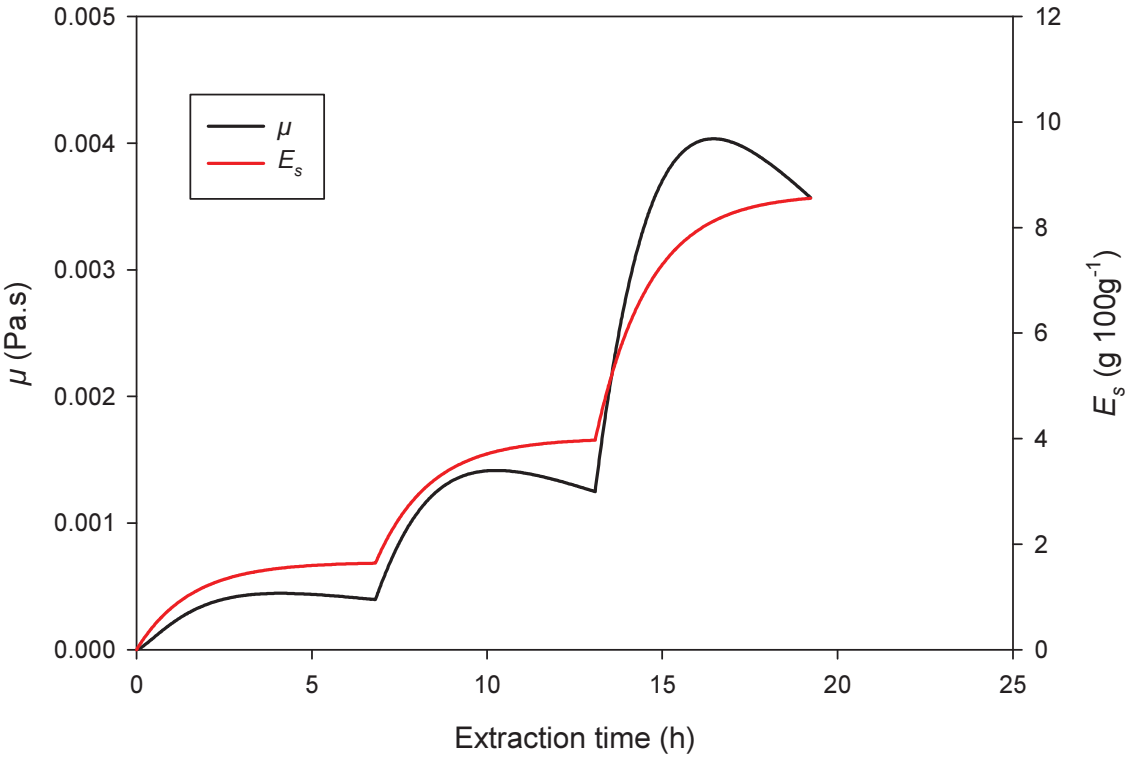

Figure 7-8 E_s and μ evolution for three stage extraction to equilibrium at 120°C

Consider now a design with consideration of the product viscosity. Ideally, one would run each of the three stages of extraction for the time taken to reach maximum viscosity but this action would clearly shift the interface between the different stages shown in Figure 7-8 which in turn would have an effect on the time taken to maximum viscosity.

This problem is by-passed by setting a total desired run time (in this instance 4 hours) and testing for different scenarios of time distribution between the different stages. The following examples are introduced to illustrate the methodology developed and the major points that the analysis highlights.

The first example uses extraction times of 1, 1 and 2 hours for stages 1, 2 and 3 respectively. The longer time was chosen for stage 3 because Figure 7-8 showed that the final stage gave the largest gains in total solids. The effect of extraction time is accounted for by defining an efficiency factor ε

$$\varepsilon = \frac{y}{y_e} \qquad (7.29)$$

where y is the concentration of the extracted solution at the chosen stage extraction run time and y_e is the SNF fraction of the solution extracted when equilibrium is achieved which is determined by using the equilibrium curve.

The efficiency ε for the i^{th} stage can be determined for total solids based on the following equation

$$\varepsilon_i = 1(1 - e^{-bt_i}) \qquad (7.30)$$

where t_i is the extraction time for the i^{th} stage. Therefore for the efficiency of a 1 hour extraction stage at 120°C, b = 0.65 hr^{-1} Section 6.1.2) will be given by

$$\varepsilon = 1(1 - e^{-0.65\times1}) = 0.48 \qquad (7.31)$$

Similarly for 2, 3 and 4 hours the ε is 0.73, 0.86 and 0.93 respectively. With ε it is then possible by modifying equation 7.14 to calculate y_i such that

$$y_i = \varepsilon_1 \times (4.68\mathrm{x_{i-1}}^{1.76}) + y_{i-1} \qquad (7.32)$$

Then Equations 7.32 and 7.15 to 7.18 can be used for a stage analysis using goal seek in Excel as was used previously (an example spreadsheet is given in Table 11-5 of the Appendix). A comparison between the 3 stage extraction to equilibrium and the 3 stage extraction for 4 hours is given in Figure 7-9. The plot shows that the shorter process results in a lower E_s and a lower yield than shown in Figure 7-8 for the equilibrium extraction.

The evolution of E_s and μ was then generated as previously for the 3 stage process, but E_{se} for each stage was generated from y_e not y, is given in Figure 7-10. The viscosity profile does not pass through a maximum as shown in Figure 7-8 but increases continuously during extraction. The final E_s is 7.7 g $100g^{-1}$ which is higher than the single 4 hour extraction of 5.87 g 100 g^{-1} but lower than 3 stage process to equilibrium which gave 8.55 g 100 g^{-1}.

The final viscosity is now 0.0048 Pa.s compared to 0.0035 Pa.s in the equilibrium process and the ratio of run times and therefore throughput for the same equipment is 4.8.

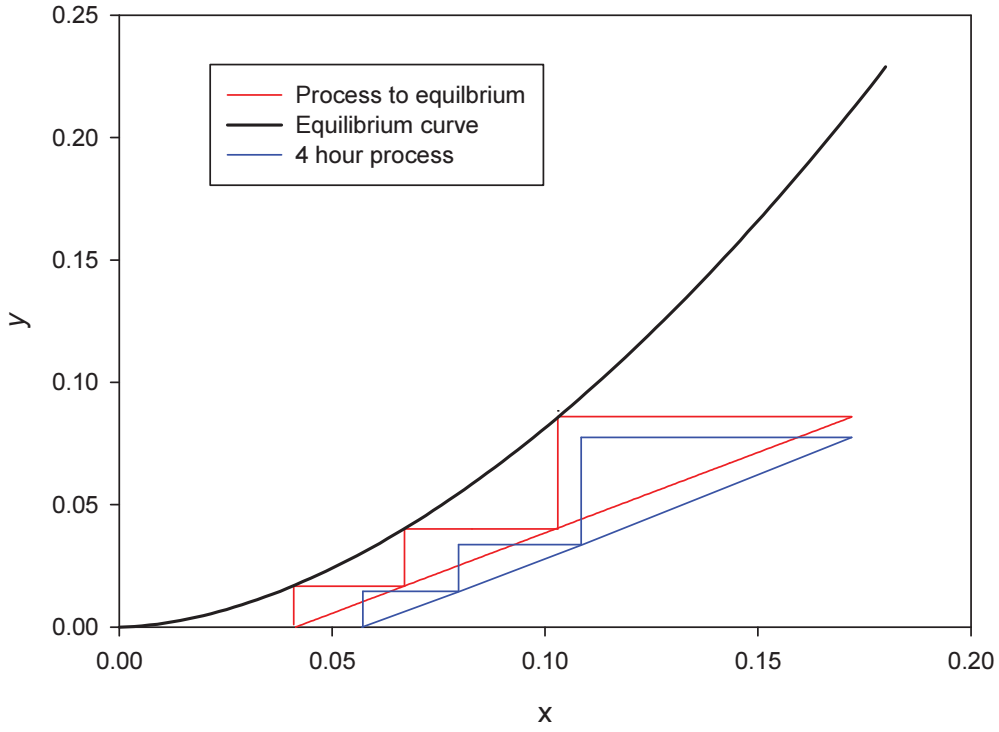

Figure 7-9 Comparison of three stage equilibrium and 1:1:2hr extraction at 120°C .

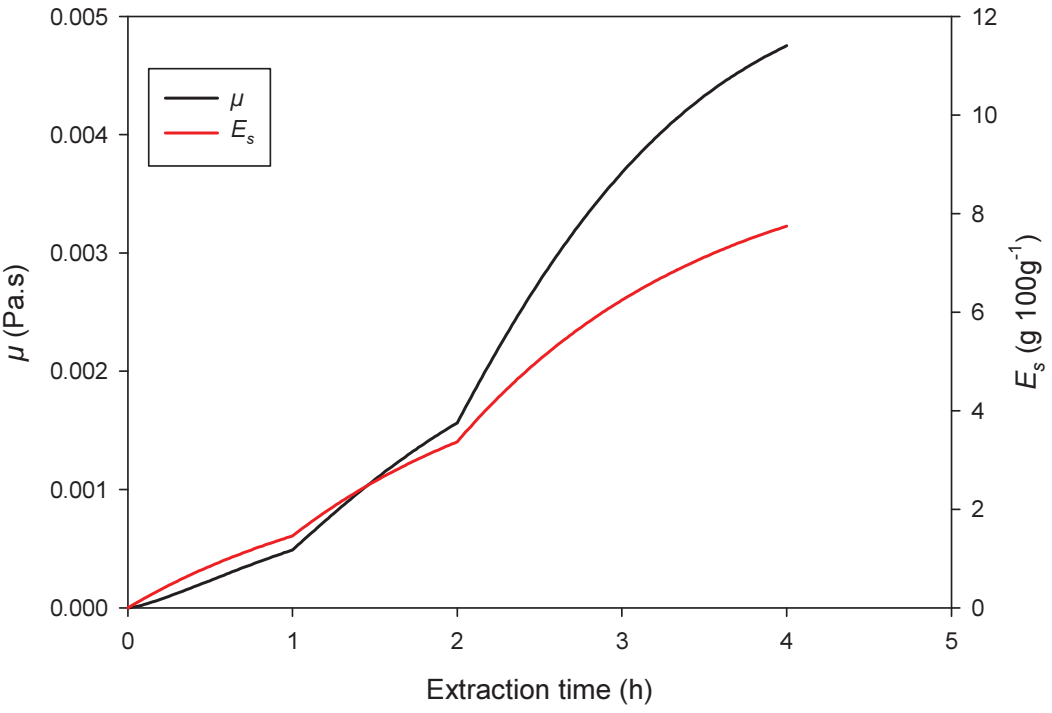

Figure 7-10 E_s and μ evolution for a 4 hour 3 stage 1:1:2 hr process at 120°C

In the next example, consider a two stage extraction process over four hours. Two alternative four hour operating regimes were analysed (1) a 2:2 hour and (2) 1:3 hour extraction. Figure 7-11 shows very slight decreases in yield and final E_s for the 1:3 process compared to the 2:2 process. Both 2 stage processes also have a lower yield and final E_s than the 3 stage 4 hour process.

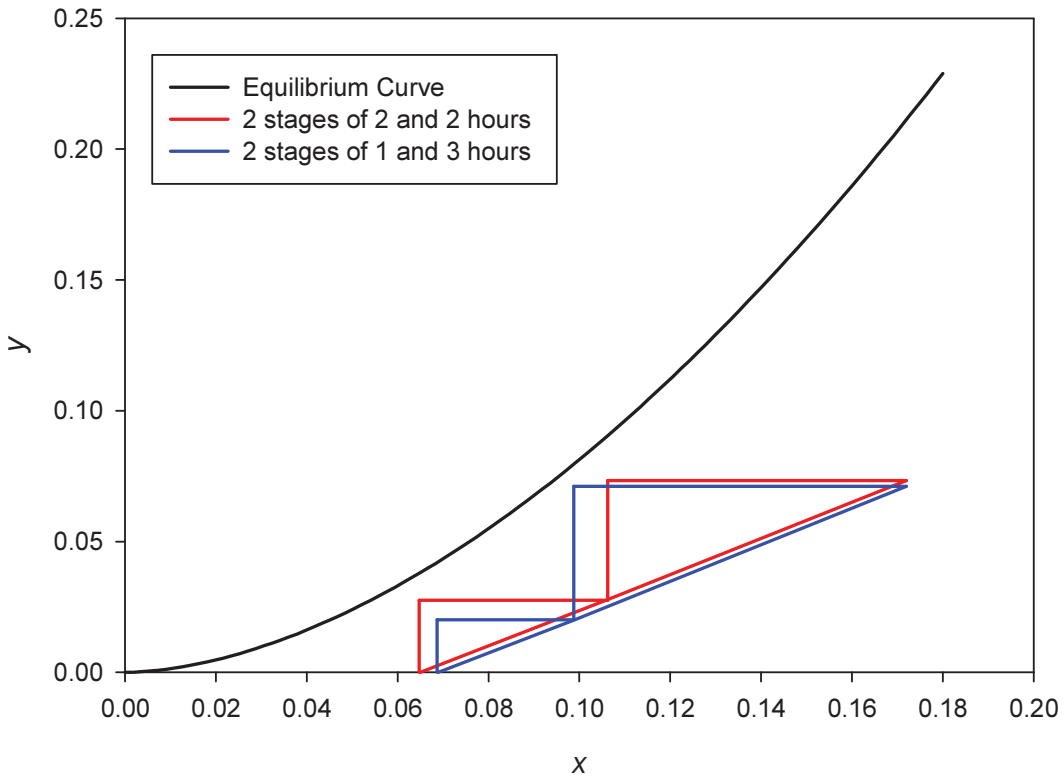

Figure 7-11 Comparison of a 2:2 hour and a 1:3 hour extraction process at 120°C

The E_s and viscosity evolution for the 2 stage processes is given in Figure 7-12. The 2:2 hour process gives a slightly better viscosity and final solids concentration than the 1:3 process and would be recommended as the better option.

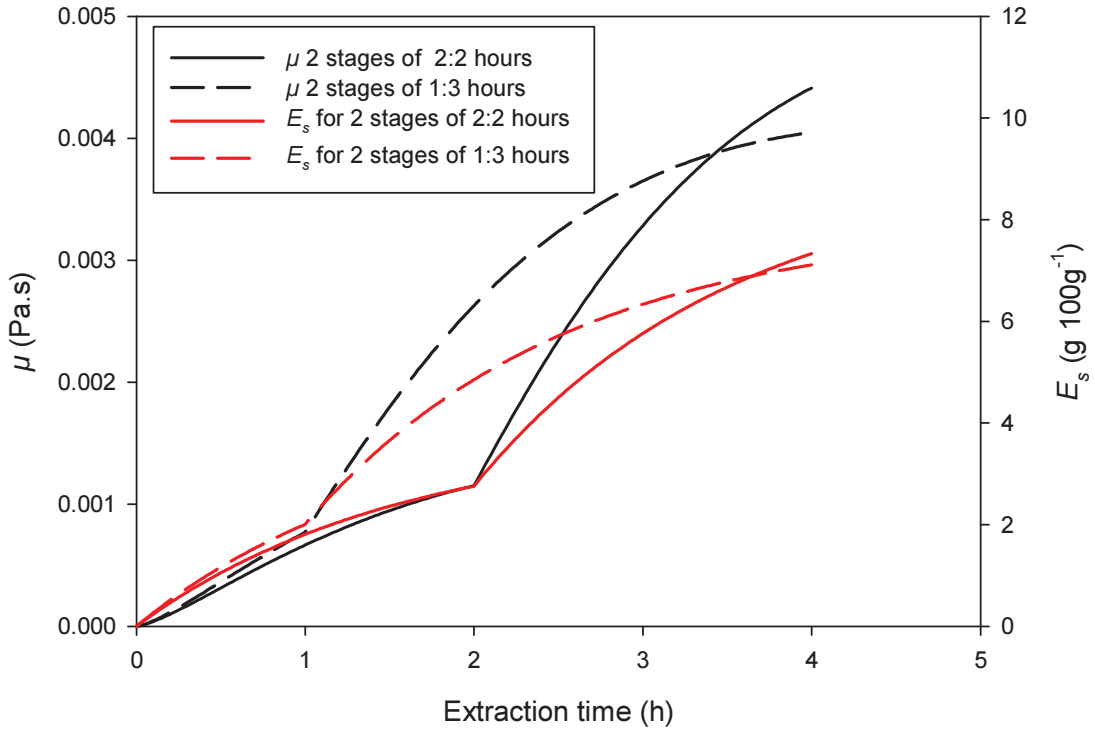

Figure 7-12 Evolution of E_s and μ for a 2 stage extraction with a total time of 4 hours at 120°C

7.2.4.4 Maximising SNF concentration in the aqueous extract solution

Another exercise was to determine if it was possible to achieve a solids concentration at the end of extraction that was high enough that further concentration was not necessary. A multi-stage process where fresh bones are added at the start of each stage was considered to see if a concentration of 16 g 100 g^{-1} could be achieved.

Therefore each stage must be analysed as follows

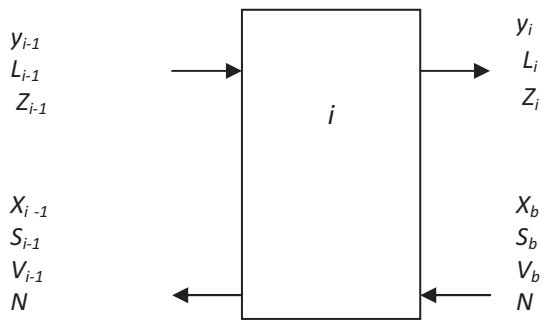

Figure 7-13 Definition of stage *i*

With fresh bones being added each for each stage, x_b, S_b and v_b and N are the values for fresh bones for each stage.

The values of y_{i-1}, L_{i-1} and Z_{i-1} must be defined either from analysis of the previous stage. For one stage using water at the start of the process $y_{i-1} = 0$. It is again assumed that (L-Z) and N remains constant through all of stages. To start the process a value of x_{i-1} is guessed and from this S_{x-1}, V_{x-1} are calculated using N. Then the concentration of the aqueous stream y_i, coming out can be calculated from the equilibrium curve using equation 7.14. Then Z_i and L_i are calculated using equations 7.15 and 7.16 respectively. The total SNF input mass to stage i is

$$I = (Z_{i-1} + S_b) \qquad (7.33)$$

The total SNF output mass is

$$O = (Z_i + S_{i-1}) \qquad (7.34)$$

The difference (D) represents the accumulation of hold-up in the system

$$D = O - I \qquad (7.35)$$

$$\text{At steady state } D = 0 \qquad (7.36)$$

All of the equations were entered into Excel with a cell for each of the values linked with the appropriate formulas. Solver was then used to resolve the mass balance by returning 0 for equation 7.36 by adjusting x_i. The resulting y_i, L_i and Z_i could then be used to analyse another step.

For example, the first stage of a process where 100 kg of green bones is added to 100 kg of water and shown in Figure 7-14. Therefore y_o is and Z_0 are both zero and L_0 is 100kg. Also x_b S_b, V_b and N are given values of fresh bones. A guess of x_o = 0.05 is made

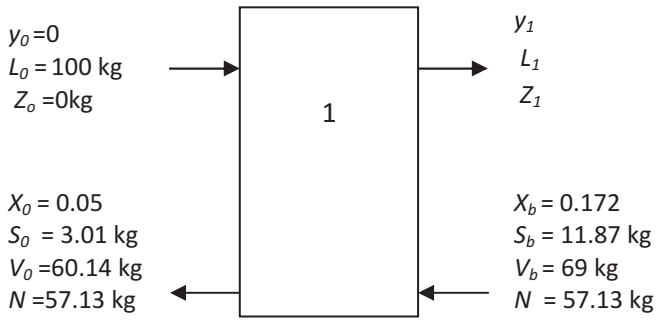

Figure 7-14 Analysis of stage 1 with addition for fresh bones

With the values in Figure 7-14 as the starting point y_1 is given by equation 7.14

$$y_1 = 4.68x_0^{1.76} = 4.68 \times 0.05^{1.76} = 0.024 \qquad (7.37)$$

Z_1 is given by equation 7.15

$$Z_1 = \frac{L_0 y_1}{(1-y_1)} = \frac{100 \times 0.024}{(1-0.024)} = 2.46\ kg \qquad (7.38)$$

L_1 is given by equation 7.16

$$L_1 = Z_1 + L_0 = 2.46 + 100 = 102.46\ kg \qquad (7.39)$$

The equation (7.36) yields

$$(z_{i-1} + S_b) - (z_i + S_{i-1}) = (0 + 11.87) - (2.46 + 3.01) = 6.4\ \text{kg} \qquad (7.40)$$

Therefore the mass balance is not resolved. Using Solver to set equation 7.37 to zero changes x_0 to 0.0853 and the final first stage analysis is presented in Figure 7-15 that can now be used to analyse the next stage.

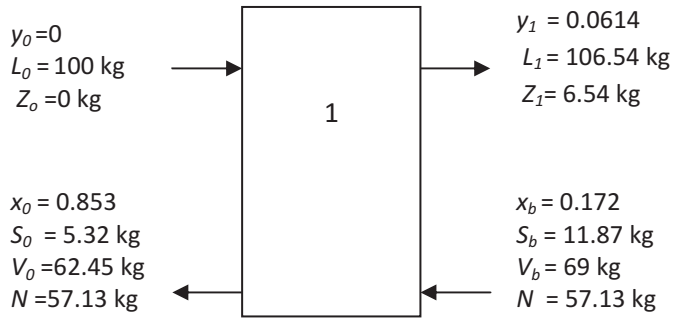

Figure 7-15 Stage 1 with fresh bones added

The above analysis can be repeated until y = 16 kg 100 kg^{-1}. Figure 7-16 shows that 5 equilibrium stages are required to achieve the desired concentration. Having already shown that a single stage extraction to equilibrium is not viable in terms of process time and because of the reduction in viscosity over that long period, so 5 stages would clearly be excessively time consuming. In addition the yield from the bones is a mere 32% and therefore a considerable amount of raw material would be required. It is concluded that this scenario is not viable and an evaporation step is required.

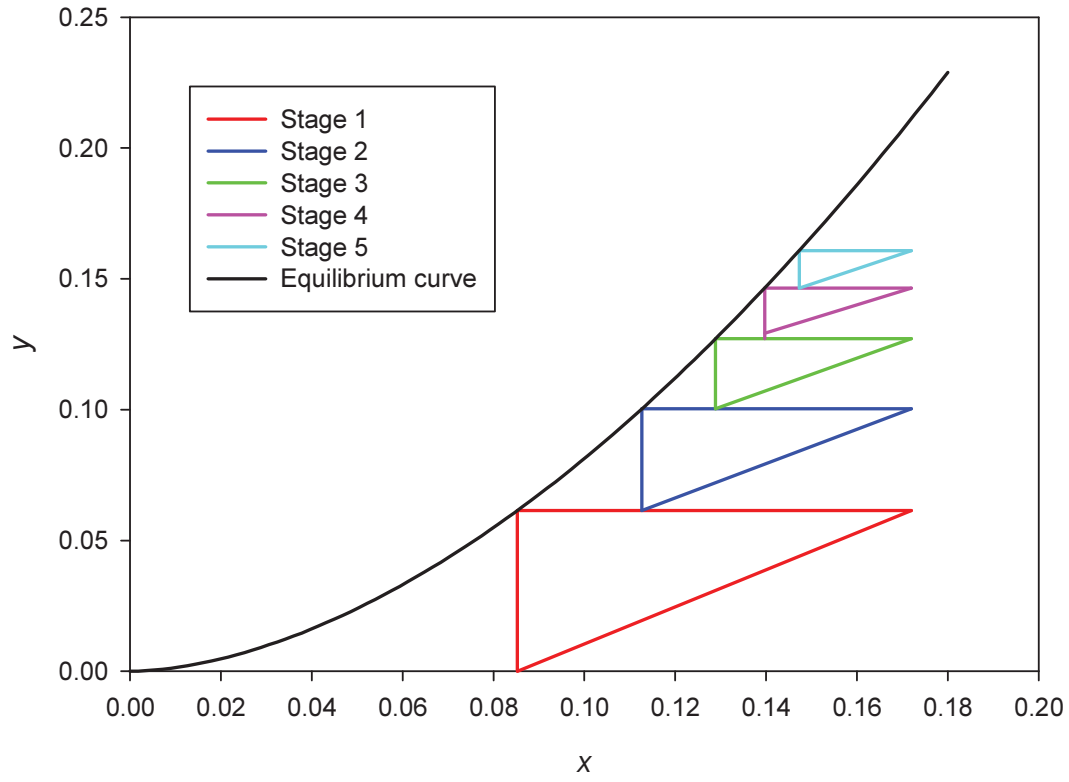

Figure 7-16 Equilibrium extraction stages at 120°C with fresh bones added at each stage until a E_s of 16 kg 100 kg^{-1} is achieved

Note that the graphical representation in Figure 7-16 is completely different from the classical representation of the classical McCabe Thiele method which is based on a single overall operating line instead of a different operating line for each stage. It also illustrates the much greater flexibility of the present stage-wise iterative analysis.

Whilst it is not practical to achieve a 16 kg 100 kg^{-1} concentration with multiple stages a two or three stage process with a short extraction time could be considered to reduce the amount of evaporation required.

The way to account for the change from equilibrium time to a set run time for this scenario is to (1) complete the analysis for the first stage to equilibrium concentration to determine the solids concentrations y_i and x_i renamed in this example as y_{ie} and x_{ie}. Then (2) an efficiency factor is defined by the time allocated to each stage using equation 7.31. From this the y_i is determined from

$$y_i = \varepsilon_i y_e \qquad (7.41)$$

Then actual Z_i can be determined using equation 7.15 and from a mass balance on the solids the actual S_{i-1} is determined using equation 7.17.

For example, if one considers a 2 hour process for the first stage of the equilibrium process presented in Figure 7-15 using equation (7.31) gives

$$\varepsilon_1 = 1\left(1 - e^{-bt_1}\right) = 1(1 - e^{-0.65\times 2}) = 0.727 \qquad (7.42)$$

Then using y_{1e} = 0.0614kg/kg, then the actual value of y_1 is given by equation 7.31

$$y_1 = \varepsilon_1 y_{1e} = 0.727 \times 0.0614 = 0.0446 \qquad (7.43)$$

Using equation 7.15

$$Z_i = \frac{L_0 y_i}{(1-y_i)} = \frac{100\times 0.0446}{(1-0.0446)} = 4.67\ kg \qquad (7.44)$$

Using equation 7.17

$$11.87 = 4.67 + S_0 - 0 \qquad (7.45)$$

Rearranging gives the actual value of S_0 in this new scenario as 7.20kg. The final analysis of stage 1 is presented in Figure 7-17.

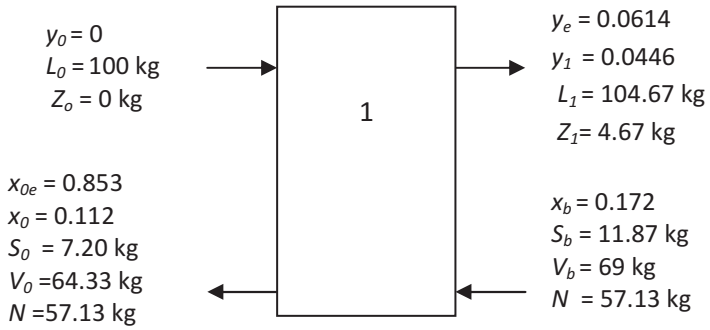

Figure 7-17 Analysis of Stage 1 for a 2 hour extraction process

The graphical representation in Figure 7-18 shows that the results for a two stage 2:2 hour and a three stage 1:1:2 hour process using fresh bones for each stage. The three stage process gives a slightly higher solids concentration of 8.36 g 100 g^{-1} compared with the two stage process that gives a solids concentration of 7.72 g 100 g^{-1}. Both are well below the desired

16% total solids. The 3 stage process with fresh bones added at each stage gives a higher concentration than the 3 stage counter-current process by 8.5%.

The yield from the bones for the two and three stage processes is 35.2% and 25.6% respectively and is well below the 49.5% for the 4 hour single stages extraction. Clearly the price of adding fresh bones in multi-stages for short processing time will be an increased raw material cost.

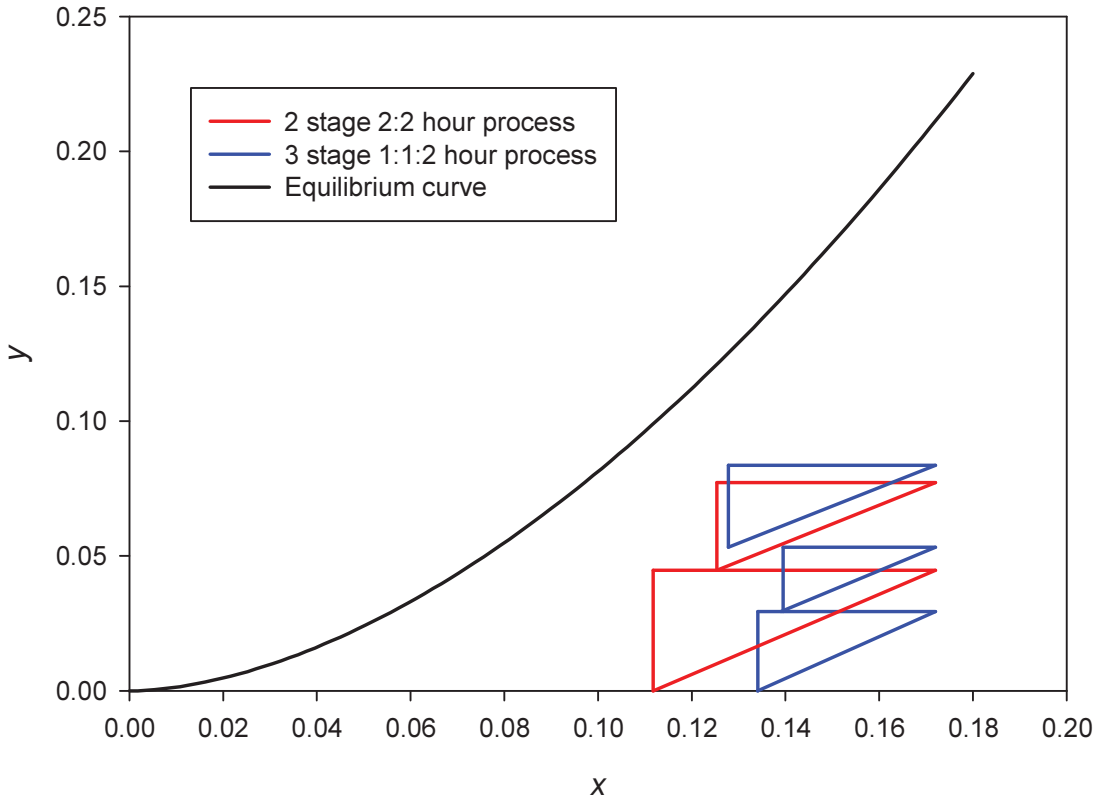

Figure 7-18 Stage analysis of a 2 stage 2:2 hour and 3 stage 1:1:2 hour extraction at 120°C

The evolution of solids and viscosity is presented in Figure 7-19, showing a steady rise in solids and viscosity in both regimes. The three stage process shows a slight advantage of higher solids concentration and viscosity, but the higher viscosity for the three stage process is simply a reflection of the higher solids concentration. When both were concentrated to 16% solids concentration they gave a viscosity of 0.014 Pa.s.

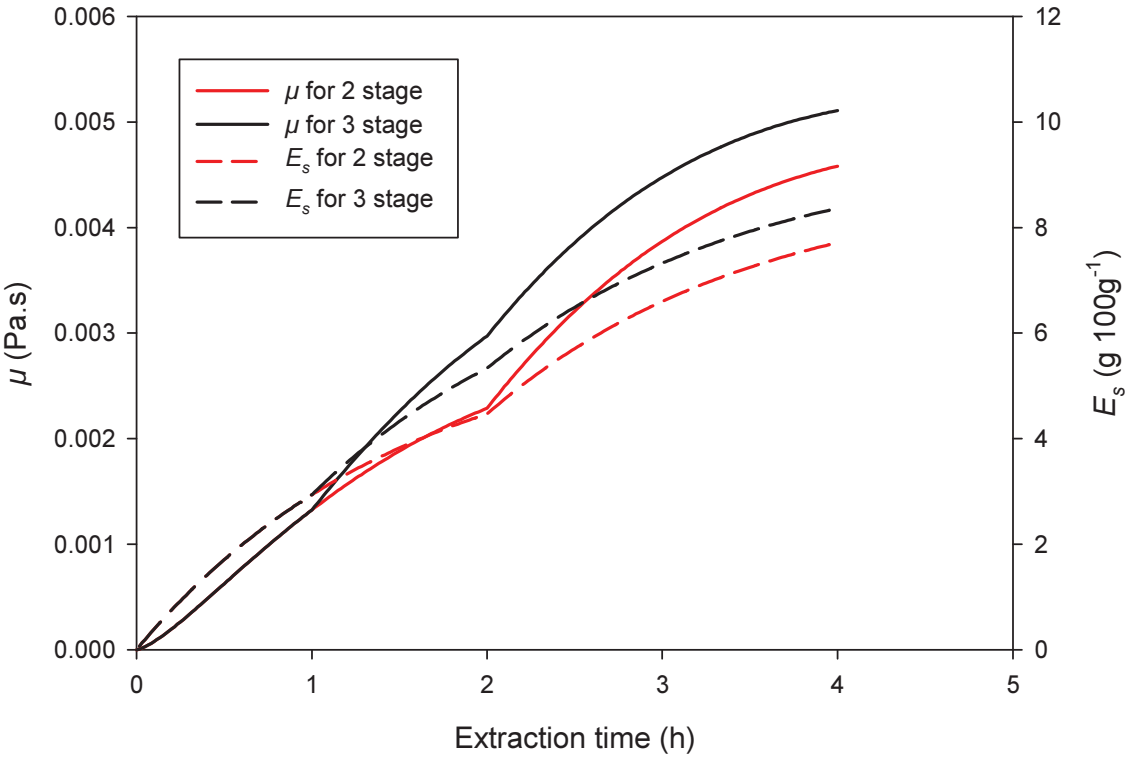

Figure 7-19 Evolution of E_s and μ for a 3 stage 1:1:2 hours and a 2 stage 2:2 hour extraction processes at 120°C

The economic consideration for adding fresh bones to each stage depends on the cost of raw bones versus the cost of evaporation. Both have a capital and operating cost component. More evaporation requires a larger evaporator (capital cost) and more energy to run (operating cost), while using more fresh bones will cost more (operating cost) and requires larger storage and handling equipment (capital cost). A balance of these costs must be considered and it is also pointed out that the price of raw materials may change while capital costs are fixed once the equipment is purchased. Therefore the future costs of raw materials and energy should be considered.

7.2.5 Comparison of different processes

The reader can see that an infinite permutation of temperature, time and number of stages can be considered. A summary of the processes compared is given in Table 7-1 to provide some general trends. Having shown how this procedure provides a reliable and quantitative analysis, it can be used by others for any particular permutation.

Table 7-1 Comparison of the different processes evaluated

Process	Extraction Process	Concentration Process	E_s (g $100g^{-1}$)	μ after extraction (Pa.s)	Yield % Extractable solids extracted	Final μ At 16% solids concentration (Pa.s)
Current EC	92°C 72	92°C 72 h	6.29	0.0026	53%	0.0108
EC optimised for μ	92°C 40.2 hours	92°C 72 h	5.91	0.0030	48%	0.0146
Current EC with VE	92°C 72 h	60°C 20 minutes	6.29	0.0026	53%	0.0138
HTSTE with VE	120°C 4 hours	60°C 20 minutes	5.87	0.0023	49%	0.0146
HT to equilibrium VE	120°C 3 stages (6.8 h, 6.3 h, 6.1 h)	60°C 20 minutes	8.6	0.0035	80%	0.0126
HTSTE (3 stage 1:1:2) VE	120°C 3 stages (1 h, 1 h, 2 h)	60°C 20 minutes	7.7	0.0048	71%	0.0146
HTSTE (2 stage 2:2) VE	120°C 2 Stages (2 h, 2 h)	60°C 20 minutes	7.33	0.0044	64%	0.0146
HTSTE (2 stage 1:3) VE	120°C 2 stages (1 h, 3 h)	60°C 20 minutes	7.11	0.0041	67%	0.0146
HTSTE (FB 3 Stage 1:1:2) VE	120°C 3stages(1, 1, 2 h) Fresh bones added each stage	60°C 20 minutes	8.36	0.0051	26%	0.0143
HTST (FB 2 Stage 2:2) VE	120°C 2stages (2,2 h) Fresh bones added each stage	60°C 20 minutes	7.72	0.0046	35%	0.0144

7.2.5.1 Economic Comparison

An economic comparison was conducted by comparing the throughput and revenue generated by a fixed size processing plant. A fixed size plant was based on a quote provided by APV for a bone extract processing plant (Mabilangan, 2010) which consisted of two 5,000 L capacity extraction vessels and a falling film evaporator for concentration with a maximum evaporation capacity of 1,500 kg hr^{-1}.

A breakdown of the cost is given in Table 7-2, where the total cost for the capital equipment C_{eq} is \$2.79M. According to (Marouli & Maroulis, 2005) the total fixed investment C_{fx} can be determined by

$$C_{fx} = f_{me}C_{eq} + f_{cv}C_{eq} \qquad (7.46)$$

where f_{me} is the installation factor that includes the installation and f_{cv} is the factor for civil works for land improvement and buildings cost. Factors for f_{me} and f_{cv} are 0.35 and 0.45 respectively (Marouli & Maroulis, 2005). Using these factors a total capital cost of \$3.67M is required.

Table 7-2 Capital Equipment costs for processing plant

Equipment	Specification	Cost
Weighing and tipping station		130,000
Hoist system (3,000 kg)	3,000 kg max	56,000
Extraction vessels (2 x 4,000 L capacity)	2 x 5,000 L steam jacketed vessels at 120°C	670,000
Extract cooling system	15,000 L hr^{-1} cooling from 125 to 95°C	57,000
Filter system (100 µm 15,000 L hr^{-1})	100 µm 15,000 L hr^{-1}	110,000
Buffer storage (pre-oil separation)	5,000 L steam jacketed tank	113,000
Solid separation and Oil removal	2,000 - 4,000 kg hr^{-1}	367,000
Oil storage system 900 L	900 L	90,000
Extract Storage system	6,000 L	135,000
Rising falling film Plate evaporator	1,800 kg hr^{-1} feed 6-20% solids 1,650 kg hr^{-1} evaporation	380,000
Concentrate storage system	900 L steam jacketed tank	209,000
CIP system	10,000 L hr^{-1} 70°C	402,000
Total Equipment costs (C_{eq})		**2,719,000**
Total Mechanical and Electrical Costs (C_{me})	=0.35 x C_{eq}	952,000
Civil and site works (C_{cv})	0.45 x C_{eq}	1,224,000
Total investment (C_{fx})		**3,672,000**

Using these factors the following processes were tested

1. The Current EC extraction process 3 days at 92°C with vacuum evaporation
2. A four hour single stage extraction at 120°C with vacuum evaporation
3. A semi-counter current 2 stage extraction process at 120°C of 2 hours for each stage with vacuum evaporation
4. A 2 stage extraction process at 120°C for 2 hours at each stage with fresh bones added for both stages followed by vacuum evaporation
5. A four hour single extraction with evaporation to the viscosity of the current product i.e. with 12% solids instead of 16%

The volume of product each week was based on the processing time with a realistic schedule and shift pattern of 2 x 8 hours 5 days per week. The two stage processes included an additional hour because of having to stop the process and start it again. The number of batches (*B*) per week from 2 vessels is given in Table 7-3.

Table 7-3 Determination of the number of batches per week

Process	Batch time	Batches per vessel per shift	Batches per week, *B*
1	3 days	0.15	3.4
2	4 h process + 1 h = 5 h	1	20
3	4 h process + 2 h = 6 h	1	20
4	4 h process + 2 h = 6 h	1	20
5	4 h process + 1 h = 5 h	1	20

The total amount of solids non-fat (*Z*) generated by each process is given by

$$Z = B \times \frac{E_s \times 2{,}500}{(1 - E_s)} \qquad (7.47)$$

The total extract produced each week L_w is given by

$$L = Z + 2{,}500B \qquad (7.48)$$

The total amount of finished product (*F*) for a final concentration is given by

$$F = \frac{Z}{E_f} \qquad (7.49)$$

Where E_f is the SNF concentration of the final product and this is 0.16 for the processes 1 to 4, but is 0.13 for process 5.

The revenue R from the product is based on \$3.00 kg^{-1} of product estimated from the \$6.00 kg^{-1} price at the supermarket less GST \$0.9 less supermarket profit \$1.02 kg^{-1} less distribution costs of \$0.99 kg^{-1}.

The operating costs C_{OP} are given by

$$C_{op} = 1.2 \times C_{MU} \qquad (7.50)$$

where C_{MU} is the material and utility costs. The material cost is based on the amount of raw bones (M), assuming that bones contain 31% fat and 11.9% total extractable solids (Section 6.2.2), could be determined by

$$M = \left(\frac{Z}{(yield \times 0.119}\right) \qquad (7.51)$$

The cost of the bones was estimated to be \$0.20 kg^{-1} (B.H.P Wilkinson, personal communication, February 14, 2013).

The cost of the utilities is based on the cost of the steam used for evaporation and extraction.

The steam used for evaporation is based on the total amount of moisture removal (W_v) per week is given by a mass balance such that

$$W_v = \left(\frac{Z - E_S\, Z}{E_S}\right) - \left(\frac{Z - 0.16 \times Z}{0.16}\right) \qquad (7.52)$$

The operating cost of the evaporator was estimated on the steam requirement (s_v). The steam requirement was estimated from 50% of V assuming that a two effect evaporator is used.

$$s_V = \frac{W_v}{2} \qquad (7.53)$$

The steam needed to heat the extraction material (s_E) is determined by the total amount to heat the material plus 10% to hold it at the required temperature. Therefore based on a specific heat capacity of 3.6 and 4.2 KJ kg^{-1} K^{-1} for the bones and water respectively and a enthalpy change for the steam of 2,200 KJ kg^{-1} the amount of steam required is

$$s_E = 1.1\left[\frac{M \times 3{,}600 + W_i \times 4{,}200)}{2{,}2003}\right] \qquad (7.54)$$

Where W_i is the processing water each week which is equal to M as the extraction ratio of bones to water is 1:1.

The steam cost is assumed to be \$40 t^{-1}.

Therefore the total operating cost (C_{op}) is given by

$$C_{op} = 1.2C_{MU} = 1.2\left(\frac{40}{100} * (1.1s_E + s_V) + 0.2 \times M\right) \quad (7.55)$$

The weekly gross profit is determined by

$$GP = R - C_{op} \quad (7.56)$$

And net profit is calculated by subtracting tax at 28% thus

$$NP = (1 - 0.28) \times GP \quad (7.57)$$

Annual return on investment is determined by the total capital investment of \$8 M

$$Annual\ ROI = \frac{GP}{C_{fx}} \quad (7.58)$$

Using this methodology it is possible to compare the processes. Table 7-4 presents the total production and raw material requirement. Clearly changing from the current 3 day extraction to a 4 hour extraction process increases the production volume by over 10 times. A simple 1 stage 4 hour process (2) can be improved in order to achieve higher production by switching to a 2 stage process with fresh bones (4), but this results in almost doubling raw material required. To lessen the amount of raw material required an improvement in yield is achieved by going to a 2 stage semi counter current process (3).

Table 7-4 Materials and utility requirements for comparison of alternative processes

Process	Z (kg week^{-1})	M (kg week^{-1})	F (kg week^{-1})	W_v (kg week^{-1})	s_v (kg week^{-1})	s_E (kg week^{-1})
1	537	8,515	3,356	6,362	2,490	6,362
2	3,118	53,473	19,488	92,873	21,154	46,436
3	3,955	51,929	24,718	104,380	20,543	52,190
4	4,183	100,430	26,143	107,515	39,730	53,758
5	3,118	53,473	25,984	86,377	21,154	43,188

A comparison of the costs and the Return On Investment (ROI) is presented in Table 7-5. The ROI is greatly increased with the four hour processes. Further improvements are seen with multi-stage processing (3) and (4) with little difference between the two, but given that the counter current process requires half the raw material that would be the preferred option. Finally option 5 that reduces the total solids is very favourable (5) and produced the best ROI.

Table 7-5 Operating costs, profit and Return on investment for the alternative processes

Process	C_{MU} ($ kg^{-1} *F*)	C_{OP} ($ kg^{-1} *F*)	*R* ($ kg^{-1} *F*)	*GP* ($ kg^{-1} *F*)	*NP* ($ kg^{-1} *F*)	Annual Profit ($)	Annual ROI
1	0.62	0.74	2.50	1.76	1.06	184,361	5%
2	0.68	0.82	2.50	1.68	1.01	1,024,197	28%
3	0.53	0.64	2.50	1.86	1.12	1,435,866	39%
4	0.90	1.08	3.00	1.92	1.15	1,565,854	43%
5	0.50	0.61	3.00	2.39	1.44	1,941,084	53%

Based on the analysis a two stage semi counter current extraction process with 2 hours for each process at 120°C followed by vacuum evaporation is recommended. The design would be based on using the same bones for the second extraction but offers the flexibility to perform the second extraction on fresh bones if raw material and handling costs are practical and favourable.

7.2.5.2 Secondary product streams and other process considerations

Another aspect for the process that should not be ignored is the processing of by-products.

7.2.5.2.1 Tallow

The amount of tallow extracted was observed to be between 16 and 25% for the processes studied. There was not time to collect the necessary data to define the equilibrium curve but the fat component was collected while the extraction kinetics were determined. There was no point in making a formal analysis under these conditions but it is estimated from the substantial data base gathered that an average 20% yield from the raw bones could be achieved. While the current EC process regards the fat as a waste product that is taken away without charge by outside contractors, the opportunity exists to utilise this stream. From past employment in the Nestle New Zealand Limited, Pet Food Plant 1998-2001, the author knows that pet food companies buy low grade tallow at roughly $0.5 kg in the 1990's and Scaria (1989) indicates a price of US $1 kg^{-1}. Indications are that good quality tallow can fetch much

higher prices nowadays \$1.5 kg^{-1} (B.H.P Wilkinson, personal communication, February 14, 2013). For a first analysis a price of \$1.0 kg^{-1} is reasonable.

Thus for the selected process an additional 5 tonnes of tallow per week is expected. Assuming a price of \$1.0 kg^{-1} this would provide an additional \$5,000 per week or increase the profit by an additional 35%. Therefore it is recommended that adding value to the tallow be further investigated.

7.2.5.2.2 Minerals

A number of preliminary extraction runs were also performed with caustic, acid and enzyme treatments (Wilkinson, 2009; Zhou, 2013). The caustic and enzyme runs indicated that the flavour of the stock obtained would probably not be acceptable to the consumer market and were not pursued further. The acid treatment was inspired from the commercial process for the manufacture of gelatine (Scaria, 1989; Nicolas-Simonnot, et al., 1997; Ockerman & Hansen, 2000). As reported briefly in section 6.2.2.2 all the soluble SNF were extracted from green bones with a series of water washes at 120°C. Then the spent bones were treated with acid in the hope of releasing more gelatine from the remaining collagen then further hot water washes were performed. The solids content of the additional water washes were nil indicating that the extraction of gelatine was completed but the first acid wash conducted at 60°C for one hour already yielded a solids content of 7.4% (Zhou, 2013). With the fast approaching deadline for submission of this thesis, there was no time to make a formal chemical analysis of the composition of the acid wash nor to make yet another detailed study of the acid extraction process, but the well-known literature on gelatine manufacture indicates clearly that the main goal of an acid wash is to remove the calcium phosphate that locks in the gelatine. Scaria (1989) page 32 estimates that the yield of calcium phosphate from dry bones is about 60% and quotes a price of US\$100 t^{-1}. Further investigation of this procedure for extraction and isolation of this by–product is also recommended.

7.2.5.2.3 Flavour compounds

The treatment of flavour compounds was also discussed in many meetings between the candidate and his supervisors. In the current EC process the flavour of the stock is achieved by roasting the bones before stock extraction. As discussed in section 2.6.3, there is a substantial amount of literature to indicate that these flavour compounds, both volatile and non-volatile, come from roasting the meat, not the bones. Hence a good alternative to the present process is to strip the meat from the bones, say by high pressure blasting, and then roast the recovered meat separately. Another approach would be to use scrap meat and roast this separately and while this may incur additional raw material costs, this may offset the

additional cost in stripping the meat from the bones. For both alternatives the oven used would be considerably smaller than the ones used presently for roasting the meat on the bones. In addition, as discussed in section 3.3.2, the flavour compounds are extracted at a much faster rate than the gelatine component of the stock. A further advantage of recovering the flavour compound separately and then adding back to the bone extracts, is consistency of flavour. Natural supplies in the primary industries can vary considerably in fat content and meat retained. Indeed if flavour needs to be enhanced, one can even contemplate purchasing scrap meat to provide even higher concentrations of flavour compounds than can be achieved with just the present supply of bones. This strategy of recovering the flavour compounds separately, even manipulating them to a desired profile and adding back to a more inert substrate is not new to the food industry. It has been used for example in the production of modern instant coffee.

Again, it was not possible to test this new process design within the present time frame and these new process proposals should be tried by future workers in the field.

7.3 Process Flow Diagram

A process flow diagram is included here to indicate what a process may look like. The process is divided into three stages, (1) pre-extraction, (2) extraction and separation and (3) concentration and packaging. Each of these is described below.

7.3.1 Pre-extraction

The process flow diagram for pre-extraction processing is given in Figure 7-20. The process involves receiving bones in bulk bins. The bins are tipped onto a conveyer using a bin tipper. The conveyer allows inspection and manually placing of bones onto trays. Trays are placed into a pre-heated oven where bones are roasted at 220°C for 20 minutes. Following roasting the bones are tipped into a steel basket to make a batch for extraction. The basket is then placed into extraction vessels using a mechanical overhead winch.

In order to reduce the size of the roasting step, the meat is removed from the bones using a high pressure water blaster. The meat is then roasted separately. Another alternative is to the use waste meat and roast it separately and the bones are extracted raw. Further experimental work is needed to optimise this process.

7.3.2 Extraction and separation

The extraction and separation process diagram is given in Figure 7-21. Extraction takes place in two steam jacketed vessels in a semi-counter current process. Fresh water is added to

spent bones for the first extraction which proceeds for two hours at 120°C. The solution from the first extraction is transferred into a vessel with fresh bones and extracted for a further 2 hours at 120°C.

After each extraction step the extract is drained and cooled through a plate heat exchanger in order to reduce the temperature to 95°C to prevent flashing. The fluid is the feed stream to the previous stage to maximise heat regeneration. The extract is pumped through a separator to remove the fat and then a filter before either flowing into the second extraction or flowing into the extraction storage vessel. The extraction storage vessel is a stirred jacketed vessel. Tomato paste can be added at this point.

The tallow and the bones from this process can be used for the processing of secondary streams.

7.3.3 Concentration and Packaging

The concentration and packaging flow diagram is given in Figure 7-22. The extract is pumped through a pre-heater to the evaporator. The pre-heater raises the temperature of the stock to the evaporation temperature. The evaporator operates under vacuum and the evaporation temperature is 55-65°C. A two effect evaporator is shown in the process flow diagram, but other alternatives can be used.

Following evaporation the concentrated solution is placed in a balance tank that acts as a buffer between the evaporator and the filling line.

From the balance tank the stock is heated to 85°C for hot filling. The liquid is filled into pouches that are then sealed. The packaged product is then cooled through a chiller and then placed into secondary packaging and put into chilled storage.

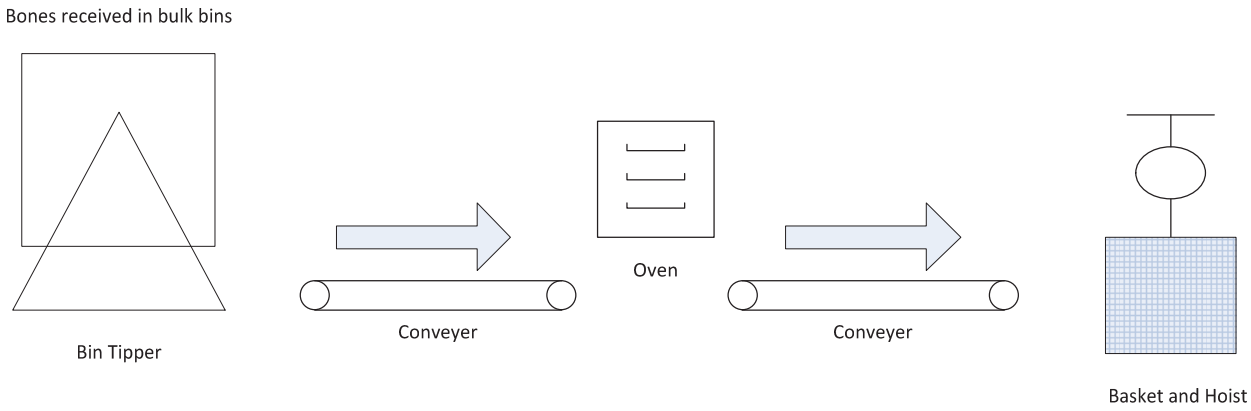

Figure 7-20 Process flow diagram for pre-extraction process

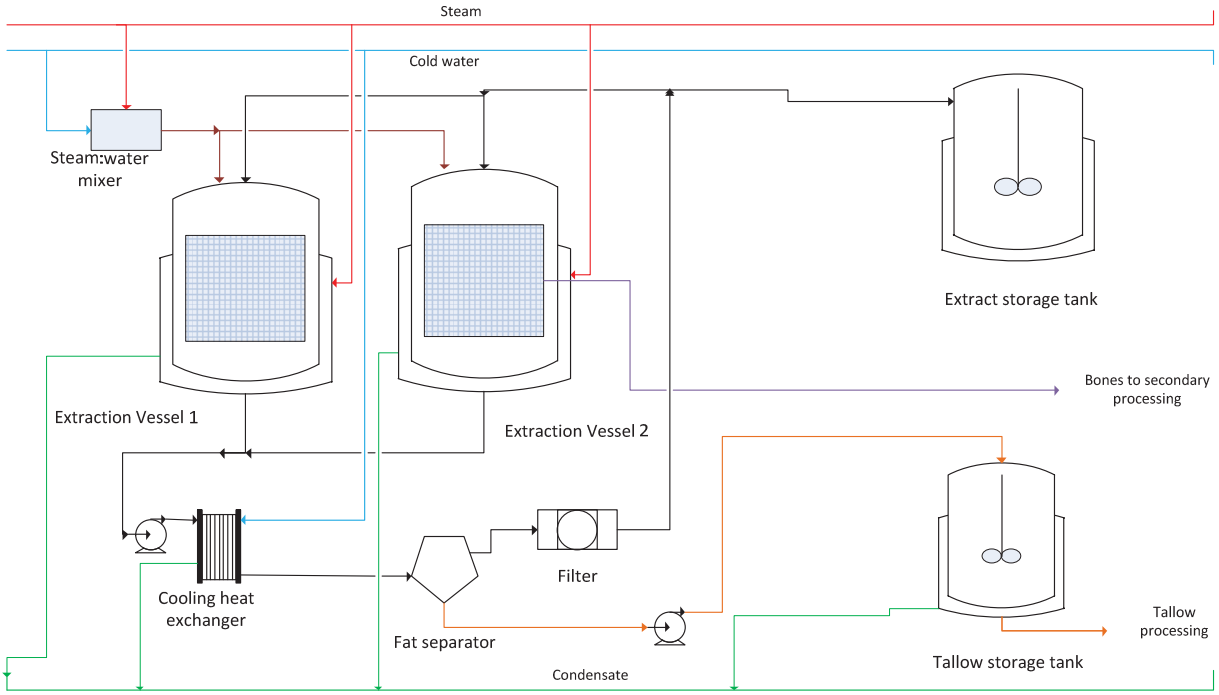

Figure 7-21 Process flow diagram for extraction and separation processes

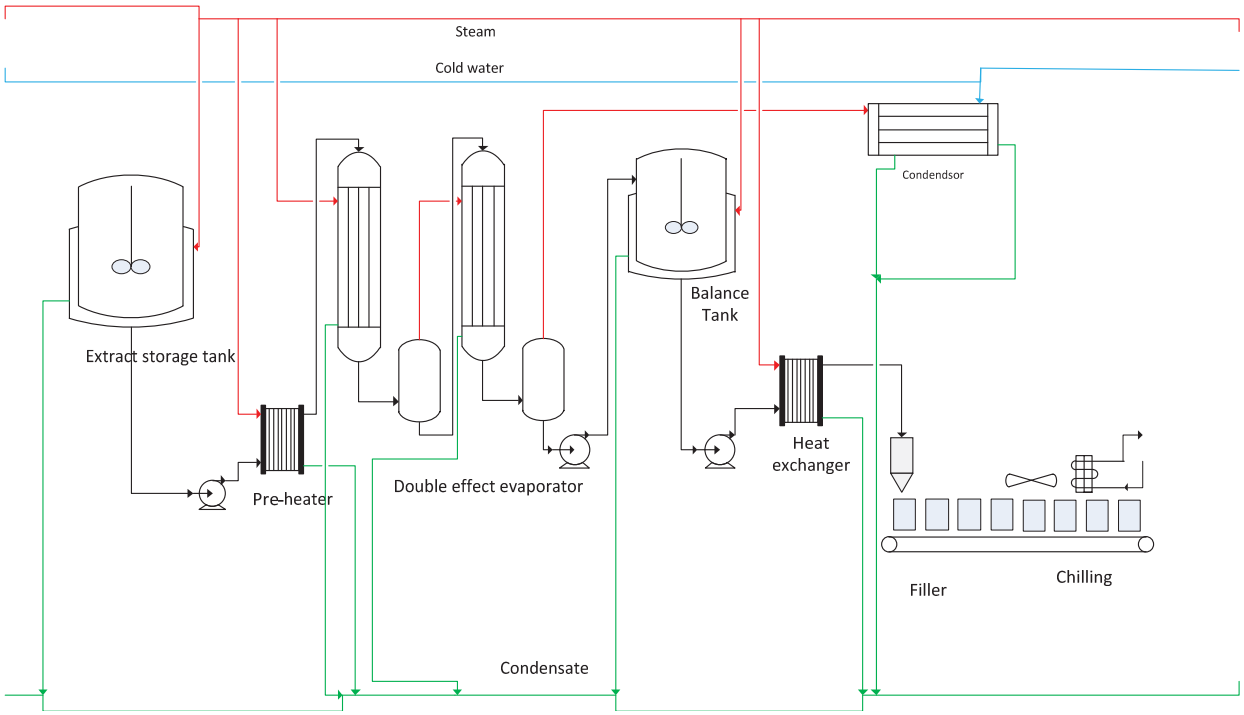

Figure 7-22 Process Flow diagram for the concentration and packaging processes

7.4 Conclusion

In order to design a process it was necessary to develop a model to combine (1) the kinetic data for changes in texture with temperature and time (2) the kinetics for extraction as a function of temperature and time and (3) the extraction equilibrium curve. A simple easy to use model was developed and provides (a) the solids concentration and (b) viscosity development as a function of time and (c) the yield from the bones. The model showed good agreement with experimental data and can be used to analyse a wide variety of processes.

A technique called stage iterative analysis was developed to analyse multiple stage-wise extractions. This differs from the traditional McCabe-Thiele method of multi stage analysis and offers improved flexibility to analyse semi- co- and counter current processes.

These techniques can be used to optimise processing through manipulation of yield, solids concentration at the end of extraction and processing time.

Analysis showed using high temperature extraction (120°C) over a short time (4 hours) followed by vacuum evaporation increased the throughput of a plant by over 10 times the current production. Multi-stage extractions in using semi-counter current arrangement further improves raw material yield, while addition of fresh bones to each stage of a multi-stage extraction further increases production capabilities.

Further improvements in economic return can be realised in developing secondary streams of tallow and calcium phosphate. An improvement in the roasting process by separating the meat from the bones will also enable a more efficient operation.

The tools and analysis will help EC to make wise decisions based on quantified analysis.

8 Overall discussion, conclusions and recommendations

The objective was to design a process for the manufacture of stock using formal engineering analysis rather than random experimental trials of potential processes. The client desired a 10 fold increase in production from 1,500 L to 15,000 L per week and an improvement in texture i.e. a thicker product.

Analysis of the current process showed that it largely involved extracting material from bones using hot water extraction at 92°C and then concentrating the extract to a desired level of total solids (16 g 100 g^{-1}). The texture of the stock solution obtained is due to the presence of gelatine extracted from the collagen material in the bones.

Despite the known time-dependency of gelatine solutions at low temperatures because of their tendency to gel, measurements of the bone extract identified Newtonian behaviour when the temperature exceeded 20°C. Therefore, the texture can be quantified by simply measuring the Newtonian viscosity at 40°C.

The viscosity of bone extract decreased when exposed to temperatures over 60°C and in order to quantify these changes the kinetics of the breakdown were measured between 60 and 120°C. The decrease of viscosity with time was found to follow first order kinetics and the effect of temperature was found to follow the Arrhenius law. In addition, the kinetics of viscosity decline were found to be independent of stock concentration. Therefore the viscosity decline for all concentrations can be represented by equations 5.6 and 5.7.

$$\frac{\mu}{\mu_0} = e^{-kt} \qquad (5.6)$$

$$k = k_{ref} e^{\frac{-E_a}{R}\left(\frac{1}{T+273} - \frac{1}{T_{ref}+273}\right)} \qquad (5.7)$$

The experimental techniques developed for thermal treatment of the stock for temperatures between 100 and 120°C were more complex and more time-consuming than the techniques used for treatments below 100°C. Further kinetic measurements in the range 100 to 120°C are recommended to improve the precision of the data. Despite this shortcoming a model fitted to the data enabled the change in viscosity of bone extract to be predicted for any concentration time and temperature regime between 60 and 120°C for concentrations up to 16% solids.

In the early phase of this project, the amount of extraction was monitored in the traditional method used in gelatine processes: by analysing the chemical compounds characteristics of gelatine, most particularly nitrogen, ash, methionine and hydroxyproline. These chemical assays proved to be expensive and time consuming as they had to be performed by a dedicated laboratory in a fellow institute. In the end, the extraction kinetics were obtained by simply following the change in soluble solids over time. This enabled a simple measurement to analyse each sample quickly and at little expense. Extraction kinetics were measured for temperatures in the range of 80 to 120°C. For temperatures of 100°C and over sealed cans were used. This required individual cans for each time step and was time consuming, but gave more reliable data over previous methods that used non-sealed containers.

The rate of extraction for all temperatures over time followed a first order kinetics rise to an equilibrium value. The rate of extraction was increased with higher temperatures and the Arrhenius law was observed for extraction temperatures within the range of 90 to 120°C. Therefore the extraction kinetics can be represented by equations 6.4 and 6.5

$$E_s = 6.35(1 - e^{-bt}) \quad (6.4)$$

$$b = 0.65e^{\frac{-119{,}500}{R}\left(\frac{1}{T+273} - \frac{1}{120+273}\right)} \quad (6.5)$$

In order to quantify the theoretical yield, the total extractable solids were determined by repeated extractions with water until an extraction was completed with no further gain in solids observed. Reducing the size of the bones and crushing them was used to speed up the process. A 7 L pressure cooker was used for the first set of runs but the temperature could not be monitored because of the pressure seal and the vessel lost a lot of steam. Large variations of extractable solids were found between samples of bones from the same batch. Some of the variation was due to the large variation of the raw material as the amount of bone, meat, connective tissue and fat varied between samples of the same batch. However, there was still concern that some of this variation was caused by the experimental technique. It is recommended that a sealed vessel with good temperature control and recording be used for further work in defining the total extractable material.

No equilibrium curve for the water extraction of bones was found in the literature and one was generated for extraction at 120°C, the chosen process temperature. Basically, the technique consisted of extracting bones with solutions already containing different concentrations of

bone extracts for long enough until the extract solution reached its asymptotic equilibrium concentration. The spent bones were then crushed and extracted with successive doses of water until no further extract was obtained. All the doses of water were pooled and the total solids on the resulting solution determined to calculate the equilibrium concentration of soluble solids left in the spent bones. This procedure was simple but time consuming because each point on the extraction curve at 120°C required a separate run in a sealed can and only a few data points were obtained. Nonetheless the equilibrium curve represented by equation 6.6 proved valuable in the process design.

$$Y_o = 4.68{X_o}^{1.76} \qquad (6.6)$$

A mathematical model was constructed to combine the kinetics of extraction with the kinetics of texture as well as equilibrium data. A novel technique called "stage wise iterative analysis" was developed to test various scenarios for multiple stage extractions. It is different from the traditional McCabe-Thiele method which starts with an overall mass balance to construct an operating line and the Ponchon-Savarit construction which identifies a delta point in the process. By taking a stage wise approach, the present technique is not confined to a rigid system setup but can deal with mixed co-current and counter-current systems or, as demonstrated in Chapter 7, with discontinuous systems where the bones entering each stage are fresh green bones instead of spent bones coming from the previous stage. Traditional techniques of analysing counter current extraction do not exhibit such flexibility. Examples shown in Chapter 7 were developed using Excel but any other platform such as Matlab or Fortran would be suitable. The key feature lies in the reasoning and technique used for analysis, not the platform used.

The model validity was tested by comparing its predictions with results of an extraction and concentration experiment using the current EC process. Agreement was within 10% of experimental data collected.

The advantage of this model is that it allows a paper analysis of many different process options with clear quantitative and graphical estimates of outcomes to facilitate managerial decisions. Only a few process configurations would be short-listed or a single one chosen for actual production trials, thus greatly reducing the time and cost of process and product development. The examples in Chapter 7 illustrate clearly the complex interactions between product quality, yields, and process design, even for a simple operation like stock manufacture.

Model simulations showed that the current EC process leads to a loss in viscosity due to long thermal exposure that is not matched by viscosity gain due to increased solids content. A simple and immediate improvement can be achieved by reducing the current extraction process to less than 21 hours. The use of vacuum evaporation would also improve the final viscosity and reduce the concentration from a 3 day to a 20 minute process.

The model also clearly demonstrated the advantage of using high extraction temperatures. An extraction process of 120°C over 4 hours achieves a similar gain in solids to the current process. The breakdown in viscosity due to high temperature is prevented by the reduced extraction time and the process even results in an improved viscosity compared to the current process. Coupled with vacuum evaporation this high temperature extraction greatly reduces processing time from 6 days to 5 hours and thus can easily achieve the desired 10 fold increase in daily production.

Use of multiple extractions in a semi-counter current manner can improve yields and thus reduce raw material costs. Multiple stage extractions with the addition of fresh bones can be used to increase the solids content of the aqueous extract and reduce the amount of evaporation that follows.

Potential is also seen in the processing of by-products from the bones. The fat that is separated in extraction can be refined into tallow with a potential yield of 30% from the bones which could be more than enough to cover the cost of the bones. There is also the potential to extract calcium phosphate in significant quantities using acid extraction of the spent bones. Further work is needed and recommended for by-product processing.

Also recommended is the further investigation to simplify the roasting step prior to extraction. This could be achieved by separating meat from the bones, or using scrap meat for roasting and extracting from raw bones. There is the potential to extract flavour from roasted meat, concentrate this separately and then blend with bone extract to independently control texture and flavour. Further work is needed.

In conclusion, by gathering kinetic and equilibrium data for stock extraction not available in the published literature, sometime with techniques that differed from those of previous workers, and developing a more flexible model for process analysis, this work has provided a sound basis for the development of a good process for manufacture of stock from bones. Unfortunately, much time was spent on trying different techniques of analysis of bone extracts

until the final methods were developed and the data gathered was not as plentiful as the author would have wished although it was sufficient to use in the process analysis.

The value of the present approach is that it identifies clearly the process parameters that have the most impact on the financial outcome and illustrates clearly the way for to achieve the overall research objectives.

8.1 Conclusions

1) The current commercial process investigated is a hot water (92°C) extraction of bones followed fat separation and concentration that produces a solids content of 16 g 100 g^{-1}. The solids are largely derived from gelatine and this provides the material with a 'thick' texture.
2) The texture of the stock can be quantified by measuring the Newtonian viscosity of the material at 40°C.
3) The viscosity of the extract increases with increasing solids content and an empirical equation is used to quantify this.
4) The viscosity decreases over time at temperatures above 60°C. The rate of decrease for the viscosity increases with temperature but is independent of solids concentration and is modelled with first order kinetics and Arrhenius law for temperatures between 60 and 120°C.
5) The extraction of bones in hot water can be followed by the easily measured the fat free soluble solids content which is easily related to the total solids content.
6) Extractions at temperatures between 100 and 120°C was achieved using 3 L sealed cans and demonstrated a rapid rise in solids compared to the current 92°C process.
7) The extraction kinetics were found to be a first order rise to an equilibrium solids concentration. The rate of reaction is greatly affected by temperature and was found to obey Arrhenius law for temperatures between 90 and 120°C.
8) The total extractable solids content in the rib bones was found to be 11.9 ± 0.25%, this is below the total collagen present in bones. The extraction of further solids by lowering the pH was demonstrated.
9) The extractable fat content of the rib bones was found to be 31 ± 4%
10) The equilibrium curve for extractable solids between the aqueous phase and the solid bones was determined for 120°C, using four data points.

11) The kinetics of extraction and viscosity could be combined to model the evolution of solids and viscosity over time for various extraction and concentration processes between 92 and 120°C.
12) The model was validated with experimental data and showed that an extraction temperature of 120°C with vacuum evaporation would easily enable the desired 10 fold increase in production and a higher viscosity.
13) The development of a stage-wise iterative analysis allows the analysis of numerous multi stage extraction processes to be compared. The analysis demonstrated that an increased yield can be achieved using multiple extractions and also demonstrated that a concentration process was necessary to achieve a solids concentration of 16 g $100g^{-1}$.

8.2 Recommendations

It is recommended that:

1) Further data be collected for measuring the change of viscosity over time at temperatures between 100 and 120°C using better temperature control and sealed containers.
2) Further data be collected for the equilibrium curve at 120°C using the present technique.
3) The measurement of extractable solids content of the bones be improved by use of a sealed container with temperature control and monitoring.
4) The models developed be used to determine an appropriate manufacturing process and the process be validated by an independent experiment.
5) An investigation be conducted as to how value can be added to the large amount of fat extracted and easily separated from the process.
6) The use of by-products of the process fat and calcium phosphate be investigated.
7) Further investigation to simplify the roasting step prior to extraction perhaps by extracting roasted scrap meat and blending with extract from raw bones to control flavour and texture.

9 List of Symbols

a^*	Colour parameter red/green
b	Rate constant for the extraction kinetics (hr^{-1})
b_{ref}	Rate constant at the reference temperature for the extraction kinetics (hr^{-1})
b^*	Colour parameter blue/yellow
B	Number of batches per week
C	Cost ($)
C_{fx}	Fixed Capital Cost ($)
C_{cv}	civil woks costs ($)
C_{op}	Operating Costs ($)
C_{MU}	Material and Utility Costs ($)
D	Accumulation of solids within a process stage (kg)
E_a	Activation Energy ($J\ mol^{-1}$)
E_s	Solids concentration in the extract ($g\ 100\ g^{-1}$)
E_f	Solids concentration in finished product ($g\ 100\ g^{-1}$))
E_{se}	Solids concentration in the extract at equilibrium ($g\ 100\ g^{-1}$)
E_{si}	Solids concentration in the extract into the concentration process ($g\ 100\ g^{-1}$)
E_{so}	Solids concentration in the extract out of the concentration process ($g\ 100\ g^{-1}$)
F	Finished Product (kg)
f_{cv}	Lang factor for site preparation
f_{me}	mechanical and electrical works cost factor
GP	Gross Profit ($)
I	Total extractable solids out of a process stage (kg)
k	Rate constant for viscosity breakdown kinetics (hr^{-1})
k_{ref}	Rate constant at the reference temperature for the viscosity breakdown kinetics (hr^{-1})
K	consistency coefficient for non-Newtonian viscosity ($Pa.s^n$)
L	the mass of the liquid stream (kg)
L^*	Colour parameter lightness
M	Raw material quantity (kg)
n	flow index behaviour in rheology or total number of processing steps in extraction
N	Absolute non-extractable SNF (kg)
NP	Nett profit ($)
O	Total extractable solids into a process stage (kg)
R	Revenue from product ($)

ROI	Return on investment (%)
S	the absolute extractable solids in the solid stream (kg)
s_E	steam required for extraction (kg)
s_v	steam required for evaporation (kg)
SNF	Solids non-fat (kg)
t	time (s) or (hr)
t_v	evaporation time (hr)
T	Temperature (°C)
V	the mass of the bone stream (kg of SNF)
v_r	rate of evaporation (kg/hr)
W_v	Water removed in the concentration process (kg)
W_i	Water into the concentration process (kg)
W_o	Water out of the concentration process (kg)
x	concentration of extractable solids non fat in fat free bones (fraction)
y	concentration of solids non-fat in the aqueous phase (fraction)
y_e	concentration of solids non-fat in the aqueous phase at equilibrium (fraction)
X_o	concentration of extractable solids non fat in the bones at equilibrium (fraction)
Y_o	concentration of solids non-fat in the aqueous phase (fraction)
y_0	yield stress (Pa)
Z	the absolute extractable solids in the liquid stream (kg)
$\dot{\gamma}$	the shear rate (s^{-1})
$(\Delta\mu)_C$	change in viscosity due to change in solids concentration (Pa.s)
$(\Delta\mu)_T$	change in viscosity due to temperature exposure (Pa.s)
τ	Shear stress (Pa)
μ	viscosity (Pa.s)
μ_o	viscosity prior to any heat treatment (Pa.s)
ε	efficiency factor

10 References

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11 Appendix

11.1 Extraction data for the current process

Table 11-1 Chemical analysis of samples from the extraction at 92°C for 67 hours

Time (h)	Total Solids Non Fat (g 100 g^{-1})	Ash (g 100 g^{-1})	Protein (g 100 g^{-1})	Hydroxyproline (mg g^{-1})	Methionine (mg g^{-1})
1	0.40	0.12			
2	0.40	0.14			
4	0.70	0.18			
8	1.50	0.19			
16	3.10	0.25	2.80	6.12	7.65
24	4.10	0.29	3.70	7.82	8.32
33	4.70	0.31			
41.5	4.80	0.25			
49	5.40	0.33	5.10	9.98	9.32
56	5.50	0.33			
67	5.66	0.33	5.20	10.56	9.53

11.2 Kinetic modelling

Table 11-2 Experimental data and fitted model for the kinetics of viscosity change with temperature treatments

Estimated parameters		Equations				
T_{ref} (°C)	90	$Predicted\ k = k_{ref} e^{\frac{-E_a}{R}\left(\frac{1}{T+273}-\frac{1}{T_{ref}+273}\right)}$				
k_{ref} (hr^{-1})	0.00704					
E_a (J mol^{-1})	98,260	$Predicted\ \frac{\mu}{\mu_0} = e^{-kt}$				
t (h)	T (°C)	Experimental μ/μ_0	Predicted k (hr^{-1})	Predicted μ/μ_0	Residual (Experimental μ/μ_0 − Predicted μ/μ_0)	Residual^2
0	100	1.000	0.0168	1.000	0.000	0.000
0.5	100	0.965	0.0168	0.992	0.027	0.001
8	100	0.860	0.0168	0.874	0.014	0.000
24	100	0.720	0.0168	0.667	-0.052	0.003
48	100	0.570	0.0168	0.445	-0.124	0.015
0	90	1.000	0.0070	1.000	0.000	0.000
0.5	90	0.998	0.0070	0.996	-0.001	0.000
2	90	0.990	0.0070	0.986	-0.004	0.000
4	90	0.953	0.0070	0.972	0.019	0.000
8	90	0.900	0.0070	0.945	0.045	0.002
24	90	0.818	0.0070	0.845	0.027	0.001
48	90	0.689	0.0070	0.713	0.025	0.001
72	90	0.624	0.0070	0.602	-0.022	0.000
0	80	1.000	0.0028	1.000	0.000	0.000
0.5	80	0.976	0.0028	0.999	0.022	0.000
8	80	0.946	0.0028	0.978	0.032	0.001
24	80	0.889	0.0028	0.935	0.046	0.002
48	80	0.823	0.0028	0.874	0.051	0.003
72	80	0.769	0.0028	0.818	0.048	0.002
0	70	1.000	0.0011	1.000	0.000	0.000
0.5	70	0.952	0.0011	0.999	0.047	0.002
8	70	0.952	0.0011	0.992	0.039	0.002
24	70	0.931	0.0011	0.975	0.045	0.002
48	70	0.909	0.0011	0.951	0.042	0.002
72	70	0.866	0.0011	0.927	0.061	0.004
0	60	1.000	0.0004	1.000	0.000	0.000
0.5	60	0.965	0.0004	1.000	0.035	0.001
24	60	0.959	0.0004	0.991	0.033	0.001
72	60	0.928	0.0004	0.973	0.046	0.002
0	62	1.000	0.0005	1.000	0.000	0.000
0.5	62	1.029	0.0005	1.000	-0.029	0.001

Table 11-2 continued

t (h)	T (°C)	Experimental μ/μ_0	Predicted k (hr^{-1})	Predicted μ/μ_0	Residual (Experimental μ/μ_0 – Predicted μ/μ_0)	Residual^2
1	62	1.014	0.0005	1.000	-0.014	0.000
1.5	62	1.006	0.0005	0.999	-0.007	0.000
2	62	1.036	0.0005	0.999	-0.037	0.001
2.5	62	1.029	0.0005	0.999	-0.030	0.001
3	62	0.999	0.0005	0.999	0.000	0.000
3.5	62	0.991	0.0005	0.998	0.007	0.000
4	62	1.021	0.0005	0.998	-0.023	0.001
0	72	1.000	0.0013	1.000	0.000	0.000
0.5	72	1.014	0.0013	0.999	-0.014	0.000
1	72	0.984	0.0013	0.999	0.015	0.000
1.5	72	1.021	0.0013	0.998	-0.023	0.001
2	72	1.014	0.0013	0.997	-0.016	0.000
2.5	72	1.021	0.0013	0.997	-0.025	0.001
3	72	0.991	0.0013	0.996	0.005	0.000
3.5	72	0.991	0.0013	0.996	0.004	0.000
4	72	0.991	0.0013	0.995	0.004	0.000
0	81	1.000	0.0031	1.000	0.000	0.000
0.5	81	1.006	0.0031	0.998	-0.008	0.000
1	81	0.999	0.0031	0.997	-0.002	0.000
1.5	81	1.021	0.0031	0.995	-0.026	0.001
2	81	0.999	0.0031	0.994	-0.005	0.000
2.5	81	0.999	0.0031	0.992	-0.006	0.000
3	81	0.999	0.0031	0.991	-0.008	0.000
3.5	81	0.999	0.0031	0.989	-0.009	0.000
4	81	0.999	0.0031	0.988	-0.011	0.000
0	92	1.000	0.0084	1.000	0.000	0.000
0.5	92	1.014	0.0084	0.996	-0.018	0.000
1	92	1.029	0.0084	0.992	-0.037	0.001
1.5	92	1.021	0.0084	0.987	-0.034	0.001
2	92	1.021	0.0084	0.983	-0.038	0.001
2.5	92	1.014	0.0084	0.979	-0.035	0.001
3	92	1.021	0.0084	0.975	-0.046	0.002
3.5	92	1.014	0.0084	0.971	-0.043	0.002
4	92	1.006	0.0084	0.967	-0.039	0.002
0	100	1.000	0.0168	1.000	0.000	0.000
0.5	100	0.999	0.0168	0.992	-0.007	0.000
1	100	0.991	0.0168	0.983	-0.008	0.000
1.5	100	0.961	0.0168	0.975	0.014	0.000
2	100	0.999	0.0168	0.967	-0.032	0.001
2.5	100	0.991	0.0168	0.959	-0.032	0.001

Table 11-2 continued						
t (h)	T (°C)	Experimental μ/μ_0	Predicted k (hr^{-1})	Predicted μ/μ_0	Residual (Experimental μ/μ_0 – Predicted μ/μ_0)	Residual^2
3	100	0.976	0.0168	0.951	-0.025	0.001
3.5	100	0.946	0.0168	0.943	-0.003	0.000
4	100	0.969	0.0168	0.935	-0.034	0.001
0	120	1.000	0.0845	1.000	0.000	0.000
1	120	0.931	0.0845	0.919	-0.012	0.000
1.5	120	0.954	0.0845	0.881	-0.073	0.005
2	120	0.879	0.0845	0.845	-0.034	0.001
2.5	120	0.743	0.0845	0.810	0.066	0.004
3	120	0.691	0.0845	0.776	0.085	0.007
3.5	120	0.676	0.0845	0.744	0.068	0.005
4	120	0.683	0.0845	0.713	0.030	0.001
Sum of residuals squared						0.093

11.3 Experimental data and fitted model for Extraction Kinetics

Table 11-3 Experimental data and fitted model for Extraction kinetics

Estimated parameters		Equations				
E_{se} (g 100 g^{-1})	6.35	$Predicted\ b = b_{ref} e^{\frac{-E_{ae}}{R}\left(\frac{1}{T+273} - \frac{1}{T_{ref}+273}\right)}$				
T_{ref} (°C)	120					
b_{ref} (hr^{-1})	0.65	$Predicted\ E_s = E_{se}(1 - e^{-bt})$				
E_a (J mol^{-1})	119,483					
T (°C)	t (h)	Experimental E_s (g 100g^{-1})	Predicted b (hr^{-1})	Predicted E_s (g 100g^{-1})	Residual (Predicted E_s – Experimental E_s)	Residual^2
92	1	0.4	0.04	0.23	0.17	0.03
92	2	0.4	0.04	0.46	-0.06	0.00
92	4	0.7	0.04	0.88	-0.18	0.03
92	8	1.5	0.04	1.64	-0.14	0.02
92	16	3.1	0.04	2.87	0.23	0.05
92	24	4.1	0.04	3.79	0.31	0.10
92	33	4.7	0.04	4.54	0.16	0.02
92	41.5	4.8	0.04	5.06	-0.26	0.07
92	49	5.4	0.04	5.40	0.00	0.00
92	56	5.5	0.04	5.64	-0.14	0.02
92	67	5.66	0.04	5.92	-0.26	0.07
120	1	2.418	0.61	2.94	-0.52	0.27
120	2	4.9972	0.61	4.55	0.45	0.20
120	3	5.4002	0.61	5.42	-0.02	0.00
120	4	6.156	0.61	5.90	0.25	0.06
120	5	6.07	0.61	6.16	-0.09	0.01
120	3	5.93	0.61	5.42	0.51	0.26
120	4	5.74	0.61	5.90	-0.16	0.03
110	1	1.3218	0.23	1.35	-0.02	0.00
110	2	2.2702	0.23	2.41	-0.14	0.02
110	3	3.4658	0.23	3.26	0.21	0.04
110	4	3.4389	0.23	3.93	-0.49	0.24
100	1	1.0478	0.09	0.53	0.52	0.27
100	2	1.2896	0.09	1.01	0.27	0.08
100	3	1.7732	0.09	1.46	0.31	0.10
100	4	2.3374	0.09	1.87	0.47	0.22
80	1	0.394		Data not used		
80	3	0.788		Data not used		
80	6	0.985		Data not used		
80	24	3.2		Data not used		
80	48	4.665		Data not used		
Sum of Residuals						**2.21**

11.4 Model for evolution of solids and viscosity

Table 11-4 Spreadsheet for model with a 4 hour extraction and 20 minutes concentration to a SNF concentration of 16 g 100 g^{-1}

time	*time*	*T*	*k*	*b*	E_{sj}	ΔE	$E_{s(j+1)}$	μ_j	$\Delta\mu_C$	$\Delta\mu_T$	$\mu_{(j+1)}$
(m)	(h)	(°C)	(hr^{-1})	(hr^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
0	0										
1	0.017	120	8.55E-02	0.65	0.00	0.07	0.07	0.00E+00	6.62E-06	0.00E+00	6.62E-06
2	0.033	120	8.55E-02	0.65	0.07	0.07	0.14	6.62E-06	1.10E-05	9.43E-09	1.76E-05
3	0.05	120	8.55E-02	0.65	0.14	0.07	0.20	1.76E-05	1.34E-05	2.50E-08	3.10E-05
4	0.067	120	8.55E-02	0.65	0.20	0.07	0.27	3.10E-05	1.53E-05	4.41E-08	4.62E-05
5	0.083	120	8.55E-02	0.65	0.27	0.07	0.33	4.62E-05	1.68E-05	6.58E-08	6.29E-05
6	0.1	120	8.55E-02	0.65	0.33	0.06	0.40	6.29E-05	1.80E-05	8.97E-08	8.09E-05
7	0.117	120	8.55E-02	0.65	0.40	0.06	0.46	8.09E-05	1.91E-05	1.15E-07	9.98E-05
8	0.133	120	8.55E-02	0.65	0.46	0.06	0.53	9.98E-05	2.00E-05	1.42E-07	1.20E-04
9	0.15	120	8.55E-02	0.65	0.53	0.06	0.59	1.20E-04	2.08E-05	1.71E-07	1.40E-04
10	0.167	120	8.55E-02	0.65	0.59	0.06	0.65	1.40E-04	2.15E-05	2.00E-07	1.62E-04
11	0.183	120	8.55E-02	0.65	0.65	0.06	0.71	1.62E-04	2.22E-05	2.30E-07	1.84E-04
12	0.2	120	8.55E-02	0.65	0.71	0.06	0.77	1.84E-04	2.27E-05	2.62E-07	2.06E-04
13	0.217	120	8.55E-02	0.65	0.77	0.06	0.83	2.06E-04	2.32E-05	2.94E-07	2.29E-04
14	0.233	120	8.55E-02	0.65	0.83	0.06	0.89	2.29E-04	2.37E-05	3.26E-07	2.52E-04
15	0.25	120	8.55E-02	0.65	0.89	0.06	0.95	2.52E-04	2.41E-05	3.59E-07	2.76E-04
16	0.267	120	8.55E-02	0.65	0.95	0.06	1.01	2.76E-04	2.44E-05	3.93E-07	3.00E-04
17	0.283	120	8.55E-02	0.65	1.01	0.06	1.07	3.00E-04	2.48E-05	4.27E-07	3.24E-04
18	0.3	120	8.55E-02	0.65	1.07	0.06	1.12	3.24E-04	2.51E-05	4.62E-07	3.49E-04
19	0.317	120	8.55E-02	0.65	1.12	0.06	1.18	3.49E-04	2.53E-05	4.97E-07	3.74E-04

Table 11-4 Continued

time	*time*	*T*	*k*	*b*	E_{sj}	ΔE	$E_{s(j+1)}$	μ_j	$\Delta\mu_C$	$\Delta\mu_T$	$\mu_{(j+1)}$
(m)	(h)	(°C)	(hr^{-1})	(hr^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
20	0.333	120	8.55E-02	0.65	1.18	0.06	1.24	3.74E-04	2.55E-05	5.33E-07	3.99E-04
21	0.35	120	8.55E-02	0.65	1.24	0.06	1.29	3.99E-04	2.58E-05	5.68E-07	4.24E-04
22	0.367	120	8.55E-02	0.65	1.29	0.05	1.35	4.24E-04	2.59E-05	6.04E-07	4.49E-04
23	0.383	120	8.55E-02	0.65	1.35	0.05	1.40	4.49E-04	2.61E-05	6.40E-07	4.75E-04
24	0.4	120	8.55E-02	0.65	1.40	0.05	1.45	4.75E-04	2.62E-05	6.76E-07	5.00E-04
25	0.417	120	8.55E-02	0.65	1.45	0.05	1.51	5.00E-04	2.63E-05	7.13E-07	5.26E-04
26	0.433	120	8.55E-02	0.65	1.51	0.05	1.56	5.26E-04	2.64E-05	7.49E-07	5.52E-04
27	0.45	120	8.55E-02	0.65	1.56	0.05	1.61	5.52E-04	2.65E-05	7.86E-07	5.77E-04
28	0.467	120	8.55E-02	0.65	1.61	0.05	1.66	5.77E-04	2.66E-05	8.23E-07	6.03E-04
29	0.483	120	8.55E-02	0.65	1.66	0.05	1.71	6.03E-04	2.67E-05	8.59E-07	6.29E-04
30	0.5	120	8.55E-02	0.65	1.71	0.05	1.76	6.29E-04	2.67E-05	8.96E-07	6.55E-04
31	0.517	120	8.55E-02	0.65	1.76	0.05	1.81	6.55E-04	2.67E-05	9.33E-07	6.81E-04
32	0.533	120	8.55E-02	0.65	1.81	0.05	1.86	6.81E-04	2.67E-05	9.70E-07	7.06E-04
33	0.55	120	8.55E-02	0.65	1.86	0.05	1.91	7.06E-04	2.67E-05	1.01E-06	7.32E-04
34	0.567	120	8.55E-02	0.65	1.91	0.05	1.96	7.32E-04	2.67E-05	1.04E-06	7.58E-04
35	0.583	120	8.55E-02	0.65	1.96	0.05	2.00	7.58E-04	2.67E-05	1.08E-06	7.83E-04
36	0.6	120	8.55E-02	0.65	2.00	0.05	2.05	7.83E-04	2.67E-05	1.12E-06	8.09E-04
37	0.617	120	8.55E-02	0.65	2.05	0.05	2.10	8.09E-04	2.67E-05	1.15E-06	8.34E-04
38	0.633	120	8.55E-02	0.65	2.10	0.05	2.14	8.34E-04	2.66E-05	1.19E-06	8.60E-04
39	0.65	120	8.55E-02	0.65	2.14	0.05	2.19	8.60E-04	2.66E-05	1.23E-06	8.85E-04
40	0.667	120	8.55E-02	0.65	2.19	0.04	2.23	8.85E-04	2.65E-05	1.26E-06	9.11E-04
41	0.683	120	8.55E-02	0.65	2.23	0.04	2.28	9.11E-04	2.64E-05	1.30E-06	9.36E-04
42	0.7	120	8.55E-02	0.65	2.28	0.04	2.32	9.36E-04	2.64E-05	1.33E-06	9.61E-04
43	0.717	120	8.55E-02	0.65	2.32	0.04	2.36	9.61E-04	2.63E-05	1.37E-06	9.86E-04
44	0.733	120	8.55E-02	0.65	2.36	0.04	2.41	9.86E-04	2.62E-05	1.40E-06	1.01E-03
45	0.75	120	8.55E-02	0.65	2.41	0.04	2.45	1.01E-03	2.61E-05	1.44E-06	1.04E-03
46	0.767	120	8.55E-02	0.65	2.45	0.04	2.49	1.04E-03	2.60E-05	1.47E-06	1.06E-03

Table 11-4 Continued

time	*time*	*T*	*k*	*b*	E_{sj}	ΔE	$E_{s(j+1)}$	μ_j	$\Delta\mu_C$	$\Delta\mu_T$	$\mu_{(j+1)}$
(m)	(h)	(°C)	(hr^{-1})	(hr^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
47	0.783	120	8.55E-02	0.65	2.49	0.04	2.53	1.06E-03	2.59E-05	1.51E-06	1.08E-03
48	0.8	120	8.55E-02	0.65	2.53	0.04	2.57	1.08E-03	2.58E-05	1.54E-06	1.11E-03
49	0.817	120	8.55E-02	0.65	2.57	0.04	2.62	1.11E-03	2.57E-05	1.58E-06	1.13E-03
50	0.833	120	8.55E-02	0.65	2.62	0.04	2.66	1.13E-03	2.56E-05	1.61E-06	1.16E-03
51	0.85	120	8.55E-02	0.65	2.66	0.04	2.70	1.16E-03	2.55E-05	1.65E-06	1.18E-03
52	0.867	120	8.55E-02	0.65	2.70	0.04	2.73	1.18E-03	2.54E-05	1.68E-06	1.20E-03
53	0.883	120	8.55E-02	0.65	2.73	0.04	2.77	1.20E-03	2.53E-05	1.72E-06	1.23E-03
54	0.9	120	8.55E-02	0.65	2.77	0.04	2.81	1.23E-03	2.51E-05	1.75E-06	1.25E-03
55	0.917	120	8.55E-02	0.65	2.81	0.04	2.85	1.25E-03	2.50E-05	1.78E-06	1.27E-03
56	0.933	120	8.55E-02	0.65	2.85	0.04	2.89	1.27E-03	2.49E-05	1.82E-06	1.30E-03
57	0.95	120	8.55E-02	0.65	2.89	0.04	2.93	1.30E-03	2.47E-05	1.85E-06	1.32E-03
58	0.967	120	8.55E-02	0.65	2.93	0.04	2.96	1.32E-03	2.46E-05	1.88E-06	1.34E-03
59	0.983	120	8.55E-02	0.65	2.96	0.04	3.00	1.34E-03	2.45E-05	1.91E-06	1.37E-03
60	1	120	8.55E-02	0.65	3.00	0.04	3.04	1.37E-03	2.43E-05	1.95E-06	1.39E-03
61	1.017	120	8.55E-02	0.65	3.04	0.04	3.07	1.39E-03	2.42E-05	1.98E-06	1.41E-03
62	1.033	120	8.55E-02	0.65	3.07	0.04	3.11	1.41E-03	2.40E-05	2.01E-06	1.43E-03
63	1.05	120	8.55E-02	0.65	3.11	0.03	3.14	1.43E-03	2.39E-05	2.04E-06	1.45E-03
64	1.067	120	8.55E-02	0.65	3.14	0.03	3.18	1.45E-03	2.37E-05	2.07E-06	1.48E-03
65	1.083	120	8.55E-02	0.65	3.18	0.03	3.21	1.48E-03	2.36E-05	2.10E-06	1.50E-03
66	1.1	120	8.55E-02	0.65	3.21	0.03	3.24	1.50E-03	2.34E-05	2.13E-06	1.52E-03
67	1.117	120	8.55E-02	0.65	3.24	0.03	3.28	1.52E-03	2.33E-05	2.16E-06	1.54E-03
68	1.133	120	8.55E-02	0.65	3.28	0.03	3.31	1.54E-03	2.31E-05	2.19E-06	1.56E-03
69	1.15	120	8.55E-02	0.65	3.31	0.03	3.34	1.56E-03	2.30E-05	2.22E-06	1.58E-03
70	1.167	120	8.55E-02	0.65	3.34	0.03	3.38	1.58E-03	2.28E-05	2.25E-06	1.60E-03
71	1.183	120	8.55E-02	0.65	3.38	0.03	3.41	1.60E-03	2.27E-05	2.28E-06	1.62E-03
72	1.2	120	8.55E-02	0.65	3.41	0.03	3.44	1.62E-03	2.25E-05	2.31E-06	1.64E-03
73	1.217	120	8.55E-02	0.65	3.44	0.03	3.47	1.64E-03	2.24E-05	2.34E-06	1.66E-03

Table 11-4 Continued

time	*time*	*T*	*k*	*b*	E_{sj}	ΔE	$E_{s(j+1)}$	μ_j	$\Delta\mu_C$	$\Delta\mu_T$	$\mu_{(j+1)}$
(m)	(h)	(°C)	(hr^{-1})	(hr^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
74	1.233	120	8.55E-02	0.65	3.47	0.03	3.50	1.66E-03	2.22E-05	2.37E-06	1.68E-03
75	1.25	120	8.55E-02	0.65	3.50	0.03	3.53	1.68E-03	2.20E-05	2.40E-06	1.70E-03
76	1.267	120	8.55E-02	0.65	3.53	0.03	3.56	1.70E-03	2.19E-05	2.42E-06	1.72E-03
77	1.283	120	8.55E-02	0.65	3.56	0.03	3.59	1.72E-03	2.17E-05	2.45E-06	1.74E-03
78	1.3	120	8.55E-02	0.65	3.59	0.03	3.62	1.74E-03	2.16E-05	2.48E-06	1.76E-03
79	1.317	120	8.55E-02	0.65	3.62	0.03	3.65	1.76E-03	2.14E-05	2.51E-06	1.78E-03
80	1.333	120	8.55E-02	0.65	3.65	0.03	3.68	1.78E-03	2.13E-05	2.53E-06	1.80E-03
81	1.35	120	8.55E-02	0.65	3.68	0.03	3.71	1.80E-03	2.11E-05	2.56E-06	1.82E-03
82	1.367	120	8.55E-02	0.65	3.71	0.03	3.74	1.82E-03	2.09E-05	2.59E-06	1.83E-03
83	1.383	120	8.55E-02	0.65	3.74	0.03	3.77	1.83E-03	2.08E-05	2.61E-06	1.85E-03
84	1.4	120	8.55E-02	0.65	3.77	0.03	3.79	1.85E-03	2.06E-05	2.64E-06	1.87E-03
85	1.417	120	8.55E-02	0.65	3.79	0.03	3.82	1.87E-03	2.05E-05	2.66E-06	1.89E-03
86	1.433	120	8.55E-02	0.65	3.82	0.03	3.85	1.89E-03	2.03E-05	2.69E-06	1.91E-03
87	1.45	120	8.55E-02	0.65	3.85	0.03	3.88	1.91E-03	2.01E-05	2.71E-06	1.92E-03
88	1.467	120	8.55E-02	0.65	3.88	0.03	3.90	1.92E-03	2.00E-05	2.74E-06	1.94E-03
89	1.483	120	8.55E-02	0.65	3.90	0.03	3.93	1.94E-03	1.98E-05	2.76E-06	1.96E-03
90	1.5	120	8.55E-02	0.65	3.93	0.03	3.95	1.96E-03	1.97E-05	2.79E-06	1.97E-03
91	1.517	120	8.55E-02	0.65	3.95	0.03	3.98	1.97E-03	1.95E-05	2.81E-06	1.99E-03
92	1.533	120	8.55E-02	0.65	3.98	0.03	4.01	1.99E-03	1.93E-05	2.84E-06	2.01E-03
93	1.55	120	8.55E-02	0.65	4.01	0.03	4.03	2.01E-03	1.92E-05	2.86E-06	2.02E-03
94	1.567	120	8.55E-02	0.65	4.03	0.02	4.06	2.02E-03	1.90E-05	2.88E-06	2.04E-03
95	1.583	120	8.55E-02	0.65	4.06	0.02	4.08	2.04E-03	1.89E-05	2.91E-06	2.06E-03
96	1.6	120	8.55E-02	0.65	4.08	0.02	4.11	2.06E-03	1.87E-05	2.93E-06	2.07E-03
97	1.617	120	8.55E-02	0.65	4.11	0.02	4.13	2.07E-03	1.86E-05	2.95E-06	2.09E-03
98	1.633	120	8.55E-02	0.65	4.13	0.02	4.15	2.09E-03	1.84E-05	2.97E-06	2.10E-03
99	1.65	120	8.55E-02	0.65	4.15	0.02	4.18	2.10E-03	1.83E-05	3.00E-06	2.12E-03
100	1.667	120	8.55E-02	0.65	4.18	0.02	4.20	2.12E-03	1.81E-05	3.02E-06	2.13E-03

Table 11-4 Continued

time	*time*	*T*	*k*	*b*	E_{sj}	ΔE	$E_{s(j+1)}$	μ_j	$\Delta\mu_C$	$\Delta\mu_T$	$\mu_{(j+1)}$
(m)	(h)	(°C)	(hr^{-1})	(hr^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
101	1.683	120	8.55E-02	0.65	4.20	0.02	4.22	2.13E-03	1.79E-05	3.04E-06	2.15E-03
102	1.7	120	8.55E-02	0.65	4.22	0.02	4.25	2.15E-03	1.78E-05	3.06E-06	2.16E-03
103	1.717	120	8.55E-02	0.65	4.25	0.02	4.27	2.16E-03	1.76E-05	3.08E-06	2.18E-03
104	1.733	120	8.55E-02	0.65	4.27	0.02	4.29	2.18E-03	1.75E-05	3.10E-06	2.19E-03
105	1.75	120	8.55E-02	0.65	4.29	0.02	4.31	2.19E-03	1.73E-05	3.12E-06	2.21E-03
106	1.767	120	8.55E-02	0.65	4.31	0.02	4.34	2.21E-03	1.72E-05	3.14E-06	2.22E-03
107	1.783	120	8.55E-02	0.65	4.34	0.02	4.36	2.22E-03	1.70E-05	3.16E-06	2.23E-03
108	1.8	120	8.55E-02	0.65	4.36	0.02	4.38	2.23E-03	1.69E-05	3.18E-06	2.25E-03
109	1.817	120	8.55E-02	0.65	4.38	0.02	4.40	2.25E-03	1.67E-05	3.20E-06	2.26E-03
110	1.833	120	8.55E-02	0.65	4.40	0.02	4.42	2.26E-03	1.66E-05	3.22E-06	2.27E-03
111	1.85	120	8.55E-02	0.65	4.42	0.02	4.44	2.27E-03	1.64E-05	3.24E-06	2.29E-03
112	1.867	120	8.55E-02	0.65	4.44	0.02	4.46	2.29E-03	1.63E-05	3.26E-06	2.30E-03
113	1.883	120	8.55E-02	0.65	4.46	0.02	4.48	2.30E-03	1.62E-05	3.28E-06	2.31E-03
114	1.9	120	8.55E-02	0.65	4.48	0.02	4.50	2.31E-03	1.60E-05	3.30E-06	2.33E-03
115	1.917	120	8.55E-02	0.65	4.50	0.02	4.52	2.33E-03	1.59E-05	3.31E-06	2.34E-03
116	1.933	120	8.55E-02	0.65	4.52	0.02	4.54	2.34E-03	1.57E-05	3.33E-06	2.35E-03
117	1.95	120	8.55E-02	0.65	4.54	0.02	4.56	2.35E-03	1.56E-05	3.35E-06	2.36E-03
118	1.967	120	8.55E-02	0.65	4.56	0.02	4.58	2.36E-03	1.54E-05	3.37E-06	2.38E-03
119	1.983	120	8.55E-02	0.65	4.58	0.02	4.60	2.38E-03	1.53E-05	3.38E-06	2.39E-03
120	2	120	8.55E-02	0.65	4.60	0.02	4.62	2.39E-03	1.52E-05	3.40E-06	2.40E-03
121	2.017	120	8.55E-02	0.65	4.62	0.02	4.64	2.40E-03	1.50E-05	3.42E-06	2.41E-03
122	2.033	120	8.55E-02	0.65	4.64	0.02	4.66	2.41E-03	1.49E-05	3.43E-06	2.42E-03
123	2.05	120	8.55E-02	0.65	4.66	0.02	4.67	2.42E-03	1.48E-05	3.45E-06	2.43E-03
124	2.067	120	8.55E-02	0.65	4.67	0.02	4.69	2.43E-03	1.46E-05	3.47E-06	2.44E-03
125	2.083	120	8.55E-02	0.65	4.69	0.02	4.71	2.44E-03	1.45E-05	3.48E-06	2.46E-03
126	2.1	120	8.55E-02	0.65	4.71	0.02	4.73	2.46E-03	1.44E-05	3.50E-06	2.47E-03
127	2.117	120	8.55E-02	0.65	4.73	0.02	4.75	2.47E-03	1.42E-05	3.51E-06	2.48E-03

Table 11-4 Continued

time	*time*	*T*	*k*	*b*	E_{sj}	ΔE	$E_{s(j+1)}$	μ_j	$\Delta\mu_C$	$\Delta\mu_T$	$\mu_{(j+1)}$
(m)	(h)	(°C)	(hr^{-1})	(hr^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
128	2.133	120	8.55E-02	0.65	4.75	0.02	4.76	2.48E-03	1.41E-05	3.53E-06	2.49E-03
129	2.15	120	8.55E-02	0.65	4.76	0.02	4.78	2.49E-03	1.40E-05	3.54E-06	2.50E-03
130	2.167	120	8.55E-02	0.65	4.78	0.02	4.80	2.50E-03	1.38E-05	3.56E-06	2.51E-03
131	2.183	120	8.55E-02	0.65	4.80	0.02	4.81	2.51E-03	1.37E-05	3.57E-06	2.52E-03
132	2.2	120	8.55E-02	0.65	4.81	0.02	4.83	2.52E-03	1.36E-05	3.59E-06	2.53E-03
133	2.217	120	8.55E-02	0.65	4.83	0.02	4.85	2.53E-03	1.34E-05	3.60E-06	2.54E-03
134	2.233	120	8.55E-02	0.65	4.85	0.02	4.86	2.54E-03	1.33E-05	3.62E-06	2.55E-03
135	2.25	120	8.55E-02	0.65	4.86	0.02	4.88	2.55E-03	1.32E-05	3.63E-06	2.56E-03
136	2.267	120	8.55E-02	0.65	4.88	0.02	4.89	2.56E-03	1.31E-05	3.64E-06	2.57E-03
137	2.283	120	8.55E-02	0.65	4.89	0.02	4.91	2.57E-03	1.29E-05	3.66E-06	2.58E-03
138	2.3	120	8.55E-02	0.65	4.91	0.02	4.93	2.58E-03	1.28E-05	3.67E-06	2.59E-03
139	2.317	120	8.55E-02	0.65	4.93	0.02	4.94	2.59E-03	1.27E-05	3.68E-06	2.59E-03
140	2.333	120	8.55E-02	0.65	4.94	0.02	4.96	2.59E-03	1.26E-05	3.70E-06	2.60E-03
141	2.35	120	8.55E-02	0.65	4.96	0.02	4.97	2.60E-03	1.25E-05	3.71E-06	2.61E-03
142	2.367	120	8.55E-02	0.65	4.97	0.01	4.99	2.61E-03	1.23E-05	3.72E-06	2.62E-03
143	2.383	120	8.55E-02	0.65	4.99	0.01	5.00	2.62E-03	1.22E-05	3.73E-06	2.63E-03
144	2.4	120	8.55E-02	0.65	5.00	0.01	5.02	2.63E-03	1.21E-05	3.75E-06	2.64E-03
145	2.417	120	8.55E-02	0.65	5.02	0.01	5.03	2.64E-03	1.20E-05	3.76E-06	2.65E-03
146	2.433	120	8.55E-02	0.65	5.03	0.01	5.04	2.65E-03	1.19E-05	3.77E-06	2.65E-03
147	2.45	120	8.55E-02	0.65	5.04	0.01	5.06	2.65E-03	1.18E-05	3.78E-06	2.66E-03
148	2.467	120	8.55E-02	0.65	5.06	0.01	5.07	2.66E-03	1.17E-05	3.79E-06	2.67E-03
149	2.483	120	8.55E-02	0.65	5.07	0.01	5.09	2.67E-03	1.15E-05	3.80E-06	2.68E-03
150	2.5	120	8.55E-02	0.65	5.09	0.01	5.10	2.68E-03	1.14E-05	3.81E-06	2.69E-03
151	2.517	120	8.55E-02	0.65	5.10	0.01	5.11	2.69E-03	1.13E-05	3.83E-06	2.69E-03
152	2.533	120	8.55E-02	0.65	5.11	0.01	5.13	2.69E-03	1.12E-05	3.84E-06	2.70E-03
153	2.55	120	8.55E-02	0.65	5.13	0.01	5.14	2.70E-03	1.11E-05	3.85E-06	2.71E-03
154	2.567	120	8.55E-02	0.65	5.14	0.01	5.15	2.71E-03	1.10E-05	3.86E-06	2.71E-03

Table 11-4 Continued

time	*time*	*T*	*k*	*b*	E_{sj}	ΔE	$E_{s(j+1)}$	μ_j	$\Delta\mu_C$	$\Delta\mu_T$	$\mu_{(j+1)}$
(m)	(h)	(°C)	(hr^{-1})	(hr^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
155	2.583	120	8.55E-02	0.65	5.15	0.01	5.17	2.71E-03	1.09E-05	3.87E-06	2.72E-03
156	2.6	120	8.55E-02	0.65	5.17	0.01	5.18	2.72E-03	1.08E-05	3.88E-06	2.73E-03
157	2.617	120	8.55E-02	0.65	5.18	0.01	5.19	2.73E-03	1.07E-05	3.89E-06	2.74E-03
158	2.633	120	8.55E-02	0.65	5.19	0.01	5.20	2.74E-03	1.06E-05	3.90E-06	2.74E-03
159	2.65	120	8.55E-02	0.65	5.20	0.01	5.22	2.74E-03	1.05E-05	3.91E-06	2.75E-03
160	2.667	120	8.55E-02	0.65	5.22	0.01	5.23	2.75E-03	1.04E-05	3.92E-06	2.76E-03
161	2.683	120	8.55E-02	0.65	5.23	0.01	5.24	2.76E-03	1.03E-05	3.93E-06	2.76E-03
162	2.7	120	8.55E-02	0.65	5.24	0.01	5.25	2.76E-03	1.02E-05	3.93E-06	2.77E-03
163	2.717	120	8.55E-02	0.65	5.25	0.01	5.26	2.77E-03	1.01E-05	3.94E-06	2.77E-03
164	2.733	120	8.55E-02	0.65	5.26	0.01	5.28	2.77E-03	9.96E-06	3.95E-06	2.78E-03
165	2.75	120	8.55E-02	0.65	5.28	0.01	5.29	2.78E-03	9.86E-06	3.96E-06	2.79E-03
166	2.767	120	8.55E-02	0.65	5.29	0.01	5.30	2.79E-03	9.77E-06	3.97E-06	2.79E-03
167	2.783	120	8.55E-02	0.65	5.30	0.01	5.31	2.79E-03	9.67E-06	3.98E-06	2.80E-03
168	2.8	120	8.55E-02	0.65	5.31	0.01	5.32	2.80E-03	9.58E-06	3.98E-06	2.80E-03
169	2.817	120	8.55E-02	0.65	5.32	0.01	5.33	2.80E-03	9.48E-06	3.99E-06	2.81E-03
170	2.833	120	8.55E-02	0.65	5.33	0.01	5.34	2.81E-03	9.39E-06	4.00E-06	2.81E-03
171	2.85	120	8.55E-02	0.65	5.34	0.01	5.35	2.81E-03	9.29E-06	4.01E-06	2.82E-03
172	2.867	120	8.55E-02	0.65	5.35	0.01	5.36	2.82E-03	9.20E-06	4.02E-06	2.82E-03
173	2.883	120	8.55E-02	0.65	5.36	0.01	5.38	2.82E-03	9.11E-06	4.02E-06	2.83E-03
174	2.9	120	8.55E-02	0.65	5.38	0.01	5.39	2.83E-03	9.02E-06	4.03E-06	2.83E-03
175	2.917	120	8.55E-02	0.65	5.39	0.01	5.40	2.83E-03	8.93E-06	4.04E-06	2.84E-03
176	2.933	120	8.55E-02	0.65	5.40	0.01	5.41	2.84E-03	8.84E-06	4.04E-06	2.84E-03
177	2.95	120	8.55E-02	0.65	5.41	0.01	5.42	2.84E-03	8.75E-06	4.05E-06	2.85E-03
178	2.967	120	8.55E-02	0.65	5.42	0.01	5.43	2.85E-03	8.66E-06	4.06E-06	2.85E-03
179	2.983	120	8.55E-02	0.65	5.43	0.01	5.44	2.85E-03	8.58E-06	4.06E-06	2.86E-03
180	3	120	8.55E-02	0.65	5.44	0.01	5.45	2.86E-03	8.49E-06	4.07E-06	2.86E-03
181	3.017	120	8.55E-02	0.65	5.45	0.01	5.46	2.86E-03	8.41E-06	4.08E-06	2.87E-03

Table 11-4 Continued

time	*time*	*T*	*k*	*b*	E_{sj}	ΔE	$E_{s(j+1)}$	μ_j	$\Delta\mu_C$	$\Delta\mu_T$	$\mu_{(j+1)}$
(m)	(h)	(°C)	(hr^{-1})	(hr^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
182	3.033	120	8.55E-02	0.65	5.46	0.01	5.47	2.87E-03	8.32E-06	4.08E-06	2.87E-03
183	3.05	120	8.55E-02	0.65	5.47	0.01	5.48	2.87E-03	8.24E-06	4.09E-06	2.87E-03
184	3.067	120	8.55E-02	0.65	5.48	0.01	5.48	2.87E-03	8.16E-06	4.10E-06	2.88E-03
185	3.083	120	8.55E-02	0.65	5.48	0.01	5.49	2.88E-03	8.07E-06	4.10E-06	2.88E-03
186	3.1	120	8.55E-02	0.65	5.49	0.01	5.50	2.88E-03	7.99E-06	4.11E-06	2.89E-03
187	3.117	120	8.55E-02	0.65	5.50	0.01	5.51	2.89E-03	7.91E-06	4.11E-06	2.89E-03
188	3.133	120	8.55E-02	0.65	5.51	0.01	5.52	2.89E-03	7.83E-06	4.12E-06	2.89E-03
189	3.15	120	8.55E-02	0.65	5.52	0.01	5.53	2.89E-03	7.75E-06	4.12E-06	2.90E-03
190	3.167	120	8.55E-02	0.65	5.53	0.01	5.54	2.90E-03	7.67E-06	4.13E-06	2.90E-03
191	3.183	120	8.55E-02	0.65	5.54	0.01	5.55	2.90E-03	7.60E-06	4.13E-06	2.90E-03
192	3.2	120	8.55E-02	0.65	5.55	0.01	5.56	2.90E-03	7.52E-06	4.14E-06	2.91E-03
193	3.217	120	8.55E-02	0.65	5.56	0.01	5.57	2.91E-03	7.44E-06	4.14E-06	2.91E-03
194	3.233	120	8.55E-02	0.65	5.57	0.01	5.57	2.91E-03	7.37E-06	4.15E-06	2.91E-03
195	3.25	120	8.55E-02	0.65	5.57	0.01	5.58	2.91E-03	7.29E-06	4.15E-06	2.92E-03
196	3.267	120	8.55E-02	0.65	5.58	0.01	5.59	2.92E-03	7.22E-06	4.16E-06	2.92E-03
197	3.283	120	8.55E-02	0.65	5.59	0.01	5.60	2.92E-03	7.15E-06	4.16E-06	2.92E-03
198	3.3	120	8.55E-02	0.65	5.60	0.01	5.61	2.92E-03	7.07E-06	4.17E-06	2.93E-03
199	3.317	120	8.55E-02	0.65	5.61	0.01	5.61	2.93E-03	7.00E-06	4.17E-06	2.93E-03
200	3.333	120	8.55E-02	0.65	5.61	0.01	5.62	2.93E-03	6.93E-06	4.17E-06	2.93E-03
201	3.35	120	8.55E-02	0.65	5.62	0.01	5.63	2.93E-03	6.86E-06	4.18E-06	2.94E-03
202	3.367	120	8.55E-02	0.65	5.63	0.01	5.64	2.94E-03	6.79E-06	4.18E-06	2.94E-03
203	3.383	120	8.55E-02	0.65	5.64	0.01	5.65	2.94E-03	6.72E-06	4.19E-06	2.94E-03
204	3.4	120	8.55E-02	0.65	5.65	0.01	5.65	2.94E-03	6.65E-06	4.19E-06	2.94E-03
205	3.417	120	8.55E-02	0.65	5.65	0.01	5.66	2.94E-03	6.58E-06	4.19E-06	2.95E-03
206	3.433	120	8.55E-02	0.65	5.66	0.01	5.67	2.95E-03	6.52E-06	4.20E-06	2.95E-03
207	3.45	120	8.55E-02	0.65	5.67	0.01	5.68	2.95E-03	6.45E-06	4.20E-06	2.95E-03
208	3.467	120	8.55E-02	0.65	5.68	0.01	5.68	2.95E-03	6.38E-06	4.20E-06	2.95E-03

Table 11-4 Continued

time	*time*	*T*	*k*	*b*	E_{sj}	ΔE	$E_{s(j+1)}$	μ_j	$\Delta\mu_C$	$\Delta\mu_T$	$\mu_{(j+1)}$
(m)	(h)	(°C)	(hr^{-1})	(hr^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(g 100 g^{-1})	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
209	3.483	120	8.55E-02	0.65	5.68	0.01	5.69	2.95E-03	6.32E-06	4.21E-06	2.95E-03
210	3.5	120	8.55E-02	0.65	5.69	0.01	5.70	2.95E-03	6.25E-06	4.21E-06	2.96E-03
211	3.517	120	8.55E-02	0.65	5.70	0.01	5.70	2.96E-03	6.19E-06	4.21E-06	2.96E-03
212	3.533	120	8.55E-02	0.65	5.70	0.01	5.71	2.96E-03	6.13E-06	4.21E-06	2.96E-03
213	3.55	120	8.55E-02	0.65	5.71	0.01	5.72	2.96E-03	6.06E-06	4.22E-06	2.96E-03
214	3.567	120	8.55E-02	0.65	5.72	0.01	5.72	2.96E-03	6.00E-06	4.22E-06	2.96E-03
215	3.583	120	8.55E-02	0.65	5.72	0.01	5.73	2.96E-03	5.94E-06	4.22E-06	2.97E-03
216	3.6	120	8.55E-02	0.65	5.73	0.01	5.74	2.97E-03	5.88E-06	4.22E-06	2.97E-03
217	3.617	120	8.55E-02	0.65	5.74	0.01	5.74	2.97E-03	5.82E-06	4.23E-06	2.97E-03
218	3.633	120	8.55E-02	0.65	5.74	0.01	5.75	2.97E-03	5.76E-06	4.23E-06	2.97E-03
219	3.65	120	8.55E-02	0.65	5.75	0.01	5.76	2.97E-03	5.70E-06	4.23E-06	2.97E-03
220	3.667	120	8.55E-02	0.65	5.76	0.01	5.76	2.97E-03	5.64E-06	4.23E-06	2.97E-03
221	3.683	120	8.55E-02	0.65	5.76	0.01	5.77	2.97E-03	5.58E-06	4.24E-06	2.97E-03
222	3.7	120	8.55E-02	0.65	5.77	0.01	5.78	2.97E-03	5.52E-06	4.24E-06	2.98E-03
223	3.717	120	8.55E-02	0.65	5.78	0.01	5.78	2.98E-03	5.47E-06	4.24E-06	2.98E-03
224	3.733	120	8.55E-02	0.65	5.78	0.01	5.79	2.98E-03	5.41E-06	4.24E-06	2.98E-03
225	3.75	120	8.55E-02	0.65	5.79	0.01	5.80	2.98E-03	5.35E-06	4.24E-06	2.98E-03
226	3.767	120	8.55E-02	0.65	5.80	0.01	5.80	2.98E-03	5.30E-06	4.24E-06	2.98E-03
227	3.783	120	8.55E-02	0.65	5.80	0.01	5.81	2.98E-03	5.24E-06	4.25E-06	2.98E-03
228	3.8	120	8.55E-02	0.65	5.81	0.01	5.81	2.98E-03	5.19E-06	4.25E-06	2.98E-03
229	3.817	120	8.55E-02	0.65	5.81	0.01	5.82	2.98E-03	5.14E-06	4.25E-06	2.98E-03
230	3.833	120	8.55E-02	0.65	5.82	0.01	5.82	2.98E-03	5.08E-06	4.25E-06	2.98E-03
231	3.85	120	8.55E-02	0.65	5.82	0.01	5.83	2.98E-03	5.03E-06	4.25E-06	2.98E-03
232	3.867	120	8.55E-02	0.65	5.83	0.01	5.84	2.98E-03	4.98E-06	4.25E-06	2.99E-03
233	3.883	120	8.55E-02	0.65	5.84	0.01	5.84	2.99E-03	4.93E-06	4.25E-06	2.99E-03
234	3.9	120	8.55E-02	0.65	5.84	0.01	5.85	2.99E-03	4.87E-06	4.25E-06	2.99E-03
235	3.917	120	8.55E-02	0.65	5.85	0.01	5.85	2.99E-03	4.82E-06	4.25E-06	2.99E-03

Table 11-4 Continued

time (m)	*time* (h)	*T* (°C)	*k* (hr^{-1})	*b* (hr^{-1})	E_{sj} (g 100 g^{-1})	ΔE (g 100 g^{-1})	$E_{s(j+1)}$ (g 100 g^{-1})	μ_j (Pa.s)	$\Delta\mu_C$ (Pa.s)	$\Delta\mu_T$ (Pa.s)	$\mu_{(j+1)}$ (Pa.s)
236	3.933	120	8.55E-02	0.65	5.85	0.01	5.86	2.99E-03	4.77E-06	4.26E-06	2.99E-03
237	3.95	120	8.55E-02	0.65	5.86	0.01	5.86	2.99E-03	4.72E-06	4.26E-06	2.99E-03
238	3.967	120	8.55E-02	0.65	5.86	0.01	5.87	2.99E-03	4.67E-06	4.26E-06	2.99E-03
239	3.983	120	8.55E-02	0.65	5.87	0.01	5.87	2.99E-03	4.63E-06	4.26E-06	2.99E-03
240	4	120	8.55E-02	0.65	5.87	0.01	5.88	2.99E-03	4.58E-06	4.26E-06	2.99E-03
Concentration process											
241	4.017	60	3.79E-04		5.88		6.07	2.99E-03	1.72E-04	1.89E-08	3.16E-03
242	4.033	60	3.79E-04		6.07		6.28	3.16E-03	1.86E-04	2.00E-08	3.35E-03
243	4.05	60	3.79E-04		6.28		6.49	3.35E-03	2.02E-04	2.12E-08	3.55E-03
244	4.067	60	3.79E-04		6.49		6.73	3.55E-03	2.20E-04	2.24E-08	3.77E-03
245	4.083	60	3.79E-04		6.73		6.98	3.77E-03	2.40E-04	2.38E-08	4.01E-03
246	4.1	60	3.79E-04		6.98		7.26	4.01E-03	2.63E-04	2.54E-08	4.27E-03
247	4.117	60	3.79E-04		7.26		7.55	4.27E-03	2.89E-04	2.70E-08	4.56E-03
248	4.133	60	3.79E-04		7.55		7.87	4.56E-03	3.19E-04	2.88E-08	4.88E-03
249	4.15	60	3.79E-04		7.87		8.22	4.88E-03	3.54E-04	3.09E-08	5.24E-03
250	4.167	60	3.79E-04		8.22		8.60	5.24E-03	3.94E-04	3.31E-08	5.63E-03
251	4.183	60	3.79E-04		8.60		9.01	5.63E-03	4.41E-04	3.56E-08	6.07E-03
252	4.2	60	3.79E-04		9.01		9.47	6.07E-03	4.95E-04	3.84E-08	6.57E-03
253	4.217	60	3.79E-04		9.47		9.98	6.57E-03	5.61E-04	4.15E-08	7.13E-03
254	4.233	60	3.79E-04		9.98		10.55	7.13E-03	6.38E-04	4.50E-08	7.77E-03
255	4.25	60	3.79E-04		10.55		11.19	7.77E-03	7.33E-04	4.91E-08	8.50E-03
256	4.267	60	3.79E-04		11.19		11.90	8.50E-03	8.48E-04	5.37E-08	9.35E-03
257	4.283	60	3.79E-04		11.90		12.72	9.35E-03	9.90E-04	5.91E-08	1.03E-02
258	4.3	60	3.79E-04		12.72		13.65	1.03E-02	1.17E-03	6.53E-08	1.15E-02
259	4.317	60	3.79E-04		13.65		14.73	1.15E-02	1.40E-03	7.27E-08	1.29E-02
260	4.333	60	3.79E-04		14.73		16.00	1.29E-02	1.69E-03	8.15E-08	1.46E-02

11.5 Multi Stage analysis

Table 11-5 Mass balance for stage analysis of a 3 stage 1:1:2 hour extraction process at 120°C in Excel