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Oat in fruit juice drink

– The processing behavior of oat

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OAT IN FRUIT JUICE DRINK

- The behavior of oat

The aim of the present Master´s thesis was to develop a fruit juice-based oat drink for Eckes-Granini Finland Oy Ab. Oat is a plant based raw material whose behavior differs from fruits and berries. Oat has significantly different composition from fruits. Oat treatment and process parameters had to be evaluated and confirmed. The aim was to develop a liquid grain type snack drink with clearly identifiable fruits and berry characteristics.

The theoretical part of the thesis focuses on the oat grain composition and processing of oat grain. It covers developing and processing of different fruit and berry recipes. Additionally, there are evaluations of product pasteurization process steps. Different oat materials have been evaluated. The developed recipes have been tested in the laboratory scale evaluations and, in addition four of them in the industrial scale tests. The rheological behavior of the raw material under the processing has been evaluated for the trial tested products. The empirical part of the thesis part consists of the test trials and analytical evaluations of the products.

The results of the study show that natural ingredients in the drinkable formula are challenging and deeply affected by the thermal processing. The processing parameters are important to produce a safe product that achieves consumer acceptance.

KEYWORDS:

Fruits, juice, oat, pasteurization, rheology, viscosity.

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KAURA HEDELMÄMEHUSSA

Kauran käyttäytyminen

Opinnäytetyön tavoitteena oli kehittää kauraa sisältävä mehutuote Eckes-Granini Finland Oy Ab:lle. Kaura on kasvispohjainen raaka-aine, jonka käyttäytyminen eroaa hedelmistä ja marjoista. Täysjyväkauralla on erilainen koostumus verrattuna hedelmiin. Kauran käsittely- ja prosessiparametrit tuli arvioida ja vahvistaa. Työn tarkoituksena oli kehittää nestemäinen täysjyväviljaa sisältävä välipalajuoma, josta on selkeästi havaittavissa hedelmien ja marjojen ominaisuuksia.

Opinnäytetyön teoreettisessa osassa keskityttiin kauran jyvän koostumukseen ja prosessointiin. Teoreettinen osa kattoi eri hedelmä- ja marjareseptien kehitystyön ja prosessoinnin. Lisäksi tehtiin prosessointi- ja pastörointivaiheiden tehdasmittakaavan koeajot. Erilaisia kaurakomponentteja testattiin reseptejä varten. Kehitetyt reseptit arvioitiin laboratoriomittakaavassa, ja neljä niistä testattiin tehdaskoeajoissa, joissa arvioitiin raaka-aineiden reologista käyttäytymistä. Opinnäytetyön käytännön osassa syvennyttiin tehdaskoeajojen suunnitteluun ja toteutukseen, sekä tuotteiden analyyttisiin arviointeihin.

Opinnäytetyön tuloksista selviää, että juotavaan tuotteeseen käytetty luontainen ja käsittelemätön raaka-aine on haastava, kun tuotetta lämpökäsitellään. Tärkeätä on asettaa oikeat prosessointiparametrit lämpökäsittelylle valmistettaessa turvallista elintarviketta.

AVAINSANAT

Hedelmä, kaura, mehu, pastörointi, reologia, viskositeetti

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List of Abbreviations or Symbols

AX	Arabinoxylan
$Ba(OH)_2$	Barium hydroxide
β-glucan	Beta-glucan
BTD	Product Balance Tank
CFD	Computational Fluid Dynamics
CIP	Cleaning in Place
DSC	Differential Scanning Calorimeter
EFSA	European Food Safety Association
G’	Storage Modulus
FT2	Magnetic flow meter position in heating process
H_2O_2	Hydrogen peroxide
HCl acid	Hydrochloric acid
HMW	High Molecule Weight
HTST	High Temperature Short Time -method for pasteurization
kDa	kilo Dalton
LMW	Low Molecule Weight
M1 Pump	Feeding screw pump in the heating process
M2 Pump	Wing rotor pump in the heating process
MES-system	Manufacturing Execution System
MPa	Mega Pascal
●OH	Hydroxyl radical
Pa s	Pascal second
PID values	Proportional Integral Derivative-values
PT10	Process position for the product pressure measurement
PU	Pasteurization Unit

Re	Reynolds number
RTD	Residence Time Distribution
SF-Juice	Semi-Finished Juice

1 Introduction

Eckes-Granini Finland Oy Ab is the leading manufacturing company of juice, drink, and syrup products. The company is located in Turku. There has been over 150 years the manufacturing of juices and beverages from fruits and berries. The strategic brands are Marli, Mehukatti and God Morgon The company is part of the leading European juice business group Eckes-Granini Group GmbH with the headquarter located in Nieder-Olm, Germany.

The fruit juice-based business with added value from grain and other natural ingredients is growing fast due to the changing different consumer needs and behaviors. The vegan origin diet has increased among the consumers during the past decade. The consumer is searching for healthy food and drink alternatives that consider the environmental aspects as well. The company should notice the wishes and demands occurring in the market and offer the product portfolio fitting to the consumer needs. Oat has become a well-known ingredient for various food and beverage applications. Whole grain oat has many nutritional benefits as well. (Eckes-Granini Finland Internal discussions 2021.)

The target for this thesis was to develop a fruit and berry-based drinkable product with oat. The novelty product considered the characteristics and demands of oat together with fruit and berries. The research problem which needed to be solved was the requirements of novel oat-based fruit and berry juice drink which treatment must go through the thermal production process. The pasteurization process of oat flour with fruit juice components, makes the oat beverage challenging to process. The aim was to develop an industrial scale product which fulfills the requirements from technical, chemical and consumer acceptance point of views. Oat had to be as native origin as possible and locally grown Finnish oat.

The thesis work structure followed first the theoretical evaluation of oat itself. Oat behavior in the aqueous solution was important for understanding the fundamental engineering to know how material was subjected to variety of

forces and deformations. The science of rheology was of value here because rheology is the science of deformation and flow of matter. In the thesis practical part oat has been treated in the recipe development process and production processes. The industrial scale production tests and suitability studies have been carried out. The material research was based for the main demands which were the locally grown oat, the finished goods needed to be drinkable and liquid while having the characteristics of snack (product to be consumed between the meals). The recipe development was used for the formulation and the sensorial evaluations were conducted together with the stability studies and chemical sample evaluations as well. The results and conclusions are presented in the experimental part.

2 Oat

A development process of a new drinkable combination of grain and fruits differs from the pure fruit and berry-based juice drink. Especially when the fruit based raw materials which are traditionally used for the formula of juices, have been processed from the whole fruits into the semi-finished raw material. When using the processed semi-finished fruit based raw materials, there are normally no big challenges to create the recipe formula and manufacture the semi-finished juice drink e.g., with the thermal processing. Particularly there are plenty of different fruit-based, alternatives available for the semi-finished raw materials. (Eckes-Granini Finland Oy Ab Internal discussions 2021.)

The grain dosing to the liquid product makes the formulation challenging and there are new dimensions of the product life cycle management which should be considered. Especially oat with elevated levels of dietary fiber in the food application of high-water content has challenges of texture control in the mixing and the heat treatment processes. Whole-grain oats are quite different for the food formulation than specific and modified oat fractions. β-glucan fibers which are naturally present in oat can increase the viscosity and change the structure of the drinkable product. Usually, a major part of fibers is filtered out of liquid oat products e.g., modified oat drink products. The structure engineering of thermally processed oat foods and beverage-type foods are less used fields. (Eckes-Granini Finland Oy Ab Internal discussions 2021.)

Native β-glucan produces non-acceptable high viscosities and a slimy mouth feel (Kivelä et al. 2010, 611).

Firstly, the rheology of liquid product and the rheological properties are essential to understand during the product development and designing the process equipment's such as pumps, pipelines, agitators, mixers, colanders, and heat exchangers. The fluids can be characterized either by their viscosity or consistency. (Eckes-Granini Finland Oy Ab Process Instructions 2021.)

Food processing is included on complex flow processes. Rheological characterization of the individual food ingredients as well as the formulated food product is an integral part of food science. Rheological research in food science is linked to the development of food products and could address the industrial processing and production of food. The relationship of food flow in the production process and in the human consumption plays an important role. (Fischer & Windhab, 2010, 36.)

Lyly et al. (2003, 536 - 541) studied that beverage made with the bran-type preparations were more viscous and had higher perceived thickness than beverages made with more processed, small molecular weight oat-preparations.

2.1 Oat plant and cultivation

Oat belongs to the grain family *Graminaceae* (*Poaxeae)* and the cultivated oat genus Avena *sativa L.* is a traditional ingredient in the food which has been farmed and used hundreds of years in Finland. Actually, Finland is one of the world's considerable oat producers. During the last years, the usage of oat has been significantly increasing. The oat farming area was 347 900 hectares in 2020 in Finland. The most popular variety was Niklas with 24 % of the oat area share. The other popular varieties were Matty, Meeri, Avanti and Belinda. (Viljaalan yhteistyöryhmä 2021.)

Oat has traditionally been used as oatmeal, bran, flour, or flakes. The novel oat foods and oat drinks are made of bran or β-glucan-enriched fractions. Water-soluble β-glucans are derivied from the endosperm of oat kernels. Figure 1 shows the different structural levels from oat plant to β-glucan. Oat flour is milled from the dehulled oat grains. (Grundy 2018, 1330.)

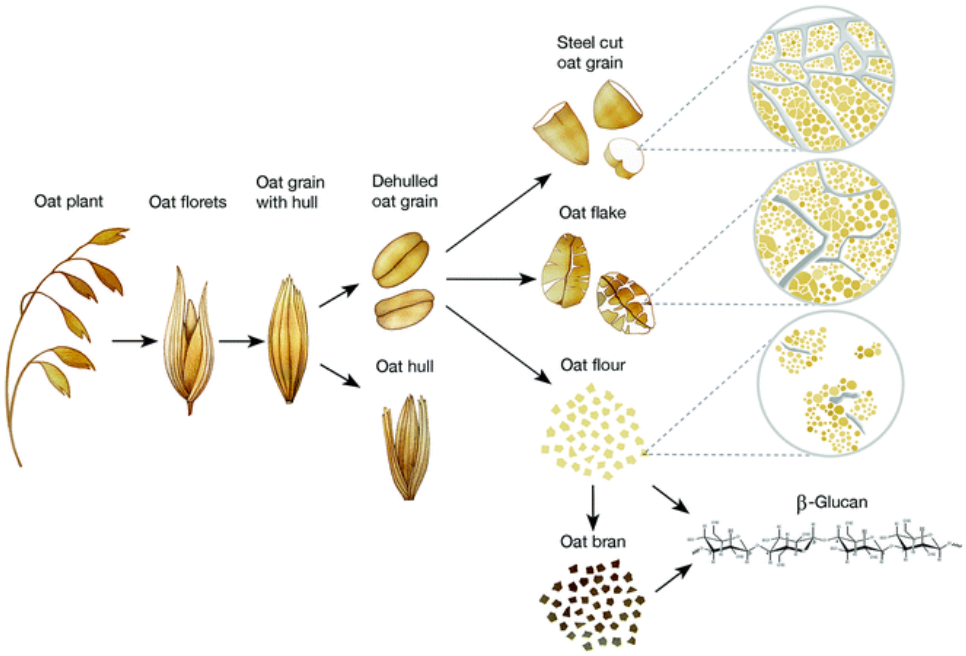

Figure 1. Differential structural levels of oat (Grundy 2018, 1330).

On the other hand, the functional properties of β-glucan are known to influence human health benefits, it is important that oat cultivars with the highest solubility and viscosity be recommended for food use (Herrera et al. 2014, 194).

2.2 Oat grain and composition

The fruit of oat is a caryopsis or grain. The anatomy of the grain is described in figure 2. Oat grain contains three main parts: bran, endosperm, and germ. The germ accounts for 3 % of the kernel weight, the bran´s weight is 38 – 40 % and starchy endosperm´s weight is 58 – 60 %. In the first place β-glucans are mainly located in the endosperm cell wall. The β - glucan content which is 3-5 % in the kernel, varies quite widely, influenced by both environment and genetics, where the genetics is being the predominant factor. (Arent & Zanniini 2013, 250 – 252.)

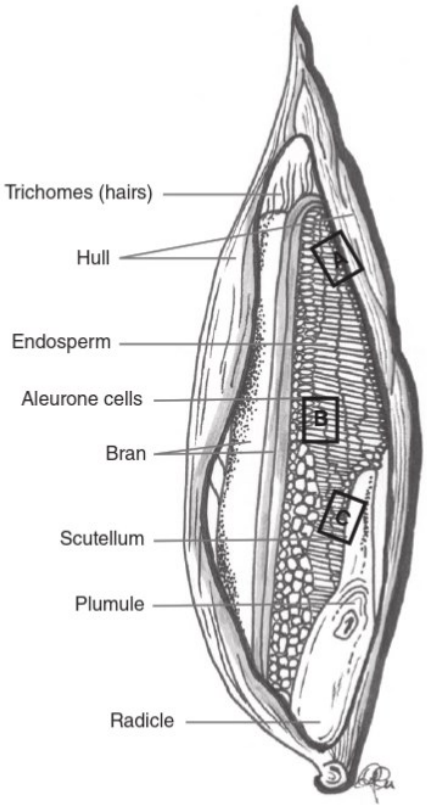

Figure 2. Oat caryopsis (Arendt & Zannini 2013, 252).

The main macro nutritional components of oat are proteins, fat, and carbohydrates. The carbohydrates consist of sugars, starch, and fiber. Oat cereals supply also important minerals, vitamins, and other micronutrients. The protein content of grain is 16 %. The components like soluble fiber, essential amino acids and β-glucan are reliable sources for the healthy diet. (Arendt & Zannini 2013, 251 – 254.)

The oat bran has the main phytochemicals such as saponins avenacosides A and B. The content of saponins is 1 g/kg. (Food Chemistry 2004, 765.) Due to the (presence of a lipid-soluble aglycone and water-soluble sugar chain(s) in their structure (amphiphilic nature), saponins are surface active compounds with detergent, wetting, emulsifying, and foaming properties. (Wang et al. 2005, 341-347.)

For instance Ralla et al. (2018, 256 – 261) concluded the effect of oat bran extract was highly surface-active and formed negatively charged submicron sized emulsion droplets at a low emulsifier-to-oil ratio, and resisted a range of pH, heat, and time-induced stresses. Oat bran phytate which is naturally present in cereals can act as a chelator, preventing the reaction of hydrogen peroxide with iron. Chelators can thus act as antioxidants by binding metal ions that would otherwise take part in the Fenton reaction. (Liyana-Pathirana & Shahidi 2006, 1156.)

H.J.H Fenton discovered in 1894 that several metals have a special oxygen transfer properties which improved the use of hydrogen peroxide. Some metals had a strong catalytic power to generate highly reactive hydroxyl radicals (. OH). Since this discovery, the iron catalysed hydrogen peroxide has been called Fenton's reaction. (Lenntech 2022.)

Basically, there is still largely unknown area what comes to the relationship of the surface properties of the cereal particles. Especially the behavior of the tribo-charging particles. The material´s surface donates or accepts electrons with contact of the other materials. (Mazumder et al. 2006, 2198.)

2.3 Dietary fiber oat β-glucan

Natural dietary fiber is found only in plant foods (Harvard T.H. Chan 2022). It consists of both soluble and insoluble fiber (Jones 2014, 5). Oat β-glucan is a viscous, and water-soluble dietary fiber part. However, it´s a non-starchy polysaccharide. Oat β-glucan was first reported in oat kernels by Morris (1942). (Wood 2011, 219-220.)

The chemical consist of β-glucan (Figure 3) is a liner unbranched β- (1→4)-D-glucopyranose units (70 %), which are separated every 2-3 units by a single β-(1→3)-linked glucose unit (30 %). (Butt et al. 2008, 70.) These (1→3)-linkages make the molecule flexible, and contribute to its high-water binding, solubility, and viscosity (Anttila et al. 2004, 81). The presence of (1 → 3)- linkages leads to twists in the chain polymer, allowing water to get in between the chains, and makes β-glucan soluble in water (Lamas de Souza et al. 2015, 243).

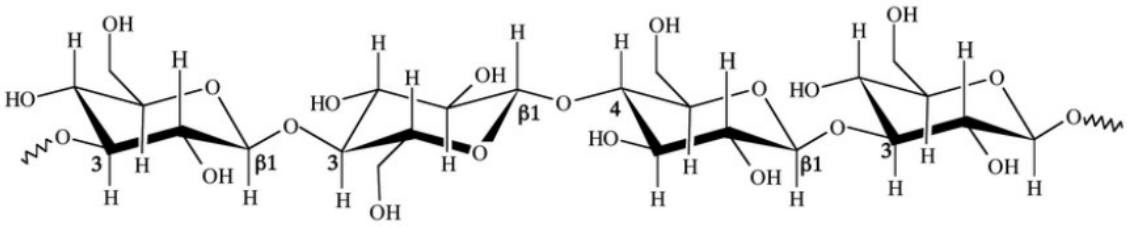

Figure 3. β-glucan molecule structure (Pillai et al. 2005, 3).

β-glucan is mainly found richly in the thinner endosperm cell walls (Fig.4) (Grundy et al. 2018, 1329). There is no β-glucan in the hull (Wood 2011, 219-220).

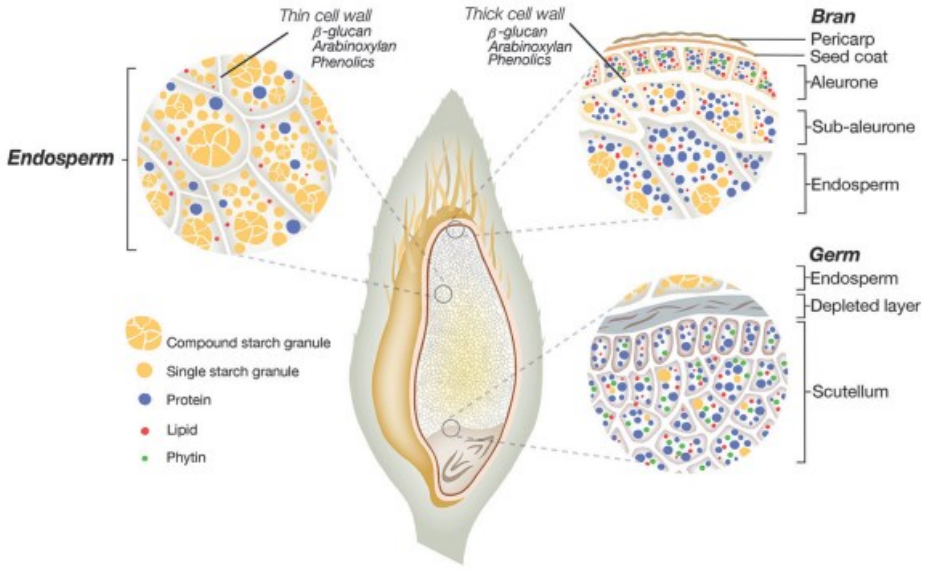

Figure 4. β-glucan locations in the grain (Grundy 2018, 1329).

The bran contains β-glucan, arabinoxylan and other nutritional components like vitamins and minerals (Grundy 2018, 1329).

2.4 The health claim related to β-glucan

The accepted European Food Safety Authority (EFSA) health claim for the β-glucan is possible to use when food have at least one (1) g of beta-glucans from oats, oat bran, barley, barley bran, or from mixtures of these sources per quantified portion.

To bear the claim information shall be given to the consumer that the beneficial effect is obtained with a daily intake of three (3) g of beta-glucans from oats, oat bran, barley, barley bran, or from mixtures of these beta-glucans. The health claim statement is following " Beta-glucans contribute to the maintenance of normal blood cholesterol levels". (EFSA 2021.)

2.5 The cultivation interaction to the content of β-glucan in the grain

Basically, the effects of growing location, oat cultivar as well as growing year, have been observed. The relationship between β-glucan levels in cereal grains and grain quality, or yield parameters, appeared to vary greatly depending upon genetic background of the cereal line being examined. (Brennan et al. 2005, 2.)

In conclusion of the study, selecting oat cultivates had a bigger effect instead of the growing location for the variation of oat flour properties (Herrera et al. 2014, 194).

β-glucan viscosity correlated positively with the daily average temperature, while β-glucan solubility index was negatively correlated with the daily average temperature. In addition, β-glucan content was positively correlated to the precipitation amount during the growing season. (Herrera et al. 2014, 195.)

2.6 Rheological behavior of β-glucan in the solutions

The molecule weight (M_w) and concentration had a determining influence on the rheology behavior in aqueous solution (Dongowski et al. 2005, 280).

The differences in the rheology have been found in the different oat varieties in the same β-glucan contents. β-glucan aqueous solubility at 37 °C was significantly influenced by growing location, oat cultivar, and the location by cultivar interaction. (Herrera et al. 2014,192.)
According to the study, the β-glucans isolated from oat products had a complex rheological behavior depending on the source material, the technological pre-treatment, and the used concentration (Dongowski et al. 2005, 289).

Gel is a non-fluid colloidal network or polymer network in which it is expanded throughout its whole volume by a fluid (IUPAC Compendium of Chemical Terminology 2012, 616). β-glucan solutions had tendency to form gels. The lower molecular weight solution was easier to form a gel than larger molecules. (Cui & Wood 2000, 159-167.) The gel formation took place with M_w less than 100 x 10^3. According to the study was found that the highest M_w sample (250 x 10^3) did not show any tendency to gel. It could be attributed to the low mobility of the long chains, retarding the chain diffusion and aggregation. The conclusion was also that with higher M_w the sample gave strength and brittleness gel. (Lazaridou et al. 2003, 704.)

The critical concentration (c**) for viscosity enhancement was increased with a decreasing molecular weight. This means that with a decreasing molecular weight, the number of molecules needed for the formation of viscosity-causing entanglements were increasing. Besides they explained that the chains of the low molecular size of the aqueous β-glucan samples were more mobile and diffused more easily. These samples had more probability of forming aggregates by lateral associations. (Lazaridou et al. 2003, 700.)

While the β-glucan concentration (c) was < 0,2 % the β-glucan solution behaved like a Newtonian solution which means that an increasing shear rate does not affect the viscosity. At the higher concentration > 0,2 % the high molecular weight β-glucans started to entangle and form viscous and pseudoplastic fluids. The pseudoplastic fluids are called equally shear-thinning fluids. (Anttila et al. 2004, 81.) While the molecular weight and concentration were doubled it could lead to a high viscosity increase – up to 15-fold increase (Doublier & Wood

1995, 335). In order to unhydrolyzed β-glucan study, no thixotropy (time depending) was evident (Doublier & Wood 1995, 336- 337). Thixotropy gel has a reduced viscosity on the application of a finite shear but recovers its original viscosity when the shear is discontinued (IUPAC Compendium of Chemical Terminology 2012, 1538).

The Newtonian viscosity increased from ca. 80 to 120 mPa s as the β-glucan concentration increased from 0,39 to 0,78 %. The M_w in the study was 1,3 x 10^6 for the unhydrolyzed β-glucan. (Doublier & Wood 1995, 336-337.)

As the study from Agbenorhevi et al. (2011, 373) showed that there was the dependence of viscosity in shear rate for the β-glucan dispersions in the different concentrations and M_W (Figure 5.).

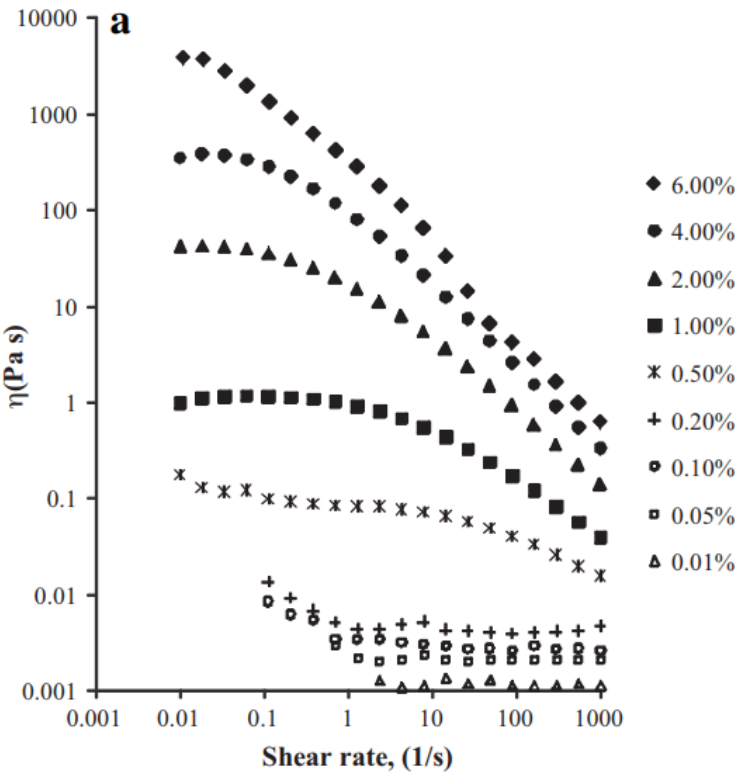

Figure 5. Viscosity dependence on shear rate (Agbenorhevi et al. 2011, 373).

At higher concentrations, pseudoplastic behaviour was showed as the shear rate increased while at lower concentrations, Newtonian behaviour was seen (Agbenorhevi et al. 2011, 374).

The molecule weight of different oat sources is described in the table 1.

Table 1. Different molecule weight and behaviour effects of oat.

([1] [2] Cui et al. 2000, 163, [3] Oat product manufacturer specification, [4] Cui et al. 2000, 163, [5] Du et al. 2019, 8).

Oat type	Molecule weight $x10^3$	Treatments
Original oat bran [1]	1 000	Untreated
Pre-treated oat bran [2]	2 000 – 2 500	Aqueous treated
Oat product [3]	686 - 911	Extrusion of oat grain
Oat with acid hydrolysis [4]	86 → 35	Heat treatment 120 - 130 ºC
Oat with chemical treatment [5]	130 → 68	Sulfation

2.6.1 β-glucan and Fenton reagents

β-glucan dietary fiber was easily degraded in the presence of Fenton reagents. These reagents were Iron (II) (0,5 nM) and peroxide (H_2O_2) (100 nM) in the oat β-glucan solution. Fenton reaction was not affected by the presence of the β-glucans in a solution at pH 2.7, hence none of the beta-glucans bound iron (II) at this pH. In the solution pH 4,7 after 2 h treatment it had 30 % less viscosity vs. the original solution. (Faure et al. 2015, 740.)

2.7 Oat arabinoxylan

Arabinoxylan (AX) is the other important dietary fiber part in oat. AX is concentrated in the bran fraction. In the whole grain oat flour the content of arabinoxylan is 2,0 – 4,5 % but only 0,2 – 0,4 % of the amount is water-extractable. The main part of AX is in the outer layer of the oat bran. (Izydorczyk 2009, 655-656.) Cereal arabinoxylans having ferulic acid residues can form gel networks stabilized by covalent crosslinks between feruloyl groups of neighbor chains. Gelation of arabinoxylans is induced by free radical generating agents such as hydrogen peroxide. (Izydorczyk 2009, 675.) AX is possible to remove by extracting the oat fractions with Ba $(OH)_2$ and β-glucan is released and becomes water-extractable (Johansson et al. 2004, 270).

2.8 Oat starch polymers

The second crucial factor of the aqueous oat solution viscosity is starch which is naturally 40 – 60 % present in the oat flour. The lowest yields of starch have been evaluated of the high protein content oat. The physiological role of starch is to store energy. Starch cannot easily be separated from the other components of the grain due hydrated bran and protein layers. The shape of granules is only weakly birefringent and irregular. Oat starch granules tend to exist in clusters. (Sayar & White 2011, 109-111.) The greatest proportion of variation for starch content was attributed to cultivar (81.1%, $p < 0.01$), and year effect was negligible (Herrera et al. 2014, 194).

Oat starch has mainly two glucose polymers: amylopectin (70 %) and amylose (25 – 30 %). Amylopectin is a highly branched polymer consisting of short α-glucan chains. (Sayar & White 2011, 111-113.) Amylopectin structure has the parts for crystal and amorphous parts (Zhou et al. 1998, 274). Amylose is a long-chain, linear polymer consisting of 1 to 4-membered α-glucans (Figure 6) (Dipak 2016, 2). Amylopectin is much larger than amylose, with molecular weight in the order of 10^6 to 10^8 (Ross 2012, 109). The high M_w of amylopectin

has one of the highest molecular weights known among naturally occurring polymers (Sayar & White 2011, 111).

When a suspension of starch granules is heated in excess water, the amylopectin douple helical structure are lost and the granule swells (Taggart & Mitchell 2009, 112). Larger granules tend to swell more on cooking, and hence granule size is a factor to be considered in starch functionality (Ross 2012, 113).

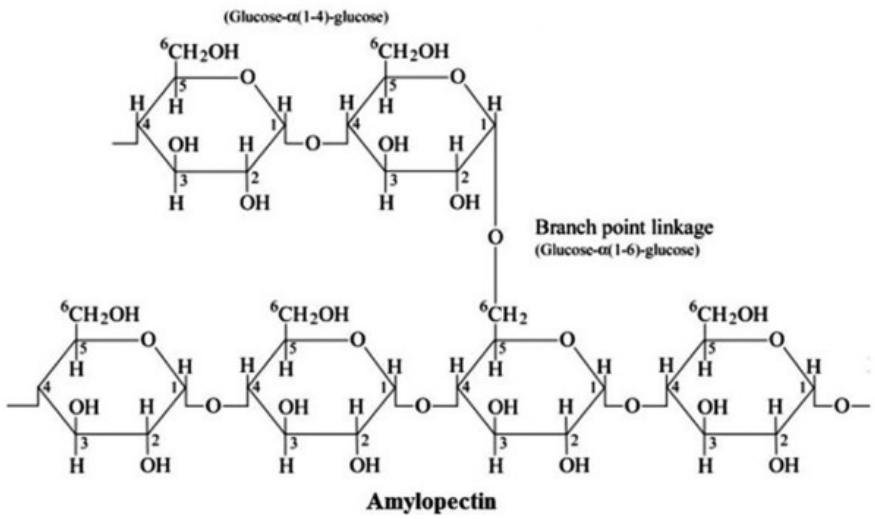

Figure 6. Amylopectin molecule structure (Dipak 2016, 2).

Amylose is smaller of these two polymers and has molecular weight 500 kDa (weight average) (Taggart & Mitchell 2009, 110). It is strongly self-aggregate via hydrogen bonds (H-bonds) and thus insoluble in cold water (Ross 2012, 109). The relative proportions of amylose and amylopectin in starch granules, together with the chain- length distribution and the frequency and spacing of branch points within the amylopectin molecule, have a major influence on the properties of the starch (Sayar & White 2011, 111-113). Figure 7 shows amylose molecule structure.

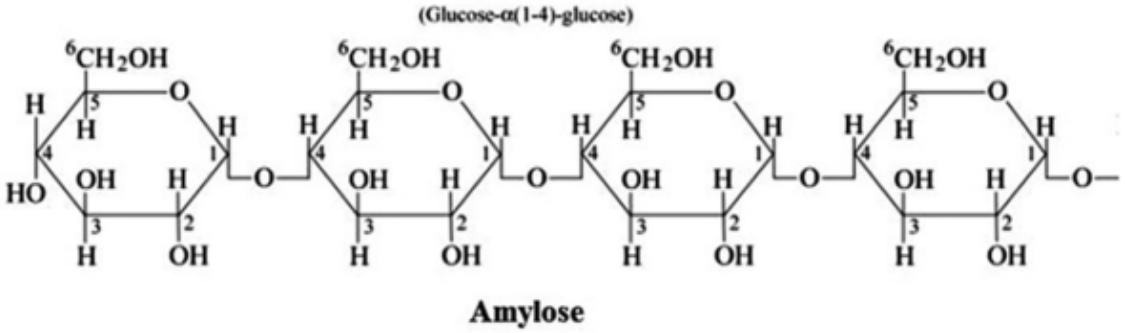

Figure 7. Structure of amylose (Dipak 2016, 2).

Oat starch has higher lipid content vs. the other cereals (Zhu 2017, 330). Tester and Karkas (1996, 276) studied that oat starch granules appeared to be rather fragile when gelatinized and swollen, and, consequently, a proportion of the cleaved amylopectin was solubilized together with amylose on heating at 80 °C. According to the study from Swikles (1985) showed that the lipid content reduced the water-binding capacity, swelling, and solubilization of oat starches (Sayer & White 2011, 111).

2.9 Oat starch behaviour in the liquid during heating and cooling

On heating, the internal ordered structure is disrupted and irreversibly destroyed. Concurrent with this, the granules swell several times their original size, and amylose, the smaller of the two starch macromolecules, is solubilized and leaches from granules. After starch is cooked and allowed to cool, it is the linear amylose that has the higher propensity to crystallize. (Ross 2012, 113.)

After cooling the polymers undergo retrogradation which means the reorganization phenomenon of amylopectin and amylose. Amylose retrogradation is a fast process whereas amylopectin retrogradation is much slower. (Sayar & White 2011, 112-113.) The second stage is the gradual firming of the gel as the terminal amylopectin chains reassociate over a period of hours to days. Starch polymers are metastable only in close-to-neutral aqueous pH solution and undergo phase separation over time. Amylopectin is sensitive to shear scission. The molecular weight of starch is key factor and

should not be underestimated. Amylopectin has one of the highest molecular weights known naturally occurring polymers. (Kasturi & Bordenave 2014, 98-99.)

The typical behavior of oat starch during the cooling was having higher torque values 75-80 % of the final setback. This was result of Paton (1977) who was the first author to present the paste behaviour of oat starch during the cooling stage. Paton described oat starch gels as being more translucent, less firm, more elastic, and more adhesive vs. corn starch gels. (Sayar & White 2011, 117.)

2.10 Oat starch gelatinization

Oat flour with a high starch content is preferred, not only because of the higher yield, but also because as a result, the content of impurities, such as lipid and β -glucan, in the starch fraction was low (Autio & Eliasson 2009, 2).
Starch granulates were able to absorb relatively high water quantity and swell. In the cold water this was limited but increased while heating up the solution. The gelatinization occurred when starch water solution was heated up and the amorphic parts absorbed water into and swell. Gelatinization was probably the most important attribute of starch. The presence of protein, fat, sugar and organic acid affected to the gelatinization process. Starch has two properties which effected to the viscosity when e.g., oat flour was added to the warm or hot water solution, gelatinization and retrogradation happened. During the cooling step, starch developed the high viscosity. Cooled oat starch was clear, less firm, elastic, more adhesive and less susceptive to retrogradation. (Peterson 2004, 24.)

High viscosity developed rapidly. The temperature at which the starch birefringence disappears was often considered the gelatinization point or gelatinization temperature. (Sayar & White 2011, 115.) Birefringence was the ability to doubly refract polarized light (Alcázar-Alay & Meireles 2015, 218).

There were no rheological changes occurred < 90 °C for the oat starch. When preheated at only 90 °C the granule structure was primary intact and most of the amylose and amylopectin was still located inside the granule. At 95 °C, the granule structure broke down and both amylose and amylopectin were co-leached from the granule. The oat variety with the highest oil content had the highest storage modulus (G'). (Autio & Eliasson 2009, 597-598.)

The microstructure partly explained the special rheological properties of oat starch dispersions during cooling (Autio & Eliasson 2009, 592).

2.11 Gelatinization measurement with Differential Scanning Calorimetry

To figure out starch behavior in the water contents, the Differential Scanning Calorimetry (DSC) is useful method to use. The typical starch DSC thermogram of gelatinization and retrogradation of cereal starch in excess water is shown in figure 8. The low-temperature Primary melting endotherm corresponds to the melting of the amylopectin crystallites in ca. 68 °C. The secondary melting is the high-temperature endotherm which corresponds to the melting of an amylose lipid complex in ca. 110 °C. (Ross 2012, 120.)

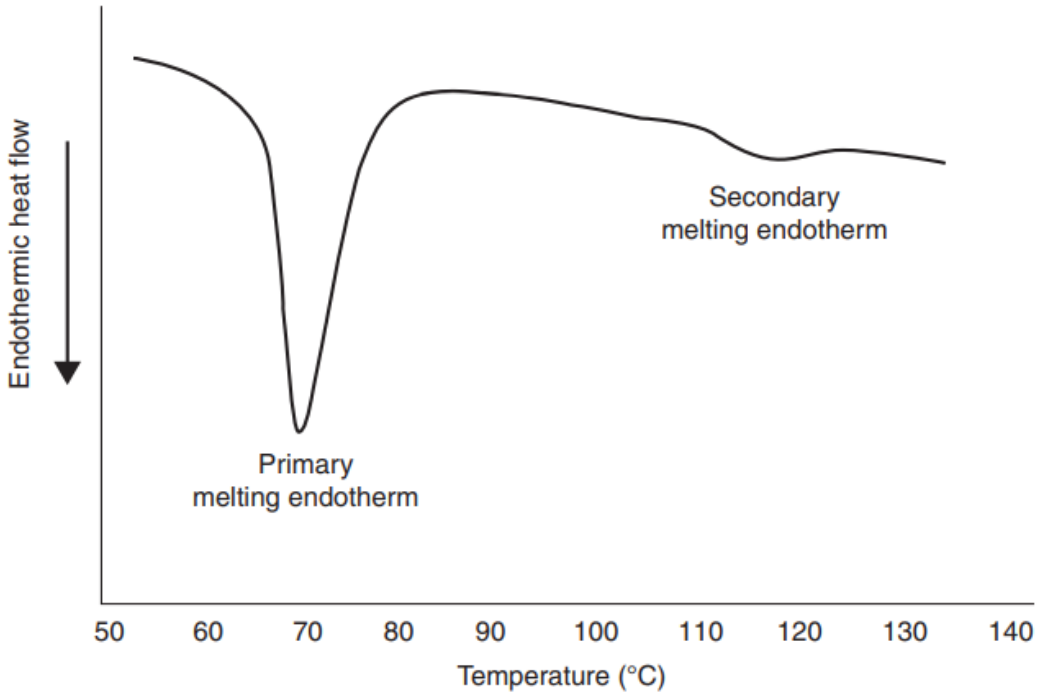

Figure 8. Differential scanning calorimetry for starch (Ross 2012, 120).

With the differential heat flow, the variety of exothermic and endothermic events were possible to observe in the sample (Ross 2012, 120).

2.12 Oat starch´s lipid and protein content effects

The results obtained by Wang and White 1994c study showed the amylose amount which leached out in the starch heating and gelatinization at temperature 95 °C was 23 %. The higher temperature increased the swelling power and solubility. (Sayar & White 2011, 116-117.)
Because of the range of lipid contents of the grain, several investigators have compared properties of starch isolated from groats differing in lipid content and found that many of the properties of oat starch were related to its lipid content. The defatted oat starch showed less swelling power and increased solubility. (Autio & Eliasson 2009, 592, 596.)

The effects of starch can also be minimized using oat bran ingredients, which are high in β-glucan and low in starch (Oat bran ingredient supplier´s e-mail September 2021).

3 Fruits and berries

Fruit is the fleshy or dry ripened ovary of a flowering plant, enclosing the seed or seeds (Britannica 2022).

Any small fleshy fruit is popularly called a berry, especially if it is edible. Raspberries, and strawberries, for example, are not true berries but are aggregate fruits. These berries are fruits that consist of a few smaller fruits. Blueberries, however, are true botanical berries. (Britannica 2022.)

3.1 Berries and Fruits used in the thesis

The fruit materials have been selected from raw materials which are suitable for Eckes-Granini Finland portfolio and production (Eckes-Granini Finland Internal discussions 2021).

3.1.1 Blueberry or bilberry

The binomial name for bilberry is *Vaccinium myrtillus.* The bilberry is a perennial, erect, 10–30 cm tall shrub with angular, green branches. It grows as wild in the forest. Its leaves are elliptic, tapering, have toothed margins, and drop for the winter. The bilberry flowers in May–July. Single, pink, bell-shaped flowers grow in the axils of the leaves. Bilberries contain vitamins C and E. They are also a reliable source of fibre. The most significant health benefit of the bilberry, however, is the anthocyanin compounds it contains. (Arktiset Aromit 2022.)
Blueberry is known as bilberry. Definition for the industrial use is running between these are under the evaluation (Association of fruit juices and nectars 2022, pre-readings.)

3.1.2 Grape

The genus name for grape is *Vitis*. There are about 60 – 80 species of vining plants in the family Vitaceae. Grape varieties are used as table fruit, dried to produce raisins, or crushed to make grape juice or wine. The grape is usually a woody vine, climbing by means on modified branches. (Britannica 2022.)

3.1.3 Pineapple

The genus name for pineapple is *ananas comosus*. It´s a perennial plant of the family Bromeliaceae. Pineapple is native to tropical and subtropical areas. The plant has 30 – 40 stiff succulent leaves closely spaced in a rosette on a thick fleshy steam. (Britannica 2022.)

3.1.4 Orange

The genus name for orange is Citrus of the family Rutaceae. Orange is round fruit which has leathery and oily rinds and edible juicy inner with flesh. Several species and varieties of orange are economically important, especially the common *Citrus x sinensis*. The orange tree often reaches height of 6 metres. Orange is rich in e.g. vitamin C and potassium. (Britannica 2022.)

3.1.5 Raspberry

The scientific name for raspberry is *Rubus idaeus.* The raspberry is a suckering shrub reaching 50–150 cm in height. Its stems are biennial and prickly, erect, or arching. Its greenish-white flowers bloom in June–July. The berry is a sweet and fragrant red aggregate drupe which detaches from the receptacle of the flower when picked. Raspberries contain vitamin C and folate. (Arktiset Aromit 2022.)

3.1.6 Strawberry

The scientific name is *Fragaria.* More than 20 species of flowering plants in the rose family. Cultivated varieties are widely grown throughout the world. Strawberries are low-growing herbaceous plants with a fibrous root system and a crown from which arise basal leaves. Berries have rich content of vitamin C. (Britannica 2022.)

3.2 Pectin in fruits and berries

Plant materials, like fruits and berries, have naturally occurring pectin which has a significant role in the middle layer of the plant cell wall, helping to bind cells together in association with cellulose, hemicellulose, and glycoproteins. Pectin is an acidic heteropolysaccharide. It has ability to form a thick gel-like solution. A plant becomes more water-soluble as it´s ripening proceeds. As the plant becomes overripe, the pectin in it is broken down. (Encyclopedia Britannica 2022.)

Pectin itself was first isolated and named by Braconnot (1825). Even there are many naturally occurring materials which contain pectin, and do not have the functional properties, especially the ability to gel in the acid sugar systems. (May 1997, 230.)

It is common to use fruit purees and concentrated juices in the fruit-based juice drink applications. The fruit juice production process starts from the harvested and inspected fruits which are stored e.g., in the bins before going through the processing plant. (Eckes-Granini Finland Internal information 2021.)

3.3 Fruit juice production with pectinase

In the extraction phase, machines crushed the fruit, and the viscous juice was separated from the fruit pulp and seeds were separated. The enzymes acted as biocatalysts which catalyzed and accelerated various biological reactions. The

enzyme called pectinases were used to breakdown pectin polymer into monomer sugars i.e., galacturonic acid. Pectinase enzyme removed the soluble pectin from the juice and amylases were used to remove the starch from the juice that caused the unwanted haze in the juice. It managed the gel formation in the juice during storage. (Verma et al. 2018, 2-3.)

The process to treat the whole fruits (like apples) into the clarified juice while removing the pectin and protein complexes is described in Fig. 9.

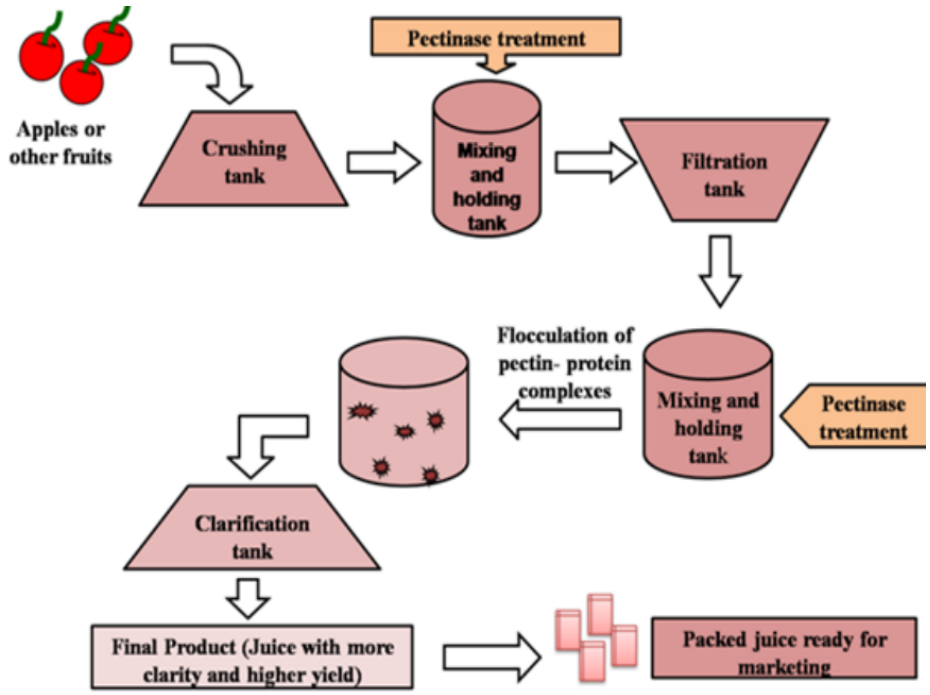

Figure 9. Fruit juice processing steps (Verma et al. 2018, 3).

To obtain the desired product, process parameters were needed to optimize. The parameters of optimization were enzyme concentration, enzyme treatment duration, incubation temperature and pH of solution. For the improvement of fruit processing, immobilization of enzymes was employed to make the fluent process and reduction of the overall production cost. By immobilized enzymes, they were able to be reused. It made the removal of the enzymes from the juice easy. (Verma et al. 2018, 2-3.)

The next process step was to homogenize or filter the fruit mass. The oxidation spoils the flavor and nutritional values. The deaeration step next to the pasteurization improved the product quality. Pasteurization was needed to kill the germs and guarantee the stability during the storage. After pasteurization process the goods were packed into aseptic packages and stored chilled or frozen. (Verma et al. 2018, 3-4.)

3.4 Fruit puree production

Fruit puree processing differed from the juice processing because all the processing involved pulp that was highly viscous and not clarified. The cleaned and selected fruits were de-stoned. Depending on specific puree requirements, the mash could either be extracted using hot break or cold break methods, depending on whether viscosity or color/taste were the prime considerations. The preparation had steps of fruit handling, like peeling of the skin, size reduction, heating to either soften the tissue and/or inactivate enzymes. The heated fruit mass was managed through finishers.

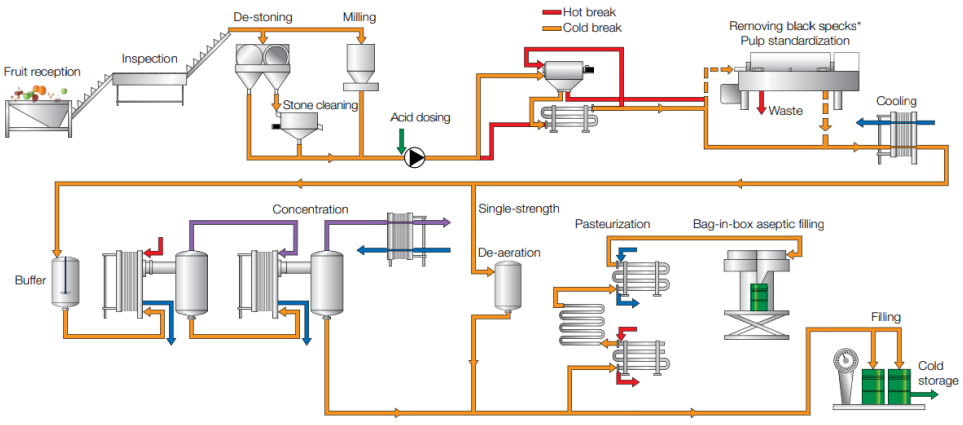

Figure 10. Fruit puree processing (Alfa Laval 2022, 4).

The puree was packed aseptically into drums or special containers for the frozen storage. For the aseptic drums, the puree was pasteurized before the filling step. (Alfa Laval 2022, 1-4.)

3.5 Fruit puree viscosity

The evaluation of the viscosity of fruit purees showed that the viscosity variation against the share rate was exponential, and the purees were non-Newtonian fluids.

Non-Newtonian is a fluid in which the components of the stress tensor are linear functions of the first spatial derivatives of the velocity components. These functions involve two material parameters (taken as constants throughout the fluid, although depending on ambient temperature and pressure). (IUPAC Compendium of Chemical Terminology 2012, 991.)

There were many factors influencing the rheological behavior of fruit puree as well concentrate. The factors were temperature, total soluble solids (Brix- value) and particle size. Apparent viscosity of all purees decreased as the shear rate increased. The viscosity behavior could be due the structural breakdown of the puree molecules when the hydrodynamic forces generated and the increased alignment of the constituent molecules. (Balestra et al. 2011, 4.)

The referred study mentions the yield stress (τ_0) was an important quality control parameter in the industrial applications. True value of the yield stress could be beneficial for the best design of food-processing systems such as thermal processing. The yield stress increased with soluble solids content. (Balestra et al. 2011,5.)

The flow behavior of fruit puree could be modelled with Herschel Bulkley equation (1) with τ = the shear stress (Pa), τ_0 = a yield stress (Pa), K = rheological constant (Pa s^n), K = rheological constant (Pa s^n), $\dot{y}$ = a shear rate (l/s), n = Flow behaviour index (dimensionless).

$$\tau = \tau_0 + K\dot{y}^n \quad (1)$$

Equation 1. Herschel-Bulkley equation for the flow behaviour of fruit puree (Krokida 2001, 181).

Most non-Newtonian foods were pseudoplastic materials (n < 1), while very few were shear-thickening (n > 1). The pseudoplastic fluids were also known as shear-thinning fluids, since their apparent viscosity decreased as the shear rate was increased. (Krokida 2001, 181.)

One of the rheological property of purees is the thixotropy. The yield stress is lost while shaking the puree and rebuilt when staying at rest (or less sheared). (Thermal processing of Fruits and Fruit Juices 2012, 423.)

4 Viscosity decreasing treatments for oat βeta-glucan

There has been a need to properly understand the threats for instability of native β-glucan in aqueous environments (Kivelä et al. 2004, 2). Some processes were existing which treat the aqueous oat flour mixture and lead to the easily produced final commercial product. There was a patented oatmeal method in which dried or wet-ground oats were mixed with water. From the aqueous suspension, the starch was digested with α- and β-amylase into maltose and finally the oat-water mixture was homogenized. By this method breaking down a substantial proportion of the viscosity producing components – namely starch and β-glucan. Both enzyme treatment and homogenization required a lot of water. In US there were 17 different documented patents on β-glucan production technology. (Zhu et el. 2016, 278.)

4.1 β-glucan molecular weight

The one main factor is the molecular weight of β-glucan. In the study from Lyly et al. the effect of concentration and molecular weight of β-glucan preparations to the sensorial quality were studied. It showed that the correlation between sensorial thickness and β-glucan molecular weight was strong while the concentration stayed the same. High M_w gave higher viscosity than low M_w. (Lyly et al. 2003, 539.)

There was the isolated β-glucan from the oat sample which had a decreased molecular weight. This affected to the lower viscosity. The oat bran samples (BG1 and BG2) with maximum 0,5 % of β-glucan content were beverage like from the viscosity point of view. The average M_w was 2×10^6 for the oat bran samples. The samples with soluble β-glucan preparations (BG3 and BG4) with M_w 60 – 160 x 10^3 could have higher concentration up to 2 % being beverage like. (Lyly et al. 2003, 537.)

4.2 High shear emulsifier treatment for β-glucan

According to Pereyra et al., 2011 the treatment with high shear emulsifier (top rotor tip speed of about 70 m/s and a shear energy of 5,000,000 W/kg) significantly lowered the whole grain oat particle size in the slurry having oat flour - water mixture with oat content 8 g in 237 ml water. The correlation was strong between particle size and viscosity. Usage of a high shear emulsifier reduction of the viscosity of oat slurry was 84 % less viscous vs. untreated slurry. The particle size reduction with high shear emulsifier was 54 % smaller than untreated control sample. The treated slurry was less pseudoplastic vs. control slurry. With the high shear emulsifier was possible to reduce the viscosity of slurries about 200 mPas with faster speed than compares to e.g., a colloid mill. (Pereyra et al. 2011, 3.)

4.3 Enzyme treatment for β-glucan

The fundamental molecular characteristics of structure and molecular weight were related to the viscosity of polysaccharide solutions. The most frequently used enzyme in the analysis of the structure of β-glucan was lichenase. (Roubroeks et al. 2000, 584.) According to the study from Roubroeks et al., the molecular weight of the untreated β-glucan was approximately 200 x 10^3. After 1 h hydrolysis the M_w was 110 x 10^3 and after 2 h 76 x 10^3. (Roubroeks et al. 2000, 587.)

As a result, in the study from Kwong et al., β-glucan was extracted from oat bran and purified to remove starch, proteins and arabinoxylan, and was subjected to enzymatic hydrolysis with lichenase to achieve β-glucan polymers of high or low viscosity. The M_W of the high-M_W (HMW) β-glucan was 580 x 10^3 g/mol. The M_W for the low-M_W (LMW) isolate was 145 x 10^3 g/mol. Solutions with HM_W β-glucan had the highest viscosity values of the tested solutions. (Kwong et al. 2013, 1467.)

4.4 Homogenization techniques influence on β-glucan

Homogenization was widely used in aqueous food applications to enhance product properties such as structure and stability (Kivelä et al. 2010, 611). The strong mechanical treatment broke down the part of polymer chains. Three homogenization techniques: a pilot scale colloid mill, a two-stage high pressure valve homogenizer, and a lab-scale microfluidizer were used in Kivelä et al. study. After the treatments were found that flow changed from shear thinning to Newtonian. Homogenization has been found to decrease the β-glucan solution viscosity and keep it during the product storage period. This could be due to the enhanced dispersibility of smaller and uniform molecules or molecule aggregates, which might slow down the reaggregation and flocculation process. (Kivelä et al. 2010, 613-615.)

Micro fluidization increased the porosity and capillary attraction of oat-based dietary fibers and enhanced the functionality of insoluble fibers (Chen et al. 2013,1826).

4.5 Oxidation treatment

Ascorbic acid (10 mM) and dehydroascorbic acid (10 mM) effects were studied in the aqueous solutions with pH 4.8 when added ionic iron (0.01 mM $FeSO4 \cdot H2O$). In the same study were included the roles of glucose (1 M,18 w/w) and oxygen. The viscosity behaviour of the solutions changed from shear thinning to Newtonian in 2 h. This has been evaluated as a results of molecular size reduction of β-glucan from 520 x 10^3 to 35 x 10^3 g/mol as a result of the ascorbic acid and iron treatment. The effect of oxygen was evaluated limiting the amount of dissolved oxygen with nitrogen supplement. The used Fenton chemistry reagents (Figure 11) were needed for the polymerization of β-glucan in the aqueous solution. The viscosity of ascorbic acid–glucose–solution remained unchanged as a function of time indicating that the proposed OH-induced degradation of β-glucan was inhibited by glucose addition (1 M). (Kivelä et al. 2009, 2.)

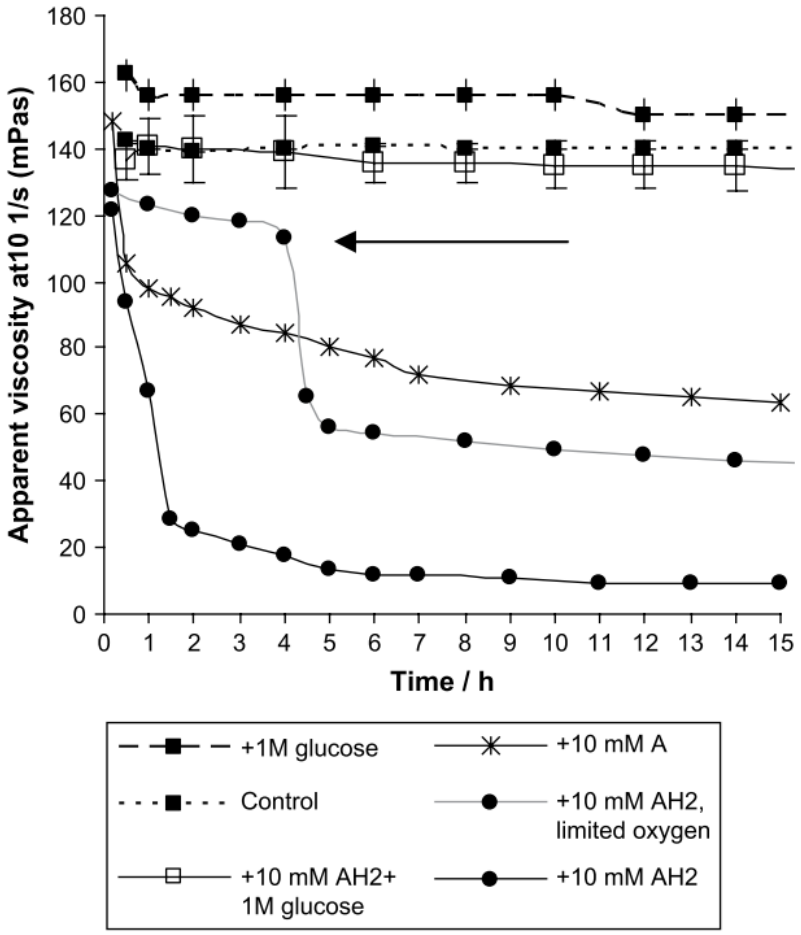

Figure 11. Fenton reagents effect to viscosity (Kivelä 2009, 2).

Endogenic H_2O_2 usually occurred in water solutions and especially in natural solutions such as food systems. Dehydroascorbic acid could also participate in the oxidative cleavage of β-glucan. (Kivelä 2009, 3.)

4.6 Acid hydrolysis of β-glucan for the oat flour preparation

According to the Finnish patent, β-glucan was hydrolysed in the acid solution. The acids were suitable for the use in food processing industry and were preferably hydrochloric acid or phosphorus acid. The invention method was based on the acid hydrolysis to reduce molecular size in a controlled manner. The treated β-glucan had the same ratio of (1→4) to (1→3) as the native β-

glucan. According to the invention the depolymerisation of β-glucan was done by effectively moisturizing β-glucan containing flour with acidic water solution and kept the oat bran concentrate elevated temperature desired retention time. The degraded β-glucan has been separated from insoluble plant fiber and incorporated into foodstuffs such as beverages and as the functional ingredient. (Kaukovirta-Norja et al. 2009, 3-5.)

4.7 Hydrogen chloride (HCl) hydrolysis for oat β-glucan slurry samples

The molecular weight dependence of viscosity versus shear rate for the four oat β-glucan samples revealed that, at the same concentration, the viscosity was higher for higher M_W samples (Fig. 12). The untreated oat β-glucan (OBG) had highest viscosity as 4.0 % and 1.0 % solution. Whereas, with HCl acid hydrolyzed samples (H05, H10 and H15) had the viscosity lower and remained more stable while the shear rate increased. (Agbenorhevi et al. 2011, 371-373.)

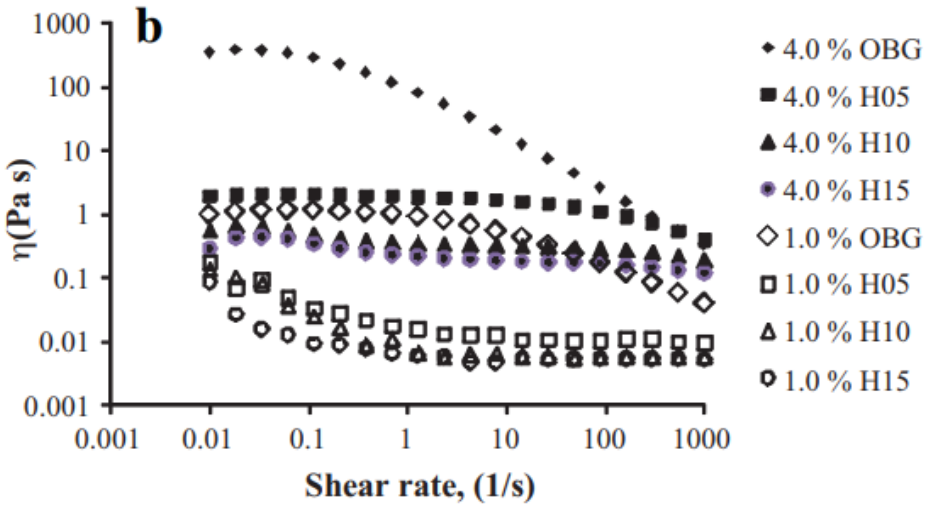

Figure 12. Oat β- glucan solution viscosities (Agbenorhevi et al. 2011, 373).

4.8 The oat extrusion process

Extrusion is a mechanical and thermal processing which involved the tested soluble oat β-glucan applications of high heat, high pressure, and shear forces. Extrusion changed dietary fiber aggregates, the gelatinization temperature as well solubility and swelling capacity became higher. Extrusion decreased the flow behaviour index and the foam ability improved. (Zhang et al. 2011, 103.)

4.9 High temperature treatment for grain

Different barley varieties were thermally treated in two phases in the study from Ain et al. 2018. When both barley varieties were boiled and roasted, these significantly modified the soluble and insoluble dietary fiber ratio. The result was more soluble fibre vs. insoluble fiber. (Ain et al. 2018, 1819.)

Heat fluidization, microwave roasting and baking processing of barley could increase the extractability and purity of β -glucan to different extents by breaking endosperm cell walls of Highland barley *Hordeum vulgare*. The decrease in molecular weight and polydispersity index of β -glucan extracted from thermally processed barley was because microwave roasting, baking and heat fluidization could depolymerize large sphere aggregates into small round fragments. (Bai 2021, 11.)

5 viscosity decreasing treatments for oat starch

Native starch is not a best product in a particular process, because it shortcomings to low shear resistance and thermal stability, thermal decomposition, and high tendency towards retrogradation. To improve such properties, starch could be subjected into modification process. There were several ways of starch modifications (physical, chemical, enzymatic and combined), designated to change one or more of its properties. (Berski et al. 2010, 665.)

5.1 The chemical acid modification

Modification of starch granule structure by acid hydrolysis (e.g. by 2.2 N HCl at 35 °C) has been used to produce soluble starch. The several studies have shown that the acid hydrolysis consists of two stages: the first fast step where the amorphous regions were loosely arranged and the second slower step caused by hydrolysis of the crystalline regions. (Sayar & White 2011, 119.)

According to Plato´s 1977 findings, the mild acid modification almost eliminated the exceptionally high viscosity measured at 80°C for native oat starch. The transition < 90 °C was not observed for the native oat starch after acid modification. (Autio & Eliassson 2009, 598.)

5.2 Starch modification with enzymes

To gain commercial solution with the enzymatic modification of starch, it was generally achieved by using amylolytic enzymes, such as α- amylase. With α-amylase target was to obtain a complex mixture of various saccharides (maltodextrins). Only the granule surface was available for the hydrolysis. Hoover & Vasanthan found already in 1992 that the usage of h porcine pancreatic α-amylase hydrolysed the native and defatted oat starch. (Sayar & White 2011, 119.) The results of enzymatic treatment implied that many of the

amylopectin molecules must be situated in the outer regions of the starch granule where they were most accessible to enzymic attack (Manners & Bathgate 1969, 169-175).

The enzyme-treated oat flour took place in at least two steps. For example, a slurry batch was prepared of oat flour and water. Enzyme was added to the slurry and held under the optimum reaction conditions followed by the enzyme deactivation steps. The method was expensive, and the yield had low rates. (Chantel et al. 2013, 1.)

In the invention from Chantel et al. 2013, described the usage of enzymes to precondition whole oat flour prior to an extrusion (continuous cooking) process. Enzyme-treated oat flour was prepared by combining a whole oat flour starting mixture and a suitable enzyme and then heating the mixture. After a suitable amount of time to begin to break down and hydrolyze the oat or barley flour, the enzyme-treated mixture was subjected to the extrusion process to continue to break down and hydrolyze the oat flour and further to gelatinize and cook the mixture. Soluble oat flour was thus prepared at low cost and high rates compared to traditional methods. (Chantel et al. 2013, 1-6.)

5.3 The leaching modification with different ingredients and technologies

The fractionation procedure was used to obtain amylose and amylopectin from starch. The corn starch was heated up to 70 - 80 ºC for 60 min which resulted for amylose and amylopectin the way, that the primary polymer leached from the starch. (Mua & Jackson 1995, 508-511.)

According to the study from Lim et al., the isolation of oat starch was done by using the high shear in water. Oat flour (25 %, w/v) was soaked in 20 °C water for 0-12 h and followed with 60 s of shearing. According to the figure 13 the yield of isolated starch showed no further improvement after soaking from 6 hours to 12 hours. (Lim et al. 1992a, 233-236.)

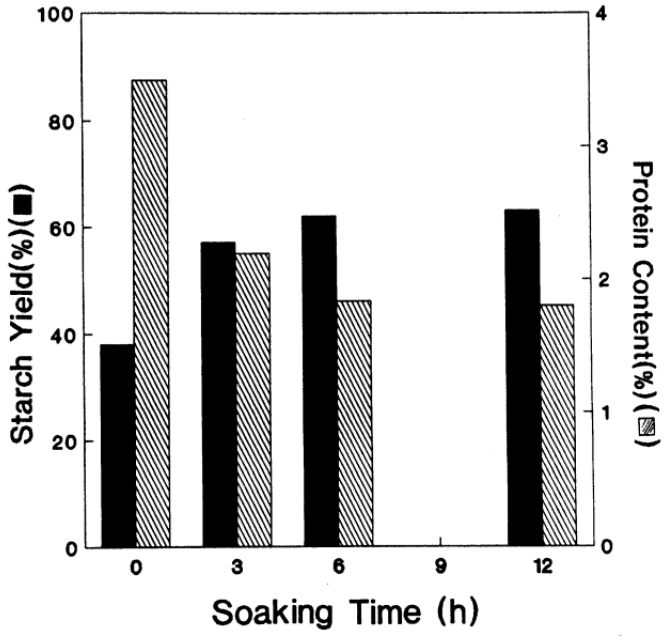

Figure 13. Starch and protein yields (%) during the soaking time in water (Lim et al. 1992a, 234).

The milling of grains was one of the physical modifications. Especially by the ball milling altered structural conformations of protein and starch. It also reduced enthalpy changes of starch-lipid complexes melting properties. (Ramadhan & Foster 2017, 55.)

Use of natural or added lipid acted as a binding agent for the damaged oat starch. This phenomenon could be used in the extrusion with limited water-content (21 – 26 %). Amylose-lipid complex has been proposed as resistant starch type 5 as its resistance to enzyme hydrolysis. (Lehtinen et al. 2004, 1-25.)

The commercial solution with oat and added rapeseed oil is available on the market. Studies have shown that oat having lipid and starch, the pasting properties were related as the viscosity of the starch decreased as the amount of free fatty acids increased. (Oat commercial solution specification 2021.)

5.4 Oat starch defatting

According to study of Wang et al., they could verify the previous discovery by Hoover & Vasanthan (1992), that lipid removal decreased pasting temperature of oat starch (Wang et al. 1994c, 453).

They suggested that defatting increased granular strength. The storage of starch gels at 25 °C for 3 h and at 4°C for 24 h, 72 h and 168 h showed that oat starch gels were significantly less firm than corn starch gels. (Wang et al. 1994c, 454.)

5.5 Oat starch extrusion

Starch was also affected by extrusion. The extrusion process released amylose and increased amylose-lipid complexes. The starch was slightly gelatinized in a controlled manner. Partial gelatinization improved the solubility of the flour and preserved the colloidal nature of the product. The advantages of the invention were the partial release of amylose, resulting in better oil binding, enhanced colloidal character and suitable viscosity less than 100 m Pa s. (Maunsell et al. 2011, 9-11.)

5.6 Starch viscosity stability to heat and acid

The ratio of viscosity after processing to viscosity before processing is an indicator of stability to heat. When there is higher the ratio, the better is the stability. Acid stability can be determined before and after acid treatment. The higher the ratio, the better the acid stability. (Rapaille & Vanhemelrijck 2012, 207.)

5.7 Sucrose content in mixtures of oat starch

Increased sucrose concentrations in mixtures of oat starch and water reduced the shear sensitivity of the swollen granules, as indicated by the breakdown ratio, and reduced the ability of this starch to develop high setback viscosity. The 10 % sucrose had higher torque vs. the 20 % sucrose. The difference during the cooling was ca. 4,7 %. (Sayer & White 2011, 117.)

6 Thermal processing

The thermal processing is used for different foods and refers to following process operations: heat, hold and cool. Target for the thermal processing is to reduce the potential contamination of a special pathogenic micro-organism. (Chen & Sun 2012, 131.)

6.1 Aseptic processing

In aseptic processing of liquid foods, the process equipment and the package are sterilized separately and brought together in a sterile environment. This involves for the sterile system the pasteurization of a liquid food product, followed by holding it for a specified period in a holding tube, cooling it, and packaging it in a sterile container. Aseptic processing needs high control of process variables and equipment. (Eckes-Granini Process Instructions 2021.)

The aseptic filling machine must be suitable for the thick product with fitting filling temperature, pressure, and seal integrity factors. (Eckes-Granini Process Instructions 2021).

6.2 Pasteurizing of the fluid

Thermal processing normally refers the processes that heat, hold, and cool a product sequentially. Pasteurizing reduces the potential contamination of a special pathogenic microorganism. (Renard 2012, 413-414.)

The fluid is thermally processed in a tubular heat exchanger. The center line velocity is twice the average value at the laminar regime. For the turbulence regime, the maximum velocity is about 1.2 times the average velocity. As such, the turbulence regime supplies a more uniform mixing condition for thermal processing. The average residence time is the length of the pipe divided by the average velocity. Notable is the microbes that travel at the maximum velocity would not be fully processed. Using the pasteurization there are several

important explanations and values to destroy the microbes. (Liu & Floros 2012, 441-449.)

6.2.1 Decimal reduction time D

Decimal reduction time or D value is the time needed at a given temperature to decrease the population of a specified microorganism by 90 % or one log cycle. For example, D 80 = 1 min means that it takes 1 minute at 80 °C to destroy 90 % (or one logarithmic reduction) of the specified microorganism. (Chen & Sun 2012,132.)

6.2.2 Thermal Resistance Constant Z

The thermal resistance constant Z is a parameter standing for the microorganism's resistance to temperature rise. (Chen & Sun 2012, 132.)

The following constates are used for fruit juices:

constate 7 is for temperature < 121,1 ºC

constate 10 is for temperature > 121,1 ºC

(Eckes-Granini Working instructions 2021.)

6.2.3 Pasteurization Unit PU

The time-temperature diagram can be described in terms of pasteurization units' accumulation. Pasteurization units supply the temperature influences sum on the microorganism evolution in product. The formula for the PU calculation is in equation 2.

$$PU = t * 10^{\frac{(Temp - Temp_{ref})}{z}} \quad (2)$$

Equation 2. PU calculation.

t = time in holding cell in minutes

Temp = actual temperature ºC

$Temp_{ref}$ = constant temperature reference (<121,1 ºC = 80 and >121,1 ºC = 121,1)

z = constant (< 121,1 ºC = 7)

(Eckes-Granini working instructions 2021.)

For time calculation in the holding cell the equation 3 is used.

$$t = V/(Q * 60) \quad (3)$$

Equation 3. Formula for calculating time in the holding cell.

V = volume (l)

Q = volume flow (l/h)

(Eckes-Granini Working Instructions 2021.)

6.3 Pasteurizing with tube heat exchanger

The heating and cooling actions are shown in the Figure 14 for the pasteurization. The hot product (3) goes to the heat exchanger (inlet) and comes out (4) (outlet). The cooling media (water) goes to the inlet (2) and

comes out (1). (Tetra Pak Presentation slides 2016,1-21.)

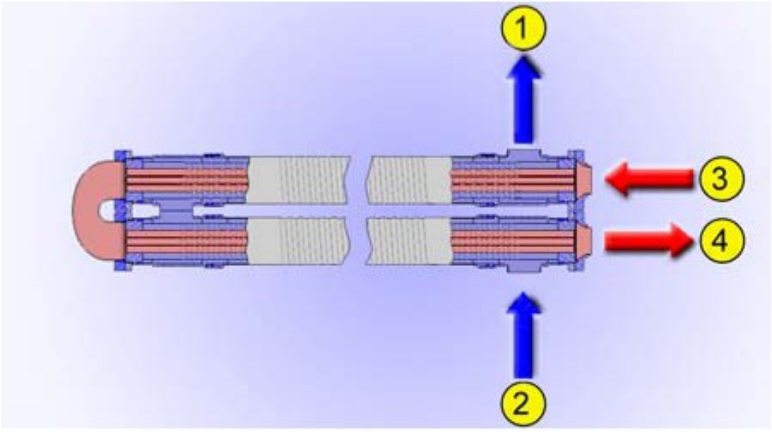

Figure 14. Heat exchanger flows (Tetra Pak presentation slides 2016, 1-21).

For tube flow the Residence Time Distribution (RTD) is associated with the velocity profile and the turbulence. The ideal cases of laminar flow and flat velocity profile rarely describe the flow in real systems. Liquid food often has moderate viscosities, flow is usually laminar in the holding tube. This promoted a considerable dispersion on the residence time. (Gutierrez et al. 2010, 248.)

The pasteurization process is divided into different sequences. Firstly, the pasteurization system must be cleaned with Cleaning in Process (CIP). The sterilization sequence follows the cleaning. After that the pasteurization unit is ready for the production. The process chart (Figure 15) describes the production sequences. In the production the term product call is used. It means that the operator can pick up the product from the order list and start the pasteurization for the product. (Eckes-Granini Process description 2021.)

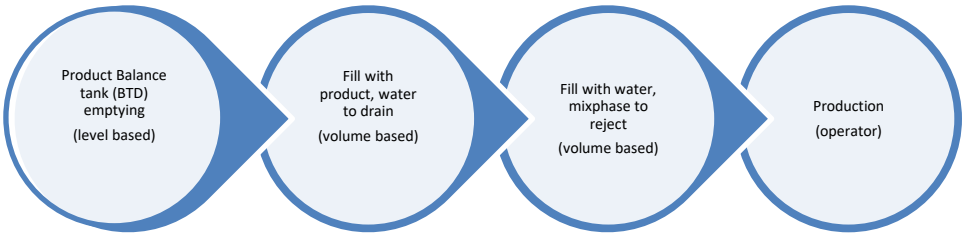

Figure 15. Sequences for the aseptic production (Eckes-Granini Process Description 2021).

The heat exchanger influence was estimated with the help of a CFD model coupling the phenomena of fluid flow, heat transfer, and product transformation (Jha et al. 2019, 237-271).

The tube heat exchanger which is equipped with spirally enhanced walls is often required for products with higher friction losses. The corrugated wall is effective when defined the Reynolds number (Re) range. The Re number is important while correlated the energy forces to the viscous forces. It describes the transport properties of a fluid. (Massini et el. 2005,1-7.) The equation 4 shows the formula for Reynolds value calculation.

$$Re = \frac{Dv\delta}{\eta} \quad (4)$$

Equation 4. Formula for Reynolds value calculation.

D = diameter of the pipe (m)

v = the average flow rate of the fluid (m/s)

δ = density of the fluid (kg/m^3)

η = viscosity of the fluid (Pa s)

In the pipe flow the Re number is considered as

- laminar flow < 2 100
- transition area from laminar to turbulent 2 100 – 3 200
- turbulent flow > 3 200.

7 Experimental part workflow

Target of the thesis was to develop a fruit and berry based liquid product with Finnish oat. The product should be without added sugar and with high content of fruit and native oat. The thermal part of the production process needed to be aseptic, and the package aseptically filled, too. The research problem which needed to be solved was the requirements of novel oat-based fruit and berry juice drink in the thermal production process. The aim for the product was also to have acceptable organoleptic characteristics.

7.1 Oat materials

The first part was to check the material alternatives for the local Finnish oat suitable for the food applications. Oats needed to be commercially available with a quality assurance certification and a product specification. The document of authenticity and nutritional information had to be confirmed and available.

There were several companies who manufacture oat flour and oat raw material applications. The oat flour samples were required.

7.2 Fruit materials

The fruits and berries were checked and selected for the recipe´s fruit base part. The aim was to develop the product without added sugar. There were fruits available which sensorially and nutritionally fit to the recipes. As the oat was a new ingredient, the fruit part idea was to keep it suitable for the oat combination and familiar for the consumers.

7.3 Other recipe materials

The usage of flavors and other ingredients had been evaluated. As oat has very dominating flavor profile and especially when the ready product needed to be

stored at the ambient temperature, the organoleptically changes during the storage time have been considered. The natural flavor was possible to reach while combining oat profiles with natural profile of berries and fruits.

Stabilator for the recipes had been evaluated as well. There were several stabilator options which were accepted for the juice drink-based product e.g., pectin, xanthan gum, guar gum from the brand purpose and legislation points of view (Eckes-Granini Finland Brand purpose). Pectin is a water-soluble polymer which has at least 75% esterification. The gel forming properties of pectin depends upon the degree of esterification. High methoxy pectin have more than 50 % esterification and low methoxy pectin has less than 50 % esterification. (Verna et al. 2018, 2.)

Oat starch with combination xanthan gum shall supply superior adhesiveness and stringiness for sweet and sour sauce applications with different polysaccharide combinations (Gibínski et al. 2005, 407).

7.4 Recipe developments

The test recipe developments had been done according to the product requirements which were described in the product development briefing (Eckes Granini Working instructions 2021). The recipes had been evaluated technically and sensorially including the stability studies. The development of recipes was done in Eckes-Granini Finland product development laboratory.

7.5 Product testing

The target was to evaluate the developed recipes in the production scale test trials. For the processing steps and parameters, the existing knowledge of beverage manufacturing and treatments were used with specific evaluation of oat-based products. The product testing was done in Eckes-Granini Finland juice preparation and filling areas.

7.6 Product evaluation

During the recipe development and product testing, the samples were evaluated in the sensory room in Eckes-Granini Finland. The chemical evaluations were done in product development and quality laboratories in Eckes-Granini Finland. The external consumer study of the developed recipes was done to clarify the consumer acceptance point of view.

8 Materials and methods

For the recipes different oat and fruit materials were evaluated and tested. There were also evaluations of the other materials suitable for beverages.

8.1 Oat materials

The different oat raw materials and ingredients were checked. The samples have been collected to the table 2. Whole grain oat included the entire germ, endosperm, and bran.

Table 2. Samples and treatments of the recipes.

Sample	Treatment	Raw material
Oat #1	Extrusion	Whole grain oat flour
Oat #2	Extrusion	Core oat flour
Oat #3	Omega 3&6	Whole grain oat with rapeseed, salt, and protein

Whole grain oat flour had been extruded from dehulled (outer layers/bran removed) and milled oats. The extrusion has rapidly precooked the flour resulting in a decrease of both the grain-based enzyme and microbe levels. As a result, the flour was easy to use and highly versatile when incorporated into food products. The flour had high water retention and improved taste (whole grain oat flour specification 1.3.2019).

The extruded oat flour from the core part has been manufactured from the peeled oat. The used part of the grain is called core oat flour (core oat flour specification 2020).

The whole grain oat with omega fatty acids 3 & 6 and oil from rapeseed has naturally lower β-glucan content. The product was not pure oat as it included rapeseed oil and rice protein as well added salt. (oat material product specification 2020.) This material has been selected to the test as it increased the oat content and gave different mouthfeel due to the bigger particles which remained insoluble in the liquid application.

The nutritional values of the tested oat samples on the table 3 were taken from the manufacturer´s raw material specifications. All tested oat materials were commercially available.

Table 3. The nutritional values of tested oat materials (g/100 g).

Oat sample	Protein	Carbohydrate	Starch	Dietary fiber	β-glucan	Fat
Oat #1	13	58	57	11	5	7
Oat #2	10	71	66	4	2	6
Oat#3	14,1	48,1	35,1	8,6	2,5	30,3

The molecule weights shown in the table 4 were collected from the manufacturer of oat and literature (Swedish Oat Fiber 2015).

Table 4. The molecule weights of tested oat materials.

Oat sample	Molecule weight / kDa
Oat #1	928
Oat #2	1730 - 2800
Oat #3	n/a

8.2 Fruit materials

The target for the product was that the sugar level come from the used fruits, berries, and oat. Table 5 shows the fruit material form and Brix-value.

Table 5. Tested fruit and berry materials Brix-values.

Fruit or berry name	Fruit or berry form	Refractometric Brix / °Bx
Apple	puree concentrate	30
Blackcurrant	puree	11,5
Grape	juice concentrate	68
Pineapple	juice concentrate	60
Orange	juice concentrate	65
Raspberry	puree	8
Strawberry	puree	8

8.3 Oat – fruit application recipes

Weighted quantity of recipe materials was dissolved in product water at room temperature using an axial flow impeller. To ensure the complete solubilization of oat, product water was heated at + 92 +/- 2 ºC. Oat was hydrated using mixer at 1 000 rpm. The heated samples were cooled down to room temperature. The degradation time for β-glucan was 1 h. Table 6 shows the recipe 1 β-glucan, oat starch, protein, dietary fiber, and iron values.

Table 6. Recipe 1 values per 100 ml.

Component	%	β-glucan	Oat starch	Protein	Dietary fiber	Iron
		g	g	g	g	mg
Fruits	80	-	-	0,507	0,181	0,22
Oat	10	0,425	5,043	1,377	0,932	0,55
Others*	10	-	-	-	-	-

Recipe 1 was evaluated in the laboratory and production scales. Others* were water for the reconstitution and flavors.

The oat component and nutritional values are presented of recipe 2 in the table 7.

Table 7. Recipe 2 β-glucan, oat starch, protein, dietary fiber, and iron values.

Component	%	β-glucan g	Oat starch g	Protein g	Dietary fiber g	Iron mg
Fruit	35,9	-	-	0,07	0,03	0,10
Berry	18,75	-	-	0,08	0,31	0,08
Oat	7	0,2275	2,9169	0,51	0,65	0,38
Others*	38,35	-	-	-	-	-

Recipe 2 was evaluated in the laboratory and production scales. Others* were water for the reconstitution, pectin, and flavors.

The oat component and nutritional values are presented of recipe 3 in the table 8.

Table 8. Recipe 3 β -glucan, oat starch, protein, dietary fiber, and iron values per 100 ml.

Component	%	β-glucan g	Oat starch g	Protein g	Dietary fiber g	Iron mg
Fruit	80	-	-	0,507	0,181	0,22
Oat	7	0,2275	2,92	0,51	0,65	0,38
Others*	13	-	-	-	-	-

Recipe 3 was evaluated in the laboratory and production scales. Others* were water for the reconstitution and flavors.

The oat component and nutritional values are presented of recipe 4 in the table 9.

Table 9. Recipe 4 β- glucan, oat starch, protein, dietary fiber, and iron values per 100 ml.

Component	%	β-glucan g	Oat starch g	Protein g	Dietary fiber g	Iron mg
Fruit	50	-	-	0,12	0,08	0,14
Oat	7	0,35	3,99	0,91	0,77	0,38
Ascorbic acid	0,033	-	-	-	-	-
Salt	0,11	-	-	-	-	-
Others*	42,857	-	-	0,46	0,69	0,28

Recipe 4 was evaluated in the laboratory and production scales. Tested recipe was version 10. Others* were water for reconstitution, plant material from cocoa beans and flavor.

Glucose content of tested recipes have been calculated from the formula and results are shown in the table 10.

Table 10. Glucose contents of the recipes 1,2,3 and 4.

Recipe No	glucose w/w-%
1	2,35
2	2,27
3	2,35
4	3,44

In the solutions with high concentration of glucose (1 M, appr. 20 w/ w-%), most indiscriminate OH-radicals will react with the glucose rather than with the high molecular weight polysaccharide (beta-glucan, 0.6 w/w-%) (Kivelä et al. 2009, 3).

The glucose levels in the tested recipes were behind the high glucose concentration mentioned in the reference to inhibit viscosity reduction. The glucose influence on the viscosity was not relevant in the tested recipes.

8.4 Different methods tested for products and recipes

In the study different chemical, physical and test trial methods were used. The methods were selected to clarify the behaviour of the developed recipes suitability for the commercial possibility.

8.4.1 Refractometric Brix-value

The Brix-value of the raw materials, semi-finished and finished products were measured as refractometric Brix. The used method is a well-known application in the food and beverage industry based on pure sucrose content in water. 1 degree Brix (ºBx) = 1 g of sucrose / 100 g of solution. In the study Bellingham RFM 340+refractomer was used.

8.4.2 Titratable acidity as citric acid

The acid content was measured by controlled addition of an alkaline titrant solution of known concentration (e.g., sodium hydroxide) until a specific endpoint was reached. The endpoint of the reaction between the acid components present in the sample and the alkaline solution (titrant) can be shown by the color change of the indicator solution (such as phenolphthalein). In the study Mettler Toledo T70 laboratory device was used.

8.4.3 pH

The pH value was an important parameter for the study of biochemical processes. The response of the pH-sensitive electrode was dependent on the H+ ion concentration and gave a signal how acidic /alkaline the solution was. The reference electrode on the other hand was not responsive to the H+ ion concentration in the sample solution and produced the same, constant potential against which the pH sensor potential was measured. The potential between the two electrodes was therefore a measure of the number of hydrogen ions in the solution, which gave the pH value of the solution. In the study Mettler Toledo T70 laboratory device was used.

8.4.4 Sample pasteurization

In lab scale study the heat treatments were carried with Miele Professional G 7883 machine. The customized pasteurizing program allowed the machine to prove the pasteurization steps from heating steps to the cooling.

The tested products were packed into glass bottles with metallic cap which enabled the heating process in the machine. The negative point was that the pressure and mechanical flow impacts were not reached by this kind of thermal test. These were evaluated with the pilot test scale in the production environment.

8.4.5 Rheological measurements

The rheological measurement was used to measure a fluid's resistance to flow when an external force was applied. This was called dynamic viscosity. Analysis was made by Mettler Rheomat RM180 laboratory device which is a rotational viscometer. The device consists of a motor driven bob (or spindle) that rotated within a fixed cylinder, which allowed for a defined geometry. The shear resistance of the sample in the gap allowed for the measurement of motor torque. The viscosity was then derived knowing the shear rate and motor torque (shear stress). Viscosity was displayed along with other parameters including temperature, torque, measuring system and stress. A stepwise rotation program which had a shear rate ranging from 100 to 1000 s^1. Rheomat calculated the lowest and highest shear rate as linear intermediate steps. In the Rheomat was used measurement system No. 11 with a measuring bob No. 1 which ø was 30 mm and l = 45 mm. Shear rate for system 11 was expressed as 6,5 - 1291 s-1 and viscosity range 0,003 - 15,4 Pa s. The recalculated viscosity (η) values were mean values.

Pasteurization effect on oat-based product viscosity was evaluated. The flow curves were obtained over a shear rate range of 100–1 000 s−1, and the temperature of measurements was +22 ºC +/-2 ºC.

8.4.6 The test trial in the production scale

The testing of developed recipe in the production process was essential to evaluate the suitability of process equipment like agitators, mixers, pumps, piping, heat exchanges and package filling machine. The knowledge of fruit-based beverage production with oat behavior understanding were combined. The best practices from the semifinished goods pre-treatment until thermal processing have been studied from the supplier materials and process technology specialist (Tetra Pak process engineer 2016-2019). Especially the product pressure and the flow rate during the thermal treatment were the key parameters while treating the new product.

Oat flour was not known to create insoluble cakes when added to the liquid. The high shear mixer with vacuum made the dosing of powders and dry matters practical into the liquid part. The product was de-aerated as the air was removed from the liquid part. This enabled higher uptime in the downstream line. To get the product homogenous with a high shear mode there was a possibility to adjust the vacuum mixer´s dynamic stator so that the product was sucked into a mixing wheel by centrifugal forces (Figure 16). The stator was lowered to down position and all products were forced through the holes in the perforated stator. The bigger particles were spitted into smaller particles. This treatment was not a homogenization step, but it treated the product with high speed and shear - depending on the parameters set up. Another benefit of this method was that the ingredients were dosed under vacuum, and below the liquid surface in the tank, prevented air entrapment, which ensured efficiency and protected product´s quality and safety.

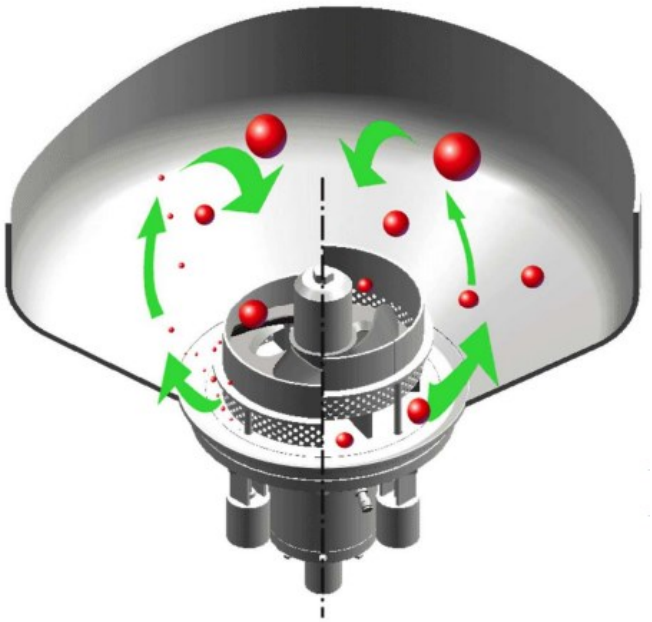

Figure 16. Vacuum mixer´s dynamic stator and flow of the particles (Tetra Pak 2019).

The vacuum mixer unit was used to mix ingredients into a stable mixture before transferring the fluid to the next process step. The target of the vacuum mixer was also to make oat starch particles smaller to reduce the viscosity and improve the sensorial characteristics.

In the aseptic process the most challenging part was the heating process step, where pasteurization unit and the parameters were selected. Typically for the beverage-based pasteurization method HTST was used (Eckes-Granini Working Instructions 2021). HTST means food pasteurization which happens in High Temperature in Short Time. Tetra Therm® Aseptic Visco® tube heat exchanger Tetra Spiraflo® (figure 17 and 18) was suitable for the oat-based products pasteurization which had non-Newtonian pseudoplastic fluid. The system allowed the high viscosity and particle having products processing in the HTST circumstances. The Z- value for microorganism's destruction could be evaluated in terms of an activation energy. The activation energy of microorganism destruction varied from 8 to 15 kJ mol−1. The quality loss

activation energy varied between 30 and 100 kJ mol−1. Therefore, the HTST process can be applied to increase the product quality while ensure the microbial safety. (Renard & Maingonat 2012, 417.)

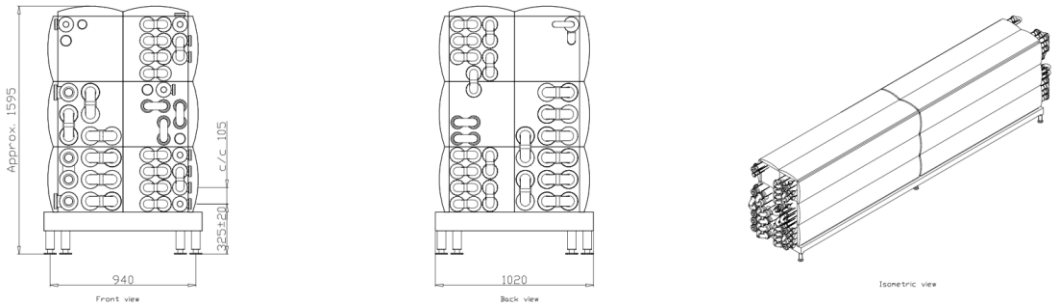

Figure 17. Tetra Therm® Aseptic Visco® tube heat exchanger Tetra Spiraflo® (Tetra Pak 2016).

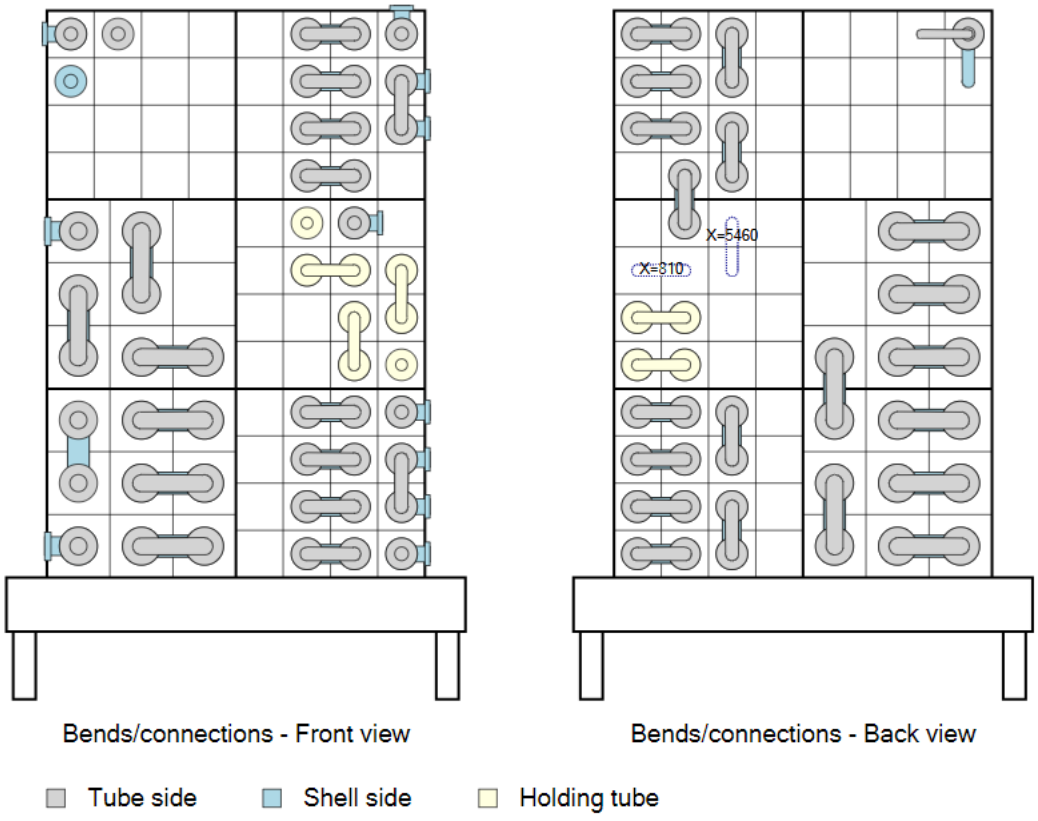

Figure 18. Tube heat exchanger front and back views (Tetra Pak 2016).

Tetra Spiralo® volume is 410 liters. The maximum pressure for tube is 5 000 kPa and for shell 2 000 kPa. The tube volume is 7,2 L, including bend volume (Tetra Pak manual).

For the pasteurization steps the product supply positive pump (M1 pump) was the first important pump in the process. In this study the juice preparation area has two options for the M1 pump: the centrifugal pump L1P1A for the low viscous product and screw pump for high viscous product. For the tested SF-Juice materials which were high viscous the mono screw pump L1P2B has been selected from the Manufacturing Execution System (MES) - recipe parameters. The viscous pump was especially made for the thick solutions. In the pump the screw rotated within a pump casing with screws situated side by side. Liquid was drawn by the screw at the inlet before pushed to the outlet in the center of the casing according to the example of the screw pump in Figure 19. The process drawing layout in Figure 21 showed the location of used pumps.

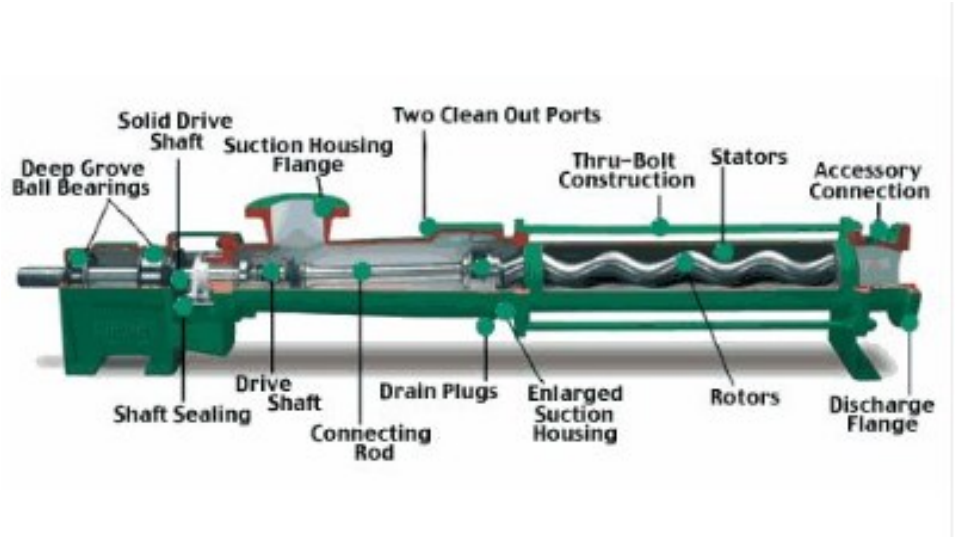

Figure 19. Screw pump (NTGD Pump).

The second pump in the process was the frequency-controlled product pump (M2) which was controlled by a flow transmitter. M2 pump in the system was wing rotor pump. Example of the wing rotor pump is in Figure 20.

Figure 20. Wing rotor pump (SFX Flow).

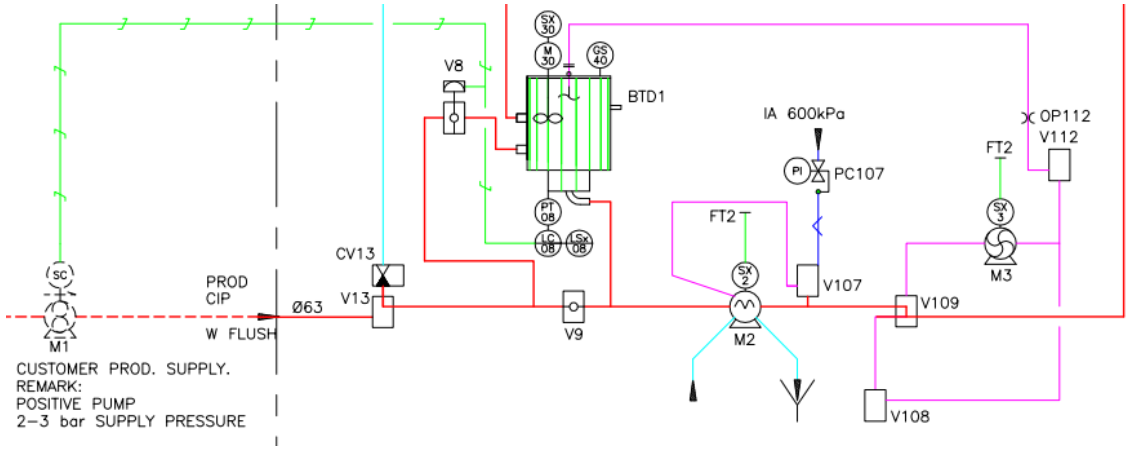

Figure 21. M1 and M2 pumps in the process layout (Tetra Pak 2016).

Pasteurization reduced contaminating pathogens to a level at which they did not pose a hazard and inactivated enzymes. The pasteurization process was divided into three sections which were heating, cooling and regeneration

sections. The most important section was heating which involved the heat exchanger to heat up temperature of product at desired set point. The pasteurization unit had a high-pressure-rated coil tubular heat exchanger that managed pressures up to 350 bar. Tube heat exchanger enabled higher in-pipe-velocity and lower system volumes. The lower system volumes meant smaller mix zones between product and water. The MES recipe parameters had the Proportional-Integral-Derivative (PID) settings and process values e.g., pasteurization temperature, holding time, product flow, cooling temperature. The advantages of PID controller were simplicity, easy to manage and reasonable performance.

The materials, recipes and changes in the manufacturing process have been selected according to the test plan.

8.4.7 Aseptic filling of the tested goods

Tetra Pak Edge filling machine was used to pack the industrial tested goods. The capacity checks were done with two different speeds. Considering the pasteurization effect of flow rate and pressure, the lower filling speed was selected. The machine also needed the specific filler parts to ensure that no particles from the product were transferred to the upper part of the seal. The seal checks were carried more often due to the new product type with particles. The thesis is not covering the filling machine detailed functions.

9 Results and discussion

The test trials were done for 4 different recipes in the production scale. Each test phase was carried from the juice preparation to the pasteurizer and to the packaging machine when pasteurization occurred according to the set parametric values.

9.1 Semifinished product manufacturing

The dosing of fruit and berry ingredients were done according to the plant´s normal juice preparation procedure. In the Manufacturing Executing System (MES) the ingredients dosing order and dosing parameters were kept. High shear mixer vacuum was used to add the oat parts from the funnel into the liquid part already dosed to the mixing phase. In the high shear mode, the stator was lowered, and all products were forced through the holes in the perforated stator (Figure16). The powders to the vacuum mixer were dosed with the funnel (Figure 22).

In the vacuum, dosing, and mixing phase the parameters were adjusted according to the slower pulses for the high viscous product which were inspected during the test phase.

Figure 22. Oat flour dosing with the funnel (Test trial recipe 2).

The semifinished product had been successfully manufactured as homogenous mixture in the vacuum mixer system according to the recipes 1 - 4. The batch related analysis of Brix, acidity and sensorial were done after each produced batch. Results are shown on the table 14.

In juice preparation area the product pump for the viscous product had been selected from the recipe parameters. The recipe parameters had the PID settings and process values.

9.2 Pasteurization of the products

The first test of the pasteurization was done with the product recipe 1 which oat content was 10 %. The test showed that the recipe was too viscous and thick product to be pasteurized. There were no successfully passed tests in the pasteurization process with recipe 1. The main reason was that the frequency converter reached the motor capacity >60 amber when the rheological behavior of the product in connection with the heat exchanger influenced the onset of flow instabilities. This was due to the fouling phenomenon of the product. The heat transfer surface caused when a liquid product met a heated surface. Fouling increased thermal resistance and thus results in reduced rates of heat transfer.

As the pasteurization step was aseptic, the system stopped automatically to the production steps while the set values for the critical process parameters were not reached due to the high effect of product pressure to the product flow and fouling. The under pasteurization occurred, and the product was not microbiologically safe anymore. Then the only possibility to continue was to make a Clean in Place (CIP) and sterilization to the unit. The test result for recipe 1 showed no result.

After the recipe 1 test, the parameters were changed to the pasteurization unit. The cooling section for the product cooling purposes was disconnected. The flow rate was lowered with 14,3 %.

According to the recipe 2 the oat content was 7 %. The pasteurization process worked for the product. The highest product pressure 25,51 bar was measured in the beginning when the system was full of the product and the filling permission was given to the filling machine. When the filling machine started to pack the product the product pressure was 14,87 – 24,51 bar. Inside the pasteurization system the pressure drops for the filler. This pressure for the filler was 3 bars during the test filling. The pasteurization values are shown on the table 11. The pasteurization filling steps with product recipe 2 were according to the diagram 1.

During the pasteurization and filling with the product the product cycle time parameters were used. Cycle time means that the filling was not running, and the product was running in the pasteurization unit. The used time for the circulation was 45 min for recipe 2.

In the diagram 1 the pasteurization unit is filled with the tested product. The time interval after each 50 l check point was recorded. The pressure increase was highest in 18:53 time point when the system was filled with oat product. The pressure dropped immediately after the filling started and new unpasteurized product run into the system.

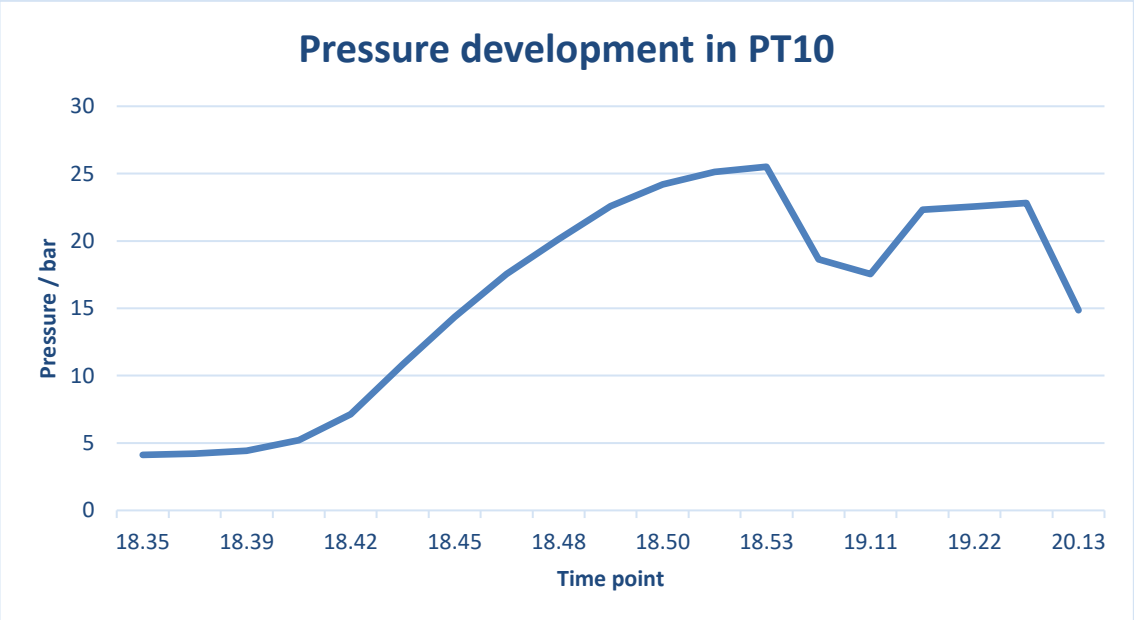

Diagram 1. The curve of pasteurization pressure development during the system was filled with product recipe 2 (Test trial Eckes-Granini 2021).

Test recipe 3 was pasteurized with the same equipment settings as the recipe 2. According to the measured values of the recipe 3 the results in diagram 2, the pressure remained significantly lower than in test with recipe 2. The product pressure was 32,8 % less in recipe 3 vs. recipe 2. Both recipes pressure graphic had similar trend development.

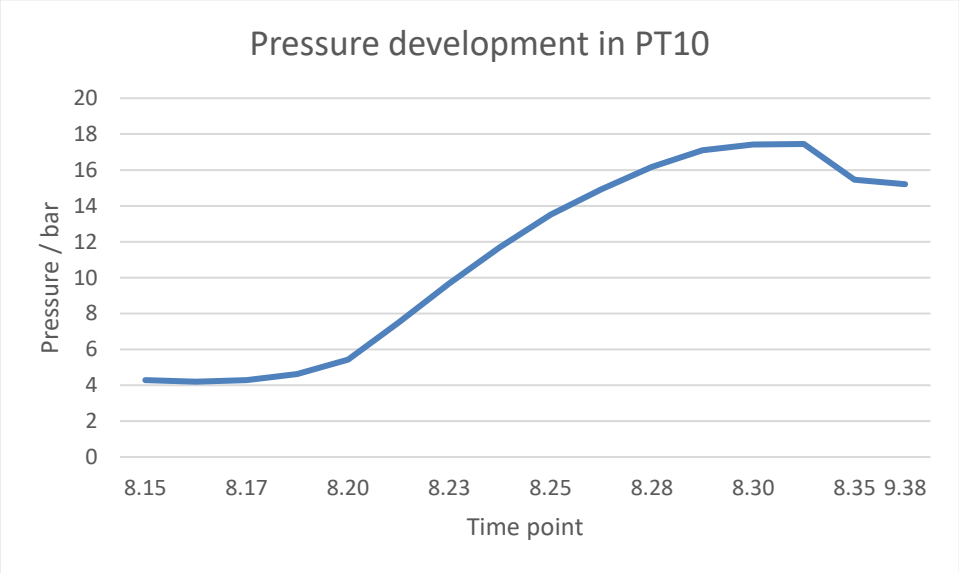

Diagram 2. Recipe 3 pressure development in test trial during the system was filled with the product (Test trial Eckes-Granini 2021).

The system was filled with the product at the time point 8:30. The pressure drop was significant after the filling machine started to pack the product.

Pasteurization parameters were collected from the unit´s panel. The unit recorded the values according to the programmed steps. In the table 11 the parameters from the production step were kept. Recipe 1 didn´t pass the pasteurization step due to too viscous product.

Table 11. Pasteurization parameters for the recipes 2, 3 and 4.

Recipe	Temperature average ºC	Holding time s	Flow rate l/h	Pump M2 %	T10 pressure bar
2	94,9	29,4	2 175	63	17,2
3	92,6	29,4	2 200	76	15,2
4	94,9	29,4	2 206	68	8,3

The residence time distribution (RTD) and Pasteurization Units (PU) were calculated, to estimate the lethality received by each element. The tested recipes 2, 3 and 4 PU results are shown in the table 12.

Table 12. Pasteurization Units (PU) of recipes 2, 3 and 4.

Recipe	PU
2	17,1
3	9,9
4	16,8

The PU calculations showed that heating behavior in the tested recipes were according to a safe thermal process. The goal in thermal processing was to ensure that the slowest heating point (cold spot) within a product container received adequate thermal treatment. PU value should be 3 - 25 according to the temperature control working instructions (Eckes-Granini Working

Instructions 2021). The recipe 3 was stable in the thermal process buffer tank (Figure 23).

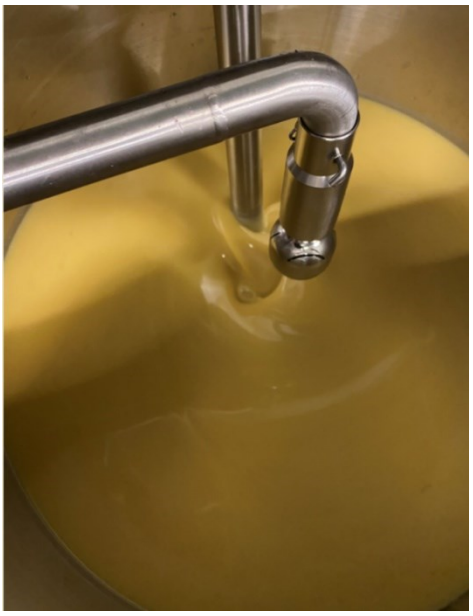

Figure 23. Fruit based recipe 3 in the industrial test phase (Test trial with recipe 3).

9.3 Pasteurization result´s evaluation

Pasteurization was a suitable processing step in viscous product to reduce pathogenic microorganisms in beverages by inactivating all non-spore-forming pathogenic. The rapid pasteurization with temperature 92 - 96 ºC during 30 to 40 s enabled safe oat grain and fruit-based beverage production. All pasteurized products were within the aseptic production limits. No deviations of microbiological results were detected.

The empirical model was based on real data, easy to develop and suitable for complicated process. The numerical representation of coupled processes was difficult at the heating wall because the high magnitude of thermal and velocity gradients that prevail there. Both granule swelling and suspension viscosity were expected to increase sharply near the corner of the domain inlet with the

heating wall. Variations along the domain's length were expected because radial distributions of temperature, velocity field and swelling degree evolved while the product progressed in the heat exchanger. (Plana-Fattori et al. 2021, 3.)

9.3.1 Reynolds value calculation results

The calculations for the Reynold value are shown in the table 13. The recipes concerned are 1,2,3 and 4. The values were calculated based on the tested product analyzed values, pasteurization test results and pasteurization unit dimension.

Table 13. Reynolds value results of tested recipes.

Recipe No	d m	v m/s	δ kg/m^3	η Pa s	Re	Flow
1	0,51	0,49	1044	1,33	196	lam.
2	0,51	0,55	1028	0,38	759	lam.
3	0,51	0,55	1058	0,30	989	lam.
4	0,51	0,54	1048	0,13	2220	trans.

The flow was laminar (lam) with recipes 1, 2 and 3. For recipe 4 the flow was in the transition from laminar to turbulent. The flow rate (velocity) value has been measured by magnetic flow meter (FT2) which location was after the final cooler section. Recipe 1 values were taken in the beginning of the pasteurization before the flow became too low. Recipe 1 values show that Re value was clearly below the recipe 2, 3 and 4 values.

9.3.2 The viscosity measurements

The viscosity (η) against shear rate (γ) was evaluated to study the rheological behavior of recipes 2, 3 and 4 which were successfully pasteurized and packed into the aseptic portion packs.

Before the thermal treatment, the viscosities in recipes 2 and 3 were relative same with the difference of 4,7 %. For recipe 4 the oat gave the higher viscosity in the beginning vs. recipe 2 and 3 (table 14).

The pasteurization increased viscosity 112 % for the recipe 2 and 78,8 % for recipe 3. There was ascorbic acid naturally present in recipe 3 which probably gave the difference. The Brix-value for recipe 3 didn´t have effect for the higher viscosity value. Recipe 4 which was treated with hot water and salt addition had less than 4,8 % change in viscosity during the heat treatment (table 14).

Recipe 3 showed 29,3 % lower viscosity than recipe 2 with the lowest shear rate (100 l/s) at the ambient temperature (23 ºC) and time point t = 1 d. The oat contents were the same 7 % in both recipes meanwhile the fruit and berry content differed significantly. After the ambient storage for 11 days the results showed 48 % lower viscosity values for recipe 2 and 60 % for recipe 3. The pectin addition to the recipe 2 showed less decrease in viscosity.

The product circulation time was evaluated for recipe 2 at the heating part in the pasteurization unit during the test trial. The measurements of circulated product showed 45 % lower viscosity with the share rate of 100 l/s vs. the uncirculated product. Physio-chemical characteristics of the test products are on the table 14.

Table 14. The physio-chemical characteristics of the evaluated fruit and oat recipes.

Viscosity was measured before heat treatment (before) and after the heat treatment (after) in the table.

Recipe	Brix ref* º Bx	Acidity g/kg	pH	Before mPa*s	After mPa*s
2	7,94	2,48	3,96	17,8	37,8
3	11,8	5,08	4,10	17,0	30,4
4	10,7	3,55	3,92	31,5	33,0

9.4 Sensorial result

In the laboratory prepared samples of recipes 2 and 3 were evaluated with the external panelist (n= 22). The total evaluation average result of organoleptic pleasure was pleasant for recipe 3 and slightly pleasant for recipe 2. The used scale was a 7-point Likert scale. After the external sensory results there have been some recipe changes which influence for the rheological properties were not affected. The external results were not included to the thesis appendix.

9.5 Chemical result

The recipes chemical values concerning vitamin C and sulfite have been analyzed. The results are in the table 15. The vitamin C result was 92,3 % higher in recipe 3 than in recipe 2. In recipe 4 no vitamin C was detected. The sulfite analysis was below the legal sulfite limit 10 mg / l. The sulfite was from the used raw materials.

Table 15. The physio-chemical characteristics of the evaluated fruit and oat recipes per 100 ml.

Recipe No	Vitamin C mg	Sulfite mg
2	0,13	0,085
3	1,70	0,440
4	0	0,625

9.6 Microbiological result of recipes 2, 3 and 4

The pasteurization and filling process steps went according to the aseptic requirements as the microbiological results in both industrial tests showed no deviations. The test trial results of the recipes 2, 3 and 4 are shown in the table 16. There was no microbiological growth in the samples.

Table 16. Microbiological results of test trial samples.

Recipe No	Bacteria cfu	Mould cfu	Yest cfu
2	0	0	0
3	0	0	0
4	0	0	0

The industrial tests showed the importance of new type of product testing when the product´s structure change was critical. The laboratory scale testing didn´t

include all the mechanical stress and impact coming from the agitators, pumps, and product flow during the processing steps. The thermal treatment with pasteurization parameters were acceptable for recipes 2, 3 and 4.

9.7 Sensorial stability evaluation

The pilot scale evaluated recipes 2 and 3 were kept in ambient and chilled temperatures over time. Oat fat oxidation in the ambient storage conditions was analyzed sensorially by the trained panelist. Both recipes showed good stability and sensory properties in structure, color, odor, and taste. Table 17 shows the results after 4 months stability test in ambient. The reference sample was kept in chilled (+6 ºC) conditions. Results are shown in the table 17. Evaluation scale was 5 - 1 while 5 = quality level excellent and 1 = poor, not commercial quality.

Table 17. Sensory results of trained panelist.

Recipe No	Structure	Color	Odor	Taste
2	4,83	4,17	4,67	4,50
3	4,83	4,83	4,83	4,33

10 Conclusions

Oat in the aqueous solution was difficult to manage in the process which includes a heat treatment of whole oat bran flour. During this study there were many evaluations and tests to treat the different samples. The major problem occurred while treating the oat with heat as starch gelatinized, and the viscosity increased. In this study there have been no enzymatic and/or fermentation steps available to separate fiber parts away. In the break down the starch is degraded into sugars. During the enzymatic treatment also protein and fiber are degraded too. The existing manufacturing processes in juice preparation area did not allow the long time consuming enzymatic or acid treatments. The oat in the application was supposed to keep as natural as possible. There were no health claim related attributes to the products assigned.

The hydrolysis in the water and oat solution with 0,1 M HCl for 12 h to achieve low hydrolysis effect was not an option due the capacity to keep the manufacturing process system blocked for such a long time.

The recipe 1 had the highest oat β-glucan and starch contents. During the test trial it was clearly noticed that oat content (10 %) was too high for processing.

The tested products with full corn oat content 7 % could be produced when having the evaluation characteristics fully considered. The slightly lower full corn oat content made the whole production process more effective with as native oat as possible.

Sensorially the developed products had characters of fruit and berry with authentic oat taste and the viscosity for the oat product could be 100 – 150 mPa s. This rate has been reached for the samples. The sensory was satisfactory after the four months storage time in ambient conditions.

There shall be regular checks during the heat treatment that the bran particles will not stick on the surfaces of the fractionation equipment. This evaluation would be interested to study.

The milling industry plays a significant role while supplying the suitable whole grain flour for beverage applications. The attention shall also be put on the type of cultivar oat M_w.

For the pasteurization process, the opportunity for PID changing parameters shall be evaluated more deeply with the equipment manufacturer professionals. The usage of CFD calculations is worth to evaluate. There shall be room to figure out the best control strategy in pasteurization process. The dynamic model can be used to reach more exact data. There are several tuning methods available, i.e., Ziegler - Nichols.

It would have been interesting to experiment the gelatinization with equipment like a microscope fitted with a polarizing filter and a hot stage-controlled heating unit. The technique is mentioned to be a way to see how the gelatinization temperature of an individual granule can be found. The swelling capacity which defines the ratio shall be also worth to evaluate. For the further evaluations also the determination of β-glucan contents shall be included e.g., using the modified AOAC 995.15 method.

As research problem of the thesis was to solve the oat-based fruit and berry juice drink production with thermal process, it has been reached. The commercially available products had been developed. The drinkable whole grain product with the acceptable sliminess, viscosity and mouthfeel was developed and tested. The nutrition value profile of the products was increased with whole oat grain flour.

References

Ain, H.B.U.; Saeed, F.; Khan, M.; Niaz, B.; Rohi, M.; Nasir, M.A.; Tufail, T.; Anbreen, F. & Anjum, F.M. 2018. Modification of barley dietary fiber through thermal treatments. Food Science & Nutrition. 2019, Vol. 7, 1816-1820.

Alcázar-Alay, S. & Meireles, M. 2015. Physicochemical properties, modifications, and applications of starches from different botanical sources. Food Science and Technology. Vol. 35, 215-236.

Alfa Laval. Purely Purees. Brochure pdf. Referred 3.8.2021. https://www.alfalaval.com.

Anttila, H.; Sontag-Strohm, T. & Salovaara, H. 2004. Viscosity of beta-glucan in oats products. Agricultural and food science. Vol.13, 80-87.

Arendt, E.K. & Zannini I, E. 2013. Cereal Grains for Food and Beverage Industries. Ebook Central Perpetual, DDA and Subscription Titles. First edition. UK: Elsevier Science & Technology. Access with Turku UAS user ID. Referred 1.10.2022.

Bai, Y-P.; Zhou, H-M.; Zhu, K-R.& Li, Q. 2021. Effect of thermal processing on the molecular, structural, and antioxidant characteristics of highland barley β-glucan. Carbohydrate polymers. Vol. 271, 1-11.

Balestra, F.; Coggi, E.; Marsilio, G.& Dalla Rosa, M. 2011. Physio-chemical and rheological changes of fruit purees during storage. Procedia Food Science. Vol.1, 576- 582.

Belitz, H.-D.; Grosh, W. & Schieberle, P. 2004. Food Chemistry. Third revised edition. Heidelberg: Springer.

Berski,W.; Ptaszek, A.; Ziobro, R.; Kowalski, G.; Grzesik, M. & Achremowicz, B. 2010. Pasting and rheological properties of oat starch and its derivatives. Carbohydrate Polymers. Vol. 83, 665 – 671.

Brennan, C. & Cleary, L. 2005. The potential use of cereal (1→3,1→4)-β-D-glucans as functional food ingredients. Journal of Cereal Science. Vol. 42, 1-13.

Chantel, R.; Chung, Y. & French, J. 2013. Soluble oat flour and method of making utilizing enzymes. Invention. US9149060B2.

Chen, D.X. & Sun, D-W. 2012. Modeling Thermal Processing Using Computational Fluid Dynamics. Thermal Food Processing: New Technologies and Quality Issues, Second Edition. 2012, 131-146.

Chen, J.; Gao, D.; Yang, L. & Gao, Y. 2013. Effect of micro fluidization on the functional properties of insoluble dietary fiber. Food Research International. Vol. 54, 1821 - 1827.

Cui, W. & Wood, P.J. 2000. Relationships between features, molecular weight, and rheological properties of cereal β-glucans. Hydrocolloids: Fundamental and Applications in Food, Biology and Medicine. Elsevier Science & Technology. 159-167.

Dipak, P. 2016. Microorganisms and α-amylase: a concise review. Innovare Journal of Sciences. Vol. 4, 1-5.

Dongowski, G.; Drzikova, B.; Snege, B.; Blochwitz, R.; Gebhardt, E. & Habel, A. 2005. Rheological behaviour of β-glucan preparation from oat products. Food Chemistry. Vol. 93, 279-291.

Doublier, J-L. & Wood, P. 1995. Rheological Properties of Aqueous Solutions of (1→3)(1→4)- β-glucan from Oats (*Avena sativa L*.). Cereal Chemistry Vol. 72(4), 335-340.

Du, B.; Meenu, M.; Liu, H. & Xu, B. 2019. A concise review on the molecular structure and function relationship of β-glucan. International Journal of Molecular Sciences. Vol. 20, 1-8.

Eckes-Granini Finland Oy Ab. Brand purpose instructions. Referred 21.1.2022.

Eckes-Granini Finland Oy Ab. 2021. Internal company discussions 15.7.2021.

Eckes-Granini Finland Oy Ab. 2021. Process Description. Referred 6.6.2022.

Eckes-Granini Finland Oy Ab. 2021. Working Instructions. Referred 8.10.2022.

EFSA. 2022 Referred to 10.1. 2022. EU Register of nutrition and health claims made on foods (v.3.6) (europa.eu). https://ec.europa.eu/food/safety/labelling_nutrition/claims/register/public. Referred 5.6.2022.

Encyclopedia Britannica. 2022. Referred to 8.10.2022. www.britannica.com.

Faure, A.M.; Koppenol, W.H. & Nyström, L. 2015. Iron (II) binding by cereal beta-glucan. Carbohydrate Polymers. Vol. 115, 739-743.

Grundy, M.M-L.; Fardet, A.; Tosh, S.M.; Rich, G.T. & Wilde, P.T.2018. Processing of oat: the impact on oat´s cholesterol lowering effect. Food & Function. Vol. 9, 1328 – 1343.

Gutierrez, C.G.C.C.; Dias, E.F.T.S.& Gut, J.A.W. 2010. Residence time distribution in holding tubes using generalized convection model and numerical convolution for non-ideal tracker detection. Journal of Food Engineering. Vol. 98, 248-256.

Harvard.T.H.Chan The Nutrition Source. Fiber. Referred to 5.11.2022. Fiber | The Nutrition Source | Harvard T.H. Chan School of Public Health.

Izydorczyk, M.S. 2009. Arabinoxylans. Handbook of Hydrocolloids. Ebook Central Perpetual, DDA and Subscription. Second edition. Elsevier Science & Technology. 653-682. Access with Turku UAS user ID. Referred 7.5.2022.

Jha, A.; Moses, J.A.& Anandharamakrishnan, C. 2019. Optmizing Beverage Pasteurization Using Computational Fluid Dynamics. Preservatives and Preservation Approaches in Beverages. Science of Beverages. Vol.15, 237-271.

Johansson, L.; Tuomainen, P.; Ylinen, M.; Ekholm, P.& Virkki, L. 2004. Structural analysis of water-soluble and -insoluble β-glucans of whole-grain oats and barley. Carbohydrate Polymers. Vol. 58, 267–274.

Jones, J. 2014. CODEX-aligned dietary fiber definitions help to bridge the “fiber gap”. Nutrition Journal. Vol. 13, 1-24.

Kasturi, P. & Bordenave, N. 2014. Starch. Oats Nutrition and Technology. Ebook Central Perpetual, DDA and Subscription Titles. First edition. UK: John Wiley & Sons, Incorporated. Access with Turku UAS user ID. Referred 24.10.2022.

Kaukovirta-Norja, A.; Helin, I.; Suortti, M.; Myllymäki, O.; Olonen, A.; Lehtinen, P. & Virkajärvi, I. 2009. Method of processing beta-glucan. WO 2009/077659 A1, 18.12.2008. Publication date 25.6.2009. 26 pages.

Kivelä, R.; Gates, F. & Sontag-Strohm, T. 2009. Degradation of cereal beta-glucan by ascorbic acid induced oxygen radicals. Journal of Cereal Science. Vol. 49, 1-3.

Kivelä, R.; Pitkänen, L.; Laine, P.; Aseyev, V. & Sontag-Strohm, T. 2010. Influence of homogenization on the solution properties of oat β-glucan. Food Hydrocolloids. Vol.24, 611-618.

Kwong, M.; Wolever, T.; Brummer, Y. & Tosh, S. 2013. Increasing the viscosity of oat β-glucan beverages by reducing solution volume does not reduce glycemic responses. British Journal of Nutrition. Vol.110, 1465-1471.

Lazaridou, A.; Billaderis, C.G. & Izydorczyk, M.S. 2003. Molecular size effects on rheological propertied of oat β-glucans in solution and gels. Food Hydrocolloids. Vol.17, 693 – 712.

Lamas de Souza, N.; Bartz, J.; Da Rosa Zavareze, E.; Diaz de Oliveira, P.; Vleira da Silva, W.; Hörnke Alves, G. & Renato Guerra Dias, A. 2015. Functional, thermal and rheological properties of oat β-glucan modified by acetylation. Food Chemistry. Vol.178, 243 - 250.

Lehtinen, P.; Myllymäki, O.; Killiäinen, K.; Lehtomäki, I.K.& Laakso, S. 2004. Method for the preparation of a starch-containing product in particle form. WO

Pat. 2004/041000 A1. Applicant: Suomen Viljava Oy. Publication date 21.5.2004. 25 pages.

Lenntech 2022. Water treatment. Referred 6.10.2022. www.lenntech.com.

Lim, W. J.; Liang, Y. T.; Seib, P. A. & Rao, C. S. 1992a. Isolation of oat starch from oat flour. Cereal Chem. Vol. 69, 233 – 236.

Liyana-Pathirana, C. & Shahidi, F. 2006. Antioxidant and free radical scavenging activities of whole wheat and milling fractions. Food Chemistry. Vol. 101, 1151–1157.

Lyly, M.; Salmenkallio-Marttila, M.; Suortti, T.; Autio, K.; Poutanen, K. & Lähteenmäki, L., 2003. Influence of oat β-glucan preparations on the perception of mouthfeel and on rheological properties in beverage prototypes. Cereal chemistry. Vol. 80, 536–541.

Manners, D.J. & Bathgate, G.N. 1969. α-1,4-glucans. Part XX. The molecular structure of the starches from oats and malted oats. Journal of the Institute of Brewing. Vol. 75, 169-175.

Massini, R.; Paciello, G.; Pagliarini, G.; Rozzi, S.& Trifiró, A. 2005. Effect of the rheological behavior on the performance of a shell and tube heat exchanger equipped with spirally enhanced walls. Eurotherm Seminar 77 - heat and mass transfer in Food Processing June 20-22, 2005.

Maunsell, C.; Myllymäki, O.; Huhtakallio, M. & Lehtomäki, I. 2011. New types of grain products, their production and use, and cosmetic formulations containing them. FI 124441 B. 18.7.2011. Publication date 19.1.2013. 35 pages.

Mazumder, M.K.; Sims, R.A.; Biris, A.S.; Srirama, P.K.; Saini, D.; Yurteri, C.U.; Trigwell, S.; De, S. & Sharma, R. 2006. Twenty-first century research needs in electrostatic processes applied to industry and medicine. Elsevier. Chemical Engineering Science. 2192-2211.

May, C.D. 1997. Thickening and Gelling Agents for Food. Second edition. UK: Springer-Science + Business Media. 230 – 260.

Mua, J-P. & Jackson, D.S. 1995. Fractionation of Regular Corn Starch: A Comparion of Aqueous Leaching and Aqueous Dispersion Methods. Carbohydrates. Cereal Chemistry. Vol. 72, 508-511.

NTGD PumpEccentric Screw Pump. Referred 13.3. 2022 https://ntgdpump.com

Oat bran ingredient´s supplier e-mail. Raw material specification. Private e-mail. 15.9.2021. Message receiver: Leena Mikkilä.

Pereyra, R. & Mutilangi, W. 2011. Methods for preparing low viscosity whole grain flour slurry via mechanical treatment. US2011/0020523 A1. 9.9.2010. Publication date 27.1.2011. 6 pages.

Peterson, D.M. 2004. Oat - a multifunctional grain. 7th International Oat Conference, Helsinki. MTT, Agrifood Research Finland.

Pillai, R.; Redmond, M. & Rödling, J. 2005. Anti-Wrinkle Therapy: Significant New Findings in the Non-Invasive Cosmetic Treatment of Skin Wrinkles with Beta-Glucan. International Journal of Cosmetic Science. 1-6.

Plana-Fattori, A.; Chantoiseau, E.; Doursat, C. & Flick, D. 2021. Modelling the heat treatment of a starch suspension inside a tubular exchanger: the influence of food product transformation on residence time distributions. HAL Open Science. 1-6.

Reiner, M. 2012. Rheology V1: Theory and Applications. Ebook Central Perpetual, DDA and subscription Titles. First edition. US: Frederick Erich. Eisevier Science & Technology. Access with Turku UAS user ID. Referred 3.3.2021.

Ross, A.S. 2012. Starch in Foods. Food Carbohydrate Chemistry. Chapter 7,107-130.

Roubroeks, J.P.; Mastromauro, D.I.; Andersson, R., Christensen, B.E. & Åman, P. 2000. Molecular Weight, Structure, and Shape of Oat (1→3),(1→4)-β-Glucan Fractions Obtained by Enzymatic Degradation with Lichenase. Biomacromolecules. Vol. 1, 584-591.

Sayar, S. & White, P.J. 2011. Oats: Chemistry and Technology. Oat starch:Physiochemical Properties and Function. Ebook Central Perpetual, DDA and Subsricption Titles. Second edition. USA: American Association of Cereal Chemists International. Access with Turku UAS user ID. Referred 28.4.2022

SFX Flow. Top Wing rotary lobe pump. Referred 13.3.2022. https://www.spxflow.com.

Skendi, A., Biliaderis, C.G., Lazaridou, A., Izydorczyk, M.S. 2003. Structure and rheological properties of water soluble β-glucan from oat cultivars of Avena sativa and Avena bysantina. Journal of Cereal Science. Vol 38, 15-31.

Taggart, P. & Mitchell, J.R. 2009. Starch. Handbook of hydrocolloids. Ebook Central Perpetual, DDA and Subscription Titles. Second edition. UK: Woodhead Publishing Series in Food Science, Technology and Nutrition Ser. Access with Turku UAS user ID. Referred 7.8.2022.

Tester R. & Karkas, J. 1996. Swelling and Gelatinization of Oat Starches. Cereal Chemistry. Vol. 73, 271-277.

Tetra Pak. 2009. Technical Manual TeM 1224516-1101 Tetra Therm® Aseptic Visco.

Tetra Pak. 2016. Presentation slides. Referred 6.6.2022.

Tetra Pak. 2016-2019. Process Engineer Mr. Tanskanen several interviews.

Tetra Pak. 2019. Vacuum Mixer Manual.

Zhang, M.; Bai, X. & Zhang, Z. 2011. Extrusion process improves the functionality of soluble dietary fiber in oat bran. Journal of Cereal Science. Vol. 54, 98-103.

Zhu, F. 2017. Structures, properties, modifications, and uses of oat starch. Food Chemistry. Vol. 229, 329-340.

Zhu, F.; Du, B.& Xu, B. 2016. A critical review on production and intertrial applications of beta-glucans. Food Hydrocolloids. Vol. 52, 275 - 288.

Verma, H.; Narnoliya, L.K. & Jadaum, J. 2018. Pectinase: A Useful Tool in Fruit Processing Industries. Nutri Food Sci Int J. Issue 5, 1 - 3.

Vilja-alan yhteistyöryhmä. 2021.. www.vyr.fi. Viljelyalat lajikkeittain. Referred 11.11.2021

Wang, L. Z.& White, P. J. 1994c. Functional properties of oat starches and relationships among functional and structural characteristics. Cereal Chem. Vol. 71, 451 - 458.

Wang, Z.-W.; Gu, M.-Y. & Li, G.-Z. 2005. Surface properties of gleditsia saponin and synergisms of its binary system. J. Disper. Sci. Technol. Vol. 26, 341– 347.

Wood, P. 2011. Oat β-glucan: properties and function. Oats- chemistry and technology. Chapter 11, 219 -248.