Exploring the Influence of Cream Processing Parameters on Butter Quality

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By

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Declaration

I, Aidan O'Loughlin, hereby declare that the material included in this thesis submitted for assessment for the programme of MSc Food Business Management and Technology is entirely my own work, under the guidance of my supervisor, Mary O'Connor. This work has not been submitted for any academic award at this University, or any other University or Higher Education Institute. Any use of the work of others has been fully acknowledged by reference in both text and bibliography.

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Abstract

This thesis was set out to explore the potential to improve the quality of winter cream, for the purposes of producing higher quality butter during the winter period. Understanding how cream processing parameters can be altered to produce a more desirable butter during the winter period was the key concept. This is an important topic for butter manufacturers as it can help add value to winter cream.

The thesis topic was evaluated through peer reviewed data. The characterising factors investigated were fatty acid composition, FFA, butter hardness and the milk fat crystalline structure within butter and cream. These areas were picked as they are the strongest indicators of butter quality.

The key finding was that there is a relationship between the alteration of cream processing parameters and the final results of the key characteristics of butter. Firstly, for the fatty acid composition, a shorter cream ripening time resulted in higher levels of UFAs such as oleic acid which are associated with the development of a softer butter. For FFA in milk, the lowest values were found from milk cooled at 4°C and pumped without incubation after cooling. For butter hardness the combination of lower ripening temperatures, high agitation, longer ripening times and the addition of LMP milk fat fractions was seen to have the biggest impact of reducing butter hardness. Lastly, in the milk fat crystallisation section, desirable β' milk fat crystals were found to develop during the first hour of cream ripening while a combination of maturing cream at 5°C along with a high agitation rate was seen to produce the highest amount of β' milk fat crystals.

In conclusion, the quality of winter cream can be improved through the alteration of cream processing parameters to produce a more desirable final butter. Future work that's recommended to be undertaken includes the usage of a spinning cone column which could help remove volatile compounds from cream.

Abbreviations

AMF – Anhydrous Milk Fat

ANOVA – Analysis of Variance

BC – Before Christ

B.D.I - Bureau of Dairy Industries

BMP – Buttermilk Powder

CF - fast cooled cream

cm - Centimetre

CMF - fast cooled and matured cream

CMS - slow cooled and matured cream

CS - slow cooled cream

DMI – Dry Matter Intake

EU – European Union

FA – Fatty Acid

FAMEs – Fatty Acid Methyl Esters

HA – High Agitation

HP – Hewlett-Packard

FFA – Free Fatty Acid

GC – Gas Chromatography

Kg – Kilogram

LA – Low Agitation

LCFA – Long Chain Fatty Acids

L/H – Litres/Hour

LMP – Low Melting Point

LSD – Least Significant Difference

MCFA – Medium Chain Fatty Acids

MF – Milk Fat

Mm/min – millimetres per minute

Mm/s – millimetres per second

NA – No Agitation

N – Newtons

NaOH – Sodium Hydroxide

pH – Potential of Hydrogen

PV – Peroxide Value

Rpm – Revolutions Per Minute

s – Second

SAXS – Small Angle X-ray scattering

SCFA – Short Chain Fatty Acids

SD – Standard Deviation

SFA – Saturated Fatty Acids

SFC – Solid Fat Content

SMP – Skim Milk Powder

TAG - Triglyceride

TMR – Total Mixed Ration

TVC – Total Viable Count

UFA – Unsaturated Fatty Acids

USD – United States Dollar

VLCFA – Very Long Chain Fatty Acids

W/W – Weight for Weight

WAXS – Wide Angle X-ray scattering

XRD – X-Ray Diffraction

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Chapter 1: Introduction

The focus of this thesis is to explore the potential to improve the quality of winter cream, for the purposes of producing higher quality butter during the winter period. In order to address this research aim, this chapter will give an overview of butter and cream and how it's produced, key characterising factors of butter and how they are defined, key manufactures, the economics of butter and downgrade product in the butter industry.

This chapter will overview the main characterising factors of butter such as the fatty acid composition, free fatty acid, butter hardness and milk fat crystalline structure and review their importance to overall butter quality.

1.1 Cream

1.1.1 Definition of Cream

A white substance known as milk is released by mammals as a means of providing their young with nutrients and immune protection. Water, lipids, protein, salt, minerals, and vitamins are all present in milk. (Jenness, 1988). Cream can be defined as a milk product which is abundant in fat, in the form of an emulsion of fat in skimmed milk obtained during the physical separation of milk which has a minimum milk fat of 10% (weight for weight (w/w))(*Codex Alimentarius Milk and Milk Products. 6TH Edition*, 2018). A separator is a device that removes cream from whole milk. As a result, the whole milk is divided into cream and skim milk.

Cream with a milk fat of 40% (w/w) is commonly used during butter production. Cream for sale to consumers can commonly be classified through its fat content. Half cream or coffee cream are common names for cream with a lower fat level (10–18%), which is widely utilized in cooking and sweets. Cream with a higher level of fat usually between 35-40% is much thicker and is commonly referred to as whipping cream as it can be whipped into a thick froth.

Cream used for butter production in Ireland is typically bovine derived. Bovine milk is derived from cows. Bovine cream is used due to its high availability and popularity worldwide. In 2019 there were over 881 million tonnes of milk produced with cow's milk representing over 81% of the global total (714 million tonnes). Asia is the world's leading region of cow's milk production with over 32% of the worldwide share with the EU being the second at 24% (Figure 1.3). Figure 1.1 outlines the global milk production levels by species from 2010 as far as 2019. Buffalo milk was the second biggest source of milk in 2019 with over 120 million tonnes produced. The remaining milk produced was sourced mainly from goats, sheep and other mammals (IDF, 2019).

The global increase in dairy consumption as shown on figure 1.2 highlights the need to maximise production of dairy products with the valorisation of winter cream considered as potential way to produce higher quality butter all year round.

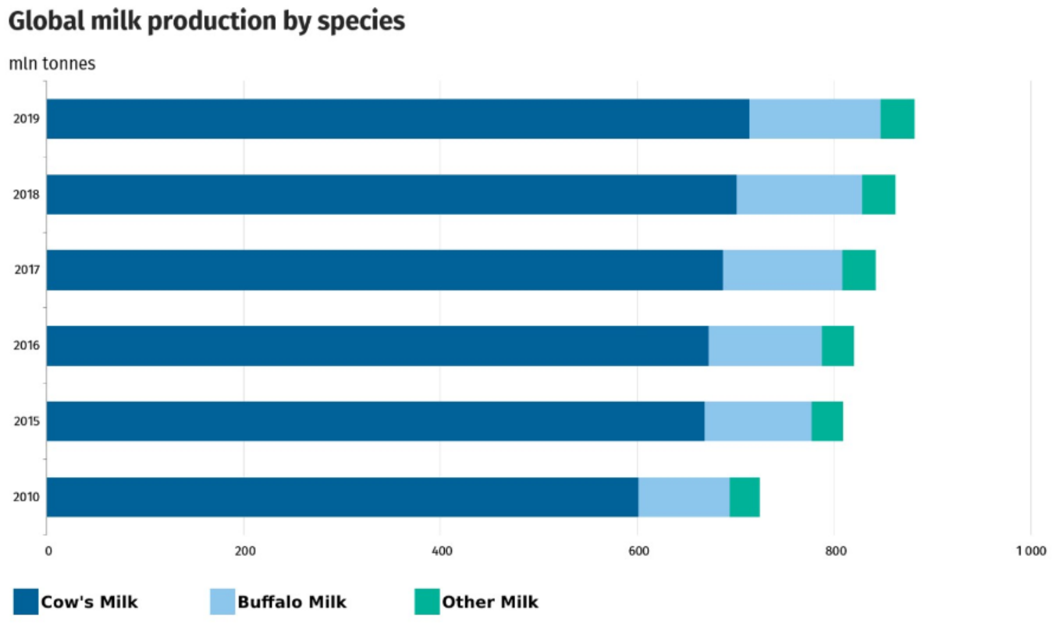

Figure 1.1: Global milk production from species 2010-2019(taken from IDF, 2019).

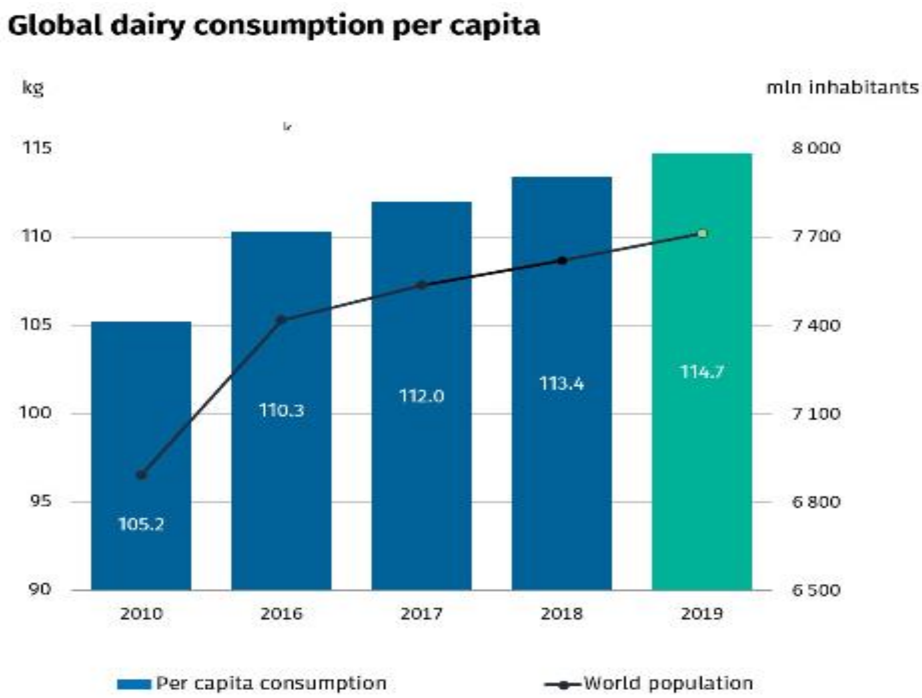

Figure 1.2: Global Dairy Consumption per capita from 2010-2019 (IDF, 2019).

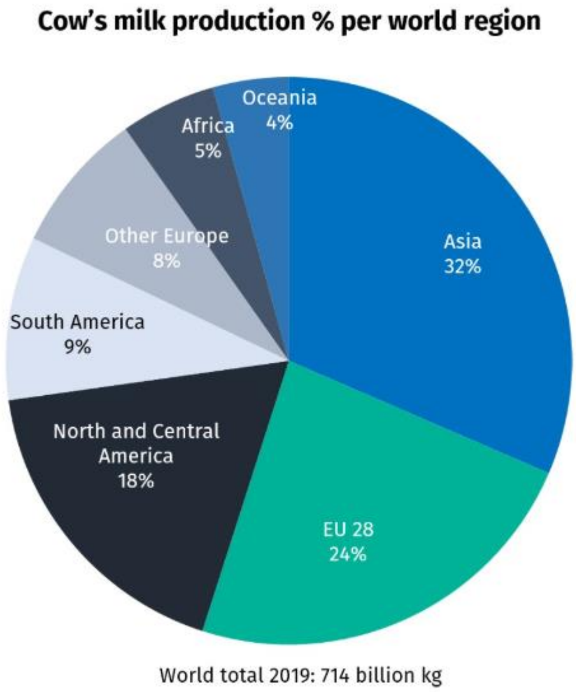

Figure 1.3 Cow's milk production % per world region in 2019 (taken from IDF, 2019).

1.1.2 Cream Production

Cream is typically produced through a centrifugal separator. The milk is introduced through vertically aligned distribution holes in the discs at a distance from the outside of the disk stack. According to their density in relation to the continuous medium, the sediment and fat globules in the milk start to settle radially outwards or inwards in the separation channels under the effect of centrifugal force. Higher density solid impurities of milk will begin to settle outwards on the edge of the separator and collect in the sediment space. The skim milk travels from the disc stack's interior to the area outside of it, where it passes through a channel between the disc stack's top and the separator bowl's conical hood to a concentric skim milk outlet. Since the cream, or fat globules, are less dense than skim milk, they flow inward in the channel towards the axis of rotation and exit at the axial outlet (*Dairy Processing Handbook*, 2021)

The whole milk which enters the separator is discharged in two flows, skim milk and cream. The cream production usually represents 10% of the total output. The amount discharged as cream determines the cream's fat content. If the whole milk contains 4% fat with an output of 20,000 l/h the total amount of fat passing through the separator can be found through the following calculation (Figure 1.4). This is important for processors of cream as finding the total amount of fat passing through the separator can aid finding the liquid discharge content.

$$\frac{4 \times 20\,000}{100} = 800 \text{ l/h}$$

Figure 1.4: Fat content calculation**: (**where 4=Milk Fat content %, 20,000 litres/h= Separator Ouput, 800 litres/h= total fat passing through seperator) (taken from *Dairy Processing Handbook*, 2021)

If we then assume that cream with a 40% fat content is needed, this amount of fat must be diluted with a quantity of skim milk. The total liquid discharged as 40% cream can then be solved through the following equation (Figure 1.5).

$$\frac{800 \times 100}{40} = 2000 \text{ l/h}$$

Figure 1.5: Liquid discharge content calculation: (40%=Cream fat content, 800 litres/h= total fat passing through separator, 2000 litres/h=total liquid discharge) (taken from *Dairy Processing Handbook*, 2021)

This confirms that 800 l/h is pure fat while the remaining 1200 l/h is skim milk. The installation of throttling valves at the outlet points for both the skim and the cream makes it attainable to adjust the volumes of the two flows in order to obtain a desired fat content in cream (*Dairy Processing Handbook*, 2021). This is useful information for butter manufacturers as this can help them manage the quantity of cream needed to make their required batch size during a production run.

1.1.3 Cream Importance

The overall quality of the raw cream is one of the key drivers of butter quality. One of the key issues I will address throughout this thesis is ways to valorise winter cream. Summer butter is made predominantly during the summer months during peak grazing season with maximum FFA values of 0.33% while winter butter is made when cows are housed. Maximum FFA values at this time of the year are 0.40%. Butter that is made with winter cream has a different texture compared to summer butter as it’s not as smooth and does not have a fresh flavour while it appears as a pale-yellow colour compared to summer butter which is a darker yellow (Dankso Foods Ltd., 2022).

1.2 Butter

1.2.1 Definition of Butter

Butter is a fatty product which is derived exclusively from milk and/or products which may be obtained from an emulsion of the type water in oil(Codex, 2018). Butter is typically made using cream which is sourced from bovine origin. The earliest evidence of a butter making process was found on a Sumerian tablet which dates back to roughly 2500 BC (McCormick, 2012). Butter generally has typical fat values of around 80% milk fat per 100g with a maximum moisture of 16% moisture per 100g. While there is no formal distinction drawn between summer and winter butter there are significant seasonal variations in the FFA values which can impact the characteristics of the butter. Summer butter which is produced from March to October has FFA typical values of <0.30% with winter butter FFA ranging from 0.30% to 0.40%.

Salt may be added to butter with a typical value of 1.6-1.7% with shelf life if refrigerated at 4°C up to 2 months while frozen salted butter has a shelf life ranging from 6-9 months. Unsalted butter has a typical shelf life of about two weeks refrigerated with frozen butter typically 5 months. The mixture of milkfat with other fat sources is prohibited (Lee *et al.*, 2018).

Butter Type	**Butter Storage Temperature**	**Shelf Life**
Salted	4°C	2 months
Salted	-18°C	6-9 months
Unsalted	4°C	2 weeks
Unsalted	-18°C	5 months

Table 1.1: Typical shelf life of salted and unsalted butter.

1.2.2 Butter Classification

Butter can be commonly classified into two categories. Firstly, is sweet cream butter and second is cultured or sour cream which is made from bacteriologically soured cream. Butter can also be classified through its salt content with either salted or unsalted varieties commercially available (*Butter and Dairy Spreads*, 2015). The below table compares the typical chemical values of the main types of butter produced in Irish butter plants.

Product	Fat	Moisture	Curd	PH	Salt	PV	FFA
Unsalted Sweet Cream Butter	82%	15.90%	1.90	6.6	0%	0.1	0.40% Max

Lactic Butter	82%	15.90%	1.90	4.7	0%	0.1	0.40% Max
Salted Sweet Cream Butter	80.5%	15.90%	1.90	6.6	1.8%	0.1	0.40% Max

Table 1.2: Typical chemical values of butter produced by Irish processors.

From (Table 1.2) we can observe from the data that the normal moisture value is 15.90% with the codex classification of butter being defined as having a moisture level of less than 16%. If butter is produced and its value exceeds this cut-off, it must either be marketed as a downgrade product at a lower price or reformed to reach the proper moisture level. Unsalted and lactic butters typically have a fat percentage of 82%, however salted sweet cream butter variations have a lower fat content to compensate for the salt. The PH value for both salted and unsalted sweet cream varieties are typically 6.6, while lactic butter contains a much lower PH of about 4.7. This in due to the addition of starter cultures in the production process which help to reduce the PH to this level. Lactic butter has a diacetyl aroma which can be attributed to the buttery smell that is present post-production. Typical diacetyl values range from 1.0-2.0ppm while anything that has a diacetyl value <0.75 should not be categorised as lactic butter. Summer butter is made predominantly during the summer months during peak grazing season with maximum FFA values of 0.33% while winter butter is made when cows are housed. Maximum FFA values at this time of the year are 0.40%.

1.2.3 Manufacturing Process

Cream from whole milk that has been separated is used to make butter. Before being separated, the whole milk is preheated in the pasteurisation unit to 63°C. Before being pumped into the cream pasteurisation facility, the warm cream is transported to the intermediate holding tank. After being separated from the cream, the skim milk is pasteurised, cooled, and pumped into storage. Skim milk powder (SMP) can be made from this skim milk by evaporating and spray-drying it which can then be sold to clients who require this product. The normal protein values for this SMP would be >32.5%, while the typical fat content would be <1.5%. The cream is pasteurized at 95°C or above in the intermediate storage tank(*Butter and Dairy Spreads*, 2015).

To eliminate any enzymes or microbes that can shorten the butter's shelf life, a higher pasteurisation temperature is necessary. The peroxidase test can be used to assess the efficiency of the heat treatment of milk. This heat treatment also lowers the danger of oxidation in butter by releasing antioxygenic sulphhy-ryl molecules. If the cream has a bad flavour or smell, vacuum deaeration might be added to the line. This is performed before pasteurisation and entails heating the cream up to the necessary temperature followed by a quick cooling to release any trapped gases and volatile compounds. The cream is then transferred to the ripening tank, where it is put through a temperature programme that will give the fat the proper crystalline structure when it solidifies during chilling. Fat starts to crystallize in cream when it is cooled below 40°C. Milk Triglycerols (TAG) crystals contribute to a product's rheological and sensory characteristics. A fat's functionality is impacted by its solid fat content as well as the crystal structure that TAGs create. The majority of milk fat, 97-98%, is made up of TAGs (Lopez, 2018). A soft butter that may be produced from hard milk fat with low iodine values would arise from the fats crystallizing at different temperatures if the cooling is gradual(*Butter and Dairy Spreads*, 2015).

As it would take several days, the low temperatures would make the fat vulnerable to bacterial development. By quickly cooling the cream to a low temperature, the rate of crystallization can be sped up. This results in rapid crystallisation growth. Low melting point triglycerides are trapped as a result, and mixed crystals are created. A low liquid to solid fat ratio would lead to the production of an unfavourable hard butter. The low-melting triglycerides can be melted out of the crystals by heating the cream to a higher temperature, which will prevent this from happening. This causes a higher level of pure crystals to form and a lower level of mixed crystals to form. In turn a softer butter will be produced and is measured according to its iodine value also known as hardness value. The ripening process usually takes 12-15 hours and when necessary acid-producing bacteria cultures are added before the temperature treatment (*Butter and Dairy Spreads*, 2015).

The cream is poured into the continuous butter-maker or churn from the ripening tank and heated to the proper temperature using a plate heat exchanger. The cream is aggressively agitated during the churning process to break down the fat globules, which causes the fat to solidify as butter grains. The fat level of the remaining liquid which is known as buttermilk decreases. Two fractions are created throughout the churning process: buttermilk and butter grains. The buttermilk is continuously drained from the churn once the butter grains have reached a certain size. Once transferred into silos, the drained buttermilk can be evaporated and spray-dried to create buttermilk powder (BMP) in a manner similar to that used with skim milk. The fat content in this BMP can range between 5-11% and can be altered to suit customer requirements (*Butter and Dairy Spreads*, 2015)

Using the butter grains that are left after draining, a continuous fat phase with a finely distributed water phase can be created. To remove moisture between the butter grains, pressure is applied. The liquid fat and fat crystals are subsequently pushed out of the fat globules under high pressure. The moisture becomes finely dispersed which continues until the desired moisture content is obtained. The resulting butter should be dry, and the operator should periodically check the moisture content throughout the working phase to make sure it meets customer specifications. The finished butter can then be sent to the packaging unit and is packed into 25kg boxes and stored at <4°C (*Butter and Dairy Spreads*, 2015).

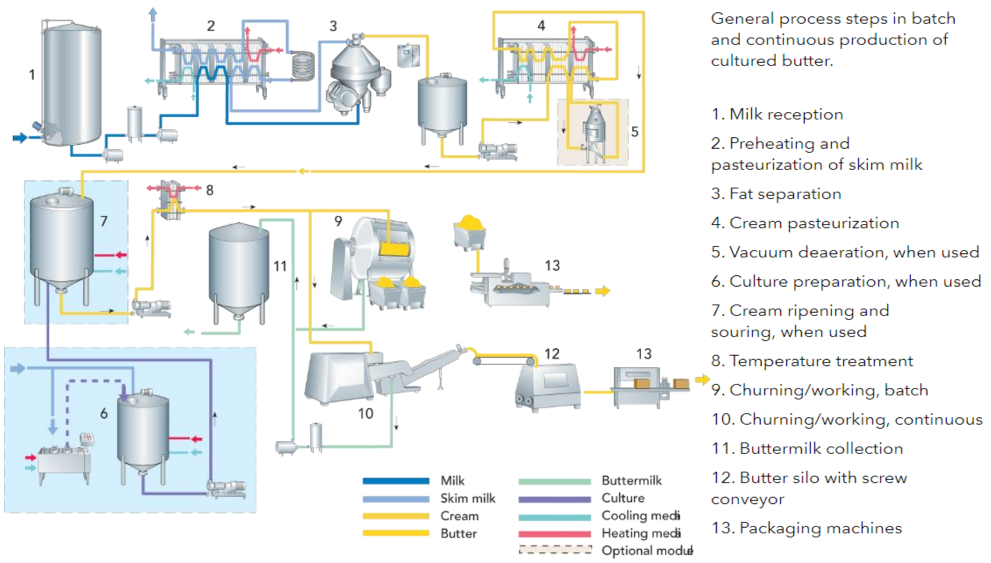

Figure 1.6: Process flow of batch production of butter which is outlined above (taken from Dairy Processing Handbook, 2021).

1.2.4 Irish Butter vs Global Butter

Butter produced in Ireland is made using milk sourced from cows primarily on pasture-based diets. The majority (about 75%) of the diet of the lactating dairy cows in Ireland consists of grazed grass, with some concentrate supplementation and small amounts of grass silage fed in both the spring and the autumn. Since it is inexpensive, pasture is used in this system. The total cost of milk production decreases as the percentage of grazed grass in this system rises (Murphy, 2005).

The way butter is produced globally has significantly changed in recent years. The amount of pasture in the diet of dairy cows has decreased in some areas as dairy farming systems have gotten more intense, and a global shift from a feeding regimen based on pasture to one focused indoors has taken place. This indoor-based feeding program commonly uses a total mixed ration (TMR) feeding approach that may include grain concentrates, forages (hay, straw, grass silage, and maize silage), as well as supplements for salt, protein, or fat (Cameron *et al.*, 2018). Countries may choose to use this strategy for a variety of reasons, such as a lack of grazing infrastructure, land cost and availability, shorter growing seasons, access to automatic milking systems, trained labour, weather variability, and lack of information about grassland grazing (Van den Pol-van Dasselaar, Hennessy and Isselstein, 2020).

In order to meet the energy needs of the high productivity dairy cows associated with TMR systems, which cannot always be met by pasture diets, indoor TMR systems often result in a greater management of nutrition and dry matter intake (DMI) (Elgersma, 2015). The TMR system is used by more than 90% of intensive dairy farms in the United States (Schingoethe, 2017) and has also become more common in the Middle East, Japan, China, and parts of Europe despite the higher labour expenses and feed costs, which can exceed 50% of the overall operating costs (Douphrate *et al.*, 2013).

Studies involving TMR versus pasture based diets have shown that pasture derived milk has a higher fat content compared to TMR while TMR produced a higher total milk yield (Gulati *et al.*, 2018). The TMR diet adds additional non-structural carbohydrates to the small intestine of ruminants for digestion which is known to increase total yield but decrease fat levels in milk (Reynolds, 2006).

1.2.5 History of Butter

The earliest production of milk would have been in the areas of Iraq and Iran around 8000-9000 BC with butter thought to have been found in milk containers(McGee, 2007). The earliest butter making process which was found on a Sumerian tablet dates back to roughly 2500 BC (McCormick, 2012). Throughout the middle-ages butter was a common food across Europe but was considered a food primarily ate by peasants. Eventually by the 16th century butter became more common across middle class society and gained a strong reputation for use as a sauce with meat and vegetables (McGee, 2007). In the 1800's both Ireland and France became well known for its butter production particularly in the areas of Normandy and Brittany. Butter during this period was typically made by hand on farms until the development of the first butter factories in the United States in the early 1860's. The 1870's saw the introduction of the centrifugal cream separator which was most successfully marketed by Carl Gustaik Patrik de Laval who was Swedish (Edwards, 1949). Butter consumption declined in the 20th century due to the onset of rationing due to World War 2 as well as the rising popularity of margarine due to its lower cost and perceived health benefits.

1.3 Butter Characterising Factors

This section will explore the various characteristics of butter such as free fatty acid, butter hardness, fatty acid composition and milk fat crystallisation and how these factors impact the overall quality of the product. These factors are primarily driven by the quality of the milk and cream used in the butter production process.

1.3.1 Fatty Acid Composition

The composition of bovine milk is shown on table 1.3. The typical milk fat value is 4.0%. The primary fatty acid in milk fat is triacylglycerols(TAG) which represent 98% of the total amount (Walstra *et al.*, 2005).

Component	Average content in Milk (%, w/w)	Range (%, w/w)
Water	87.1	85.3–88.7
Solids (no fat)	8.9	7.9–10.0
Fat (in dry matter)	31	22–38
Lactose	4.6	3.8–5.3
Fat	**4.0**	**2.5–5.5**
Protein	3.3	2.3–4.4
Casein	2.6	1.7–3.5
Mineral substances	0.7	0.57–0.83
Organic acid	0.17	0.12–0.21
Miscellaneous	0.15	—

Table 1.3: This table sets down a breakdown of the typical bovine milk composition (taken from Walstra *et al.*, 2005).

Triacylglycerols which are also commonly referred to as triglycerides are made up of three fatty acids which are individually esterified to each carbon within a glycerol molecule. This allows for the development of a stereochemically distinct fatty acid bond position: sn-1, sn-2 and sn-3 (Jones and Lichtenstein, 2020). TAG with three identical fatty acids can be classified as a simple TAG and are quite rare in nature. TAGs with that contain two or three different fatty acids can be classified as a mixed TAG and make up the majority of fat. The chain length, number, position, and conformation of the double bonds, as well as the stereochemical position of the fatty acids esterified to glycerol, all affect the triacylglycerol's melting point (Lichtenstein, 2013).

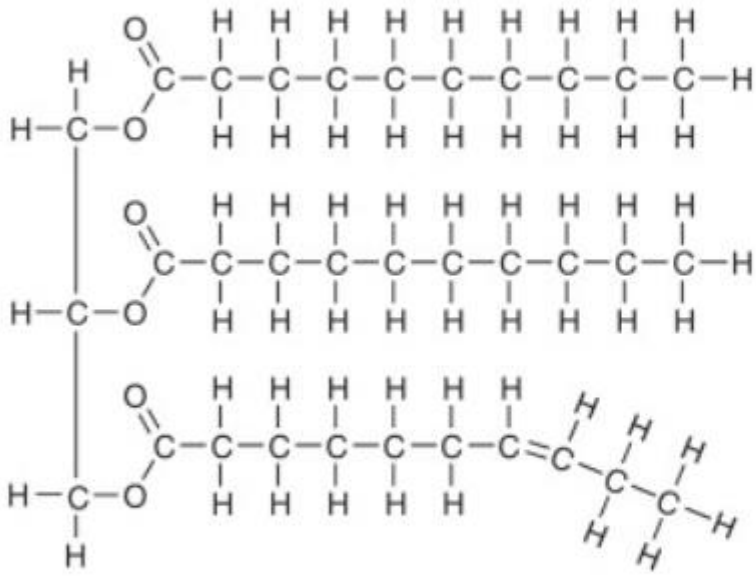

Figure 1.7: The above figure shows the molecular structure of a Triacylglycerol molecule (taken from Lichtenstein, 2013).

The fatty acid composition of butter is strongly influenced by the seasonality of Irish dairy. Seasonal calving pasture-based dairy systems, in which cows graze outdoors for 8 to 10 months per year, are possible in regions with fertile soils, temperate climates, and medium to high rainfall, such as Ireland. To maximize efficiency, herds in such systems calve in the spring (January-April), after which they are given access to pasture from the start of lactation, which coincides with the start of the grass growing season. In Ireland, 84% of dairy cows calved between January and April in 2019. The vast majority (approximately 75%) of the lactating dairy cow's diet in Ireland is grazed grass, with some concentrate supplementation and some quantities of grass silage fed in both spring and autumn (Timlin *et al.*, 2021).

Dietary systems have been shown to have an impact on the composition and quality of milk, particularly the fatty acid (FA) profile, where significant changes can be observed with changing nutrition. Figure 1.8 illustrates the average fat values in bovine milk though January to December from 2017-2019. During the winter months October – March when milk fats tend to be higher there is a significantly higher level of saturated fatty acids present such as palmitic acid (C16:0). This is linked to the higher level of concentrate that is fed to cows during this period. While when the grazing season begins in the March there is a higher level of unsaturated fatty acids present in while fat such as oleic(C18:1cis9) and linolenic acid(C18:3cis9,12,15). This is due to the higher concentrations of unsaturated fatty acids which are present in fresh grass (O'Callaghan *et al.*, 2016).

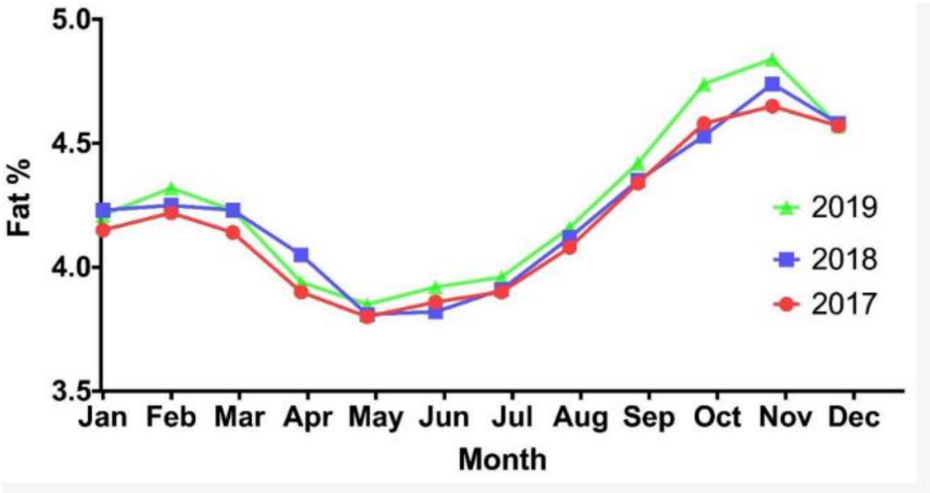

Figure 1.8: Seasonal variation in the average proportion of fat in milk produced by dairy cows in Ireland between January and December in the years 2017, 2018 and 2019 (taken from Timlin *et al.*, 2021).

Milk fat contains high quantities of unsaturated fatty acids (oleic & linoleic) as shown in table 1.4. They are of particular benefit to dairy processors as they have a lower melting point. For instance, oleic acid which is the second most abundant fatty acid in milk has a melting point of 12.8°C(Hurtaud, Delaby and Peyraud, 2007). Oleic acid can be characterised by its softness and plasticity which gives it an important role in the spreadability of butter (Jenkins and McGuire, 2006).

Fatty acid carbon number	Fatty acid common name	Average range (wt%)
4:0	Butyric	2–5
6:0	Caproic	1–5
8:0	Caprylic	1–3
10:0	Capric	2–4
12:0	Lauric	2–5
14:0	Myristic	8–14
15:0	Pentadecanoic	1–2
16:0	Palmitic	22–35
16:1	Palmitoleic	1–3
17:0	Margaric	0.5–1.5
18:0	Stearic	9–14
18:1[2]	Oleic	20–30
18:2	Linoleic	1–3
18:3	Linolenic	0.5–2

Table 1.4: Composition of the major fatty acids in milk fat (taken from Jensen, 2002).

Other examples of UFA are omega 6 (n-6) and omega 3 (n-3). Because they are not synthesized in the body, their precursors, linoleic acid and alpha-linolenic acid (C18:3n-3; ALA), are considered essential fatty acids. Consuming linoleic acid and alpha-linolenic acid has been shown in studies to help prevent heart disease and other cardiovascular events (Stark, Crawford and Reifen, 2008). Having high levels of both omega 6(n-6) and omega(n-3) unsaturated fatty acids which have good levels in summer milk due to the availability of fresh pastures would be highly beneficial in promoting good health status.

Milk contains lipoprotein lipase, which catalyses the lipolysis of triglycerides to produce free fatty acids (FFA) and partial glycerides. In the mammary gland, lipoprotein lipase is involved in the synthesis of milkfat triglycerides; its presence in milk is considered to be "spillover" because it serves no recognised biological function. Lipolysis can happen in raw milk naturally as a result of poor diet, mastitis, late lactation, or mechanical processing methods like agitation, homogenisation, or pumping that physically rupture the globule's membrane. Manufacturers of dairy products may be concerned about the potential of lipolysis since it could lead to the development of unappealing flavours in the finished product (Deeth, 2006). When FFA levels approach 1.5 mmol/L, the milk's steam foaming capacity starts to deteriorate, the surface tension decreases (due to the relatively low flavour threshold of short and medium chain FFA) and rancid off flavours in milk can appear (Deeth, 2006).

1.3.2 Free Fatty Acid

Free fatty acids (FFA) are lipid species that are released during lipolysis from adipose tissue and other cell types. FFA are beginning to perform active roles in a number of biological processes in addition to their traditional responsibilities in energy delivery and as structural elements. FFA may have an impact on endothelial, adipocyte, or macrophage gene expression. FFA can also influence the expression of genes encoding adhesion molecules, the creation of chemokines and cytokines, and the development of pro-inflammatory and pro-resolving lipid-derived species (Rodríguez-Carrio *et al.,* 2017). The development of the lipolytic flavor in milk is caused by FFA. FFA is released from glycerides by lipases, which can be found naturally in milk or made by psychrotrophic bacteria. More FFA in milk gives it a sour, bitter, and unpleasant flavour that many customers find offensive. Long-chain FFA (C14-C18) are not connected to rancidity, whereas FFA of shorter chain length (mainly C4-C12) play a key role in rancid flavour (Duncan, Christen and Penfield, 1991).

1.3.3 Butter Hardness

Butter hardness can be measured in newtons(N). The typical hardness value of butter is 1.0N. This would be considered softer butter which is typically made during summer period. The hardness of butter is dependent on four main drivers. These are stage of lactation, breed of cow, feed of cow and the weather.

During early lactation in February/March hardness values of butter are typically around 2.0N. When cows are let out in grass in mid-March/April time we see a rapid decrease in hardness with values typically decreasing below 1.0N. Then around July time hardness values tend to increase as grass growth slows down. If there was a very hot summer which included a drought butter hardness may peak in this month. Butter softens up to late spring levels in August/September due to increased growth and while a rapid decrease occurs in October/November as cows move into indoor feeding regimes.

Milk fat(MF) is predominantly composed of triacylglycerols with around 400 fatty acids(FA) with different chain lengths, degrees of saturation and stereospecific numbering position (Jensen, 2002).The TAG composition of MF can change according to the feeding regime of the cow, the stage of the lactation cycle, season and genetic factors of the animals (Capuano *et al.*, 2014). Seasonal fluctuation in MF composition mostly results from variations in feed according to season in dairy farming systems with indoor housing during the winter and pasture-based systems during the summer. In these systems, the diet mostly consists of ensiled feed and concentrate in the winter, with increased intake of fresh pasture occurring in spring and summer with or without supplemental feed, including corn silage and concentrate. Overall, the shift in the feeding schedule modifies the FA composition, which therefore alters the MF TAG composition (Pacheco-Pappenheim *et al.*, 2021). TAG seasonal composition variance in MF has been shown to result in different crystallisation behaviour throughout the year which may affect the textural properties of MF including hardness and spreadability (Mohan *et al.*, 2021).This makes the analysis of the TAG composition a vital area for butter manufactures to investigate in order to gain a better understanding of MF as an ingredient and the limitations that may be encountered due to the high variation of MF characteristics throughout the year (O'Brien and Guinee, 2016).

1.3.4 Milk Fat Crystallisation

Milk fat which is one of the main constituents of milk may be able to determine certain properties of both butter and cream. The quantity and kind of milk-fat crystals present at the application temperature have a significant impact on the functional qualities of milk fat. The stability of products containing a milk fat emulsion, such as cream, and the firmness of products in which fat is present as the continuous phase, such as butter and butter oil, are both significantly influenced by the crystalline portion of the fat. Due to the abundance of triglycerides with a wide variety of chain lengths and degrees of saturation, milk fat has a wide melting range. Additionally, the solid phase's polymorphism complicates the phase behaviour (ten Grotenhuis *et al.*, 1999). In the context of the composition of butter, polymorphism is the ability of a substance to have more than one crystal structure (Hondoh and Ueno, 2016).

A characteristic of triglycerides is the polymorphism of the crystalline phase. By using X-ray diffraction (XRD), the many polymorphic forms can be distinguished (ten Grotenhuis *et al.*, 1999). By measuring the size of the crystal unit and sub-cells, X-ray diffraction can be used to determine a crystal's polymorphism. The polymorphs diffract the x-rays in a variety of ways because of their various geometrical structures. Diffraction at high angles in fats correlates to close spacings between subcells (distances between parallel acyl groups in TAG), which enables the examination of various polymorphs

(Ribeiro *et al.*, 2015). In general, the most stable polymorph of triglycerides can be either a β′- or a β-crystal form. The density of the β-crystal is slightly higher compared to the other form which leads to more severe packing constraints for the β-crystal form. The predominant part of milk fat always remains within the β′ form and also has the highest clear point at 35°C (ten Grotenhuis *et al.*, 1999). Fats with crystals in the β′ form are of particular interest for the production of butter and margarines because of their functionality as they are softer, provide good aeration and have creaminess properties (O'Brien, 2012). The α form which is hexagonal is the least stable of the three polymorphs and has a clear point of about 20°C. There is a fourth polymer which may be found. This is called the γ form and has a lower melting point than the α form and is structurally similar to the β′ and can also be regarded as a low melting β′ modification (ten Grotenhuis *et al.*, 1999). Figure 1.9 illustrates the structure of these polymorphs.

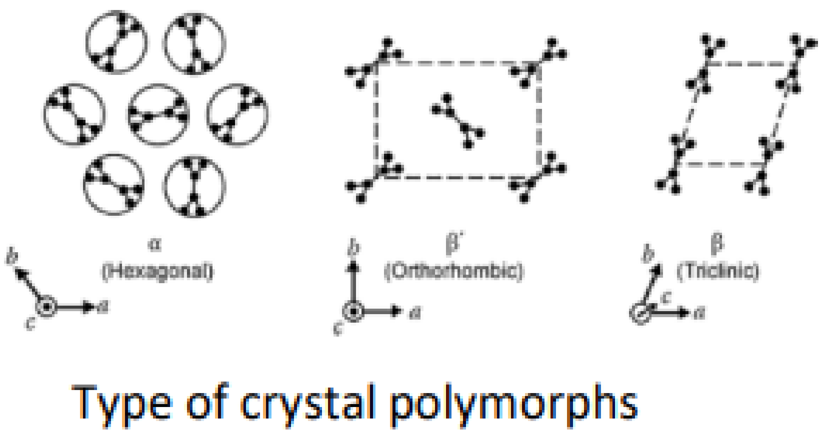

Figure 1.9: α, β′ and β crystal polymorphs (taken from Arita-Merino, 2022).

The d-spacings (short-spacings) of the crystal lattices, which are normally between 3Å and 6Å in length and correspond to the separations between the lateral packing of the fatty acid hydrocarbon chains, are what distinguish the polymorphic forms. The d-spacings of the triglyceride polymorphs are listed in Table 1.5. Triglycerides often take the form of either β′- or β-crystal as their stable polymorph. Because the density of the β-crystal form is higher than that of the β′-crystal form, the first form experiences more severe packing limitations than the later (ten Grotenhuis *et al.*, 1999).

Polymorph	Strongest X-ray short spacings (Å)	Subcell form
α	4.15	Hexagonal H
β′	3.8 and 4.2 or 3.71, 3.97, and 4.27	Orthorhombic $O_{\perp}$
β	3.5–4.0 and 4.6	Triclinic $T_{\parallel}$
γ (This is a low-melting β′-modification.)	3.7 and 4.2	Orthorhombic $O_{\perp}$

Table 1.5: Nomenclature and assignment of Polymorphs in Triglycerides (taken from D'Souza, deMan and deMan, 1990).

1.4 Economics of Butter

The global butter market size was USD 37.01 billion in 2021 with this figure anticipated to grow to USD 49.07 billion by 2028. On the onset of the global pandemic in 2020 the global market size was USD 35.61 billion (Fortune Business Insider, 2022).

In the initial months of the pandemic milk sales were disrupted due to supply chain issues. However, as time moved on the positive effect of the pandemic on sales began to be seen. As consumers had significantly more free time many turned to baking to occupy themselves through this stressful period. For others, baking was necessary due to the restriction in sales of ready to bake products (Fortune Business Insider, 2022).

Over the past number of years, the purchasing behaviour of consumers has significantly altered as people are more conscious of their health and wellness which has led to increased sales in products with natural and healthy ingredients. These naturally sourced products are perceived to be more beneficial compared to other processed food products. As a result of this trend several dairy products have become popular due to their natural properties and absence of artificial ingredients. For instance, butter contains saturated fats which are now perceived to healthier than unsaturated fats if consumed in moderation (Fortune Business Insider, 2022).

The growing demand for processed food products has also driven global butter sales in recent years. Confectionary products such as cakes, bread, biscuits and cookies require butter as a key ingredient during their manufacture with the popularity of these products expected to continue growing. Butter also has an application in ready-to-cook and ready-to-eat meals which are thriving in popularity. The continued evolution of dairy beverage products in the coming years is also forecast to increase butter sales. In addition, more people are eating outside of the home with more regularity which will continue to help the increase the usage of butter across hotels, restaurants and catering services throughout the world (Fortune Business Insider, 2022).

The increased demand for butter products illustrates the need for increase production with the valorisation of winter cream seen as a method of achieving increased output during off peak months.

1.4.1 Market Size of Butter

The global butter market can be segmented firstly by type which includes salted and unsalted (can be cultured or uncultured) butters. Salted butter has the largest global market due to its accessibility and demand. Its commonly sold as packaged butter in both foodservice channels and retail outlets. Meanwhile, unsalted butters can be further broken down into both cultured (lactic butter) and uncultured (sweet cream) products. Unsalted variations of butter have several popular applications in processed foods such as noodles, pastas and confectionary products (Fortune Business Insider, 2022).

Next, we can look at end use analysis. This area can be divided into industrial processing, retail channels(consumers) and food service channels. Industrial processing is the dominant player in this area with growth fuelled by the rising consumer demand for processed food products. By the end of 2020, industrial processing accounted for 67.81% of the total global butter market share. This increased demand for processed foods has led to the increased investment in the development of novel food products by food processors which can also be considered a contributing factor to the increased demand for butter among these manufacturers. The rapid growth of retail channels is a result of their improved distribution capabilities. The selling of packaged butter is supported well by these outlets. Consumer interest in baking at home has grown recently, either out of necessity or as a hobby. Due to the rising popularity of home cooking during the pandemic, the packed butter market has seen significant expansion (Fortune Business Insider, 2022).

Finding solutions to make the production of winter butter a more attractive proposition to butter manufacturers, third party traders and most importantly the consumer is a worthwhile area to investigate due to the rising demand globally for Irish butter. The Kerrygold butter brand which is owned by Ornua became the first Irish food brand to exceed €1 billion of annual sales in 2018 and increased to €1.3 billion by 2020. Ornua hope to increase sales of the Kerrygold brand to €2 billion by 2025 through securing a greater market share in the US where it's now the number two butter brand. This represents a doubling of the 2018 figure(Burke-Kennedy, 2021)

1.4.2 Key Manufacturers of Butter

In 2021 in the E.U there was over 2,075,357 tonnes of bulk butter produced. Of this, over 275,000 tonnes were produced in Ireland which represents 13% of total E.U output. The biggest producer in Europe was Germany with 471,057 tonnes produced which equates to 23% of total EU butter production. In 2021, there was a slight decrease in production of butter by 2.9% with 2,136,916 produced in 2020 (CLAL, 2022).

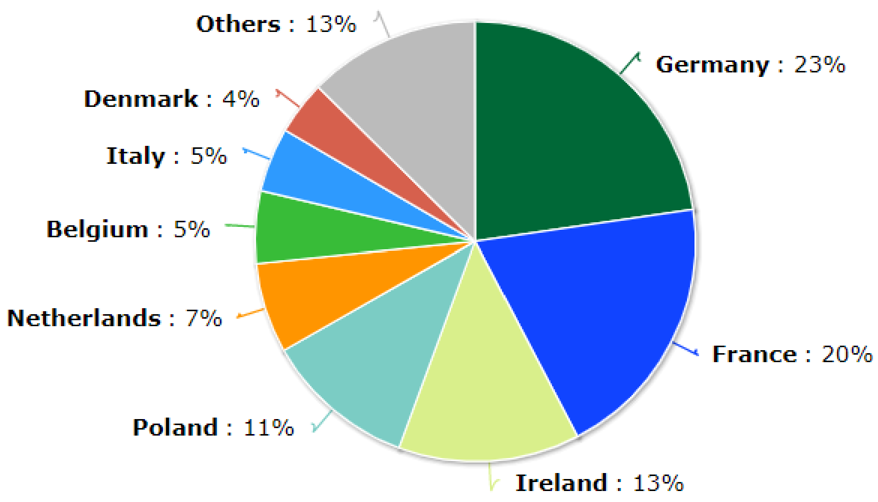

Figure 1.10: The percentage of production of Butter owned by each country in Europe in 2021, (taken from CLAL, 2022).

Ireland has seen, since the abolition of milk quotas in 2015 a major expansion of dairy farms along with the transition of traditionally beef farms to dairy farms. In order to accommodate this several milk processors throughout Ireland have had to expand in order to process the excess volume of milk. Some of the major processors in Ireland include Glanbia, Kerry, Dairygold, Aurivo, Lakelands and Tipperary Co-operative. These companies produce a wide variety of dairy products such as butter, milk powders, cheese and milk concentrates. The majority of butter produced is sold under the Ornua brand and exported to Europe while other regions where butter is supplied to include South East Asia, The Middle East and North Africa. Globally, Fonterra Co-operative Group (New Zealand), Land O'Lakes(U.S.A) and Arla Foods(Denmark) are considered some of the major players in the global butter market (Fortune Business Insider, 2022).

1.4.3 Key Users

Ornua Foods is responsible for the global marketing of several Irish dairy brands including Kerrygold butter. They have marketing teams in locations throughout the globe including Europe, Africa, Asia and the U.S which help raise awareness of the Irish dairy brands. One of the key butter markets for Ornua is Germany with Kerrygold regarded as the number one butter brand ('Ornua | Our Brands | Meet the Ornua Family of Brands', 2022).

1.4.4 Downgrade Product

Butter that doesn't match the required specification for customers can often be further processed through oiling. For instance, butter with an FFA value of greater than >0.40% oleic acid is considered rancid and can be processed further. Butter with microbial issues such as high total viable counts (TVC) (>10,000 cfu/g) can also be used for this purpose. By almost completely eliminating moisture and non-fat particles from pasteurised cream or butter, anhydrous butteroil is created. The final product has a minimum shelf life of 12 months and must have at least 99.8% milkfat and 0.10% moisture (U.S Dairy Export Council, 2018)

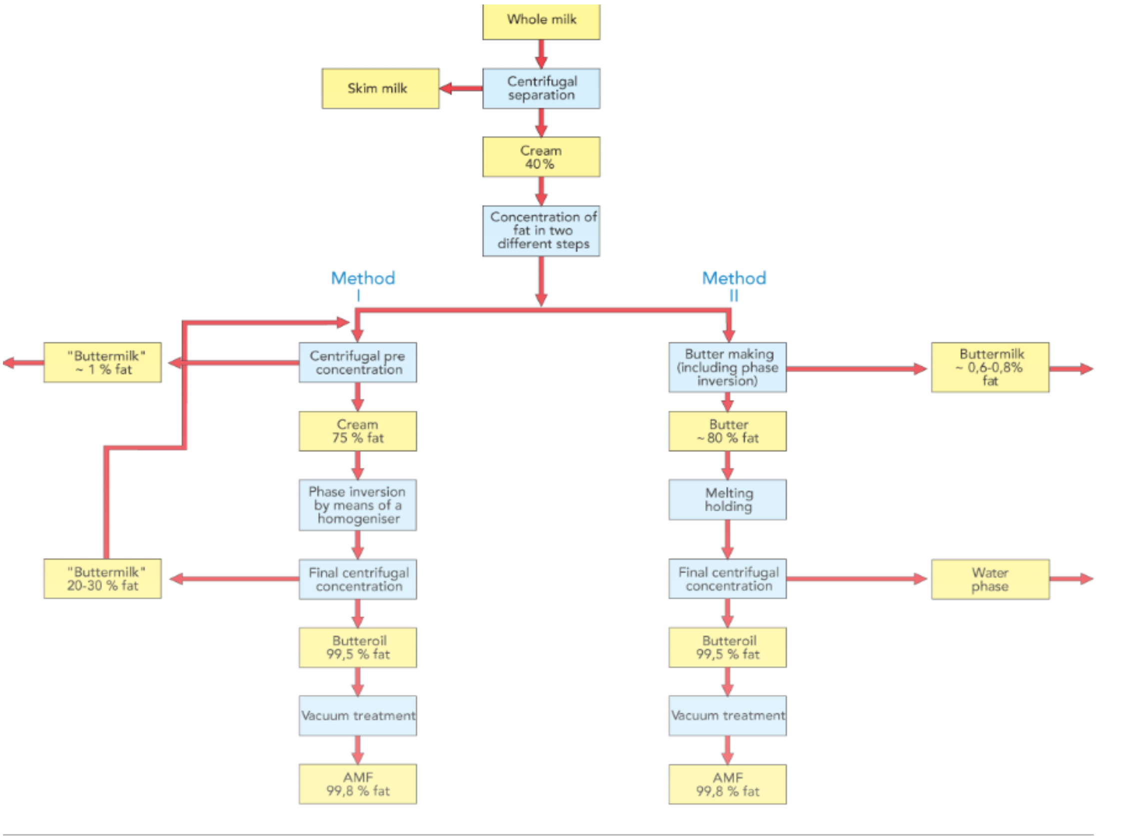

Figure 1.11: Block chart showing the principal of AMF production (taken from Dairy Processing Handbook, 2021).

1.5 Thesis Outline

This thesis will explore the potential to improve the quality of winter cream for the purposes of producing a higher quality butter during the winter period. This will be done so by reviewing studies relating to the fatty acid composition, FFA level, hardness and milk fat crystalline structure within butter and cream. The concept behind this thesis is to gain a better understanding of how cream processing parameters can be altered to produce a more desirable butter during the winter period with the four parameters previously mentioned.

Each of the sections within the results chapter will explore the impact of changing cream processing parameters and the relationship with the headings mentioned above. The aim is to form a relationship with how cream can be altered to produce a higher quality butter during the winter period.

There is a gap in the literature with regard to how cream processing parameters can be altered to produce a more desirable softer butter during the winter period. This led to the development of the research question: Exploring the Influence of Cream Processing Parameters on Butter Quality.

Chapter 2:

Materials & Methods

Exploring the Influence of Cream Processing Parameters on Butter Quality and Associated Methods

2.1 Methods

This chapter will discuss in some detail the research methodology used to demonstrate the influence of cream processing parameters on the overall quality of butter. The research method was desk-based study with material obtained from peer reviewed published research papers.

2.1.1 Thesis Outline of Research

The research was conducted to explore the potential to improve the quality of winter cream for the purposes of producing a higher quality butter during the winter period.

Chapter 1 reviewed the history of butter and cream and its main constituents. It detailed the manufacturing process of butter along with the seasonal influences on the constituents of the final product. Chapter 1 also looked at the importance of some of the key characterising factors of butter including its fatty acid composition, FFA, butter hardness and the crystalline structure. Lastly, it also reviewed the economics of butter including the market size, key manufacturers, users along with brief information regarding downgrade product.

Chapter 2 will outline the materials and methods used, to address the research question.

Chapter 3 will outline the results and findings relative to the impact of changing cream processing parameters to produce a more desirable product during the winter months. With reference to the research title, it will examine the impact of changing cream processing parameters on the fatty acid composition, FFA levels, butter hardness and milk fat crystalline structure in butter.

Chapter 4 will review and discuss the key findings on the fatty acid composition, FFA levels, butter hardness and milk fat crystalline structure in butter, allowing conclusion on the research question.

Chapter 5 will summarise the key findings and future work.

2.1.2 Scope

The scope of this thesis seeks to evaluate the potential to improve the quality of winter cream for the purposes of producing a higher quality butter during the winter period. Specifically, the focus will be on the impact of a variation of cream processing parameters on the fatty acid composition, FFA levels, hardness and milk fat crystalline structure on butter. It will be done by firstly, understanding and researching butter and cream including its history, main constituents, processing parameters and seasonal influences. Secondly, how cream processing parameters can be improved to valorise the usage of winter cream. Lastly, the growth of butter within the dairy industry will be examined

2.1.3 Data Inclusions

The data throughout this thesis was taken from quantitative studies. These studies ranged over a period of time dating back to 1990 and as recent as 2022. Due to the age of the dairy industry many older studies contain data that is still current.

2.1.4 Exclusions

Non peer reviewed data has been excluded for review data. Unsubstantiated data has also been excluded from the review.

2.1.5 Statistics

Statistical analysis has not been carried out, as part of this study, as to do so would have been inappropriate, due to the lack of available raw data. The desk-based study data was deemed statistically sound as the papers reviewed showed repeatability and reproducibility. They consisted of a sizable data quantity of tests while statistical analysis was conducted by the primary researchers. This was done so through the single factor variance analysis (one-way ANOVA) and by Tukeys's test ($p<0.05$). Two-way ANOVA was also carried out on selected papers. Fishers least significant difference (LSD) was used as a follow up to ANOVA on certain papers.

2.2 Materials

2.2.1 Study Range

The data obtained from the studies on butter and cream used were from peer reviewed research papers that were found globally. The studies were carried out using samples obtained solely from bovine dairy.

2.2.2 Challenges

The key challenge of the valorisation of winter cream was focused on. Cream processing parameters were altered for instance a variety of cream cooling and ripening times were altered to see if they could produce desirable characteristics which would lead to the production of higher quality butter during the winter period.

2.2.3 Dairy Inclusions

The inclusion criteria involved the dairy from bovine sources due to its production and consumption globally. North America holds the highest share in the global butter market followed by Europe and Asia Pacific, respectively. With global consumption of bovine milk equalling 85%, dairy from non-bovine sources have been excluded due to the low levels, in relative terms, of non-bovine dairy consumed globally.

2.2.4 Dairy Exclusions

Dairy from non-bovine sources has been excluded due to the low level used globally within the butter manufacturing industry. The impact of non-bovine butter and cream on the overall butter industry is a result negligible.

2.2.4 Butter Characteristics/Composition

This thesis focused on the impact of altering cream processing parameters with regard to the fatty acid composition, FFA levels, hardness and milk fat crystalline structure in the final butter. The above parameters were focused on due to their functionality in characterising butter during commercial sale. For instance, high levels of UFAs in butter tend to produce softer butter, FFA values of <0.40% (m/m) expressed as oleic acid are most desirable. Values obtained that are >0.40%(m/m) are considered rancid. Butter hardness for Irish butter is typically <2.0N, while the presence high levels of β' crystals tend to be associated with softer butter.

Chapter 3: Results

This chapter will outline the results and findings relative to explore the potential to improve the quality of winter cream for the purpose of producing higher quality butter during the winter period. With reference to the research title, the impact of cream processing parameters on the fatty acid composition, free fatty acid levels, butter hardness and milk fat crystallisation, will be examined. There is great scope for improvement for butter producers by altering cream used to make butter during the winter months to achieve a more desirable end product for the consumer. The fatty acid composition of butter outlines the relative levels of UFAs and SFAs in the butter. FFA measures the level of free fatty acid in butter which is an indicator of rancidity. Butter hardness measures the firmness of a butter in N. The most desirable hardness values range from 0.8-1.0N. The type of milk fat crystals produced are also examined. The quantity and kind of milk-fat crystals present at the application temperature have a significant impact on the functional qualities of milk fat. The presence of β' crystals in milk fat leads to the development of a softer final butter.

3.1 Fatty Acid Composition

3.1.1 Effect of cream cooling temperature and acidification method on the fatty acid composition of butter

A study by (Ceylan and Ozcan, 2020) examined the effect of cream cooling temperature and acidification method on the fatty acid composition of butter. Nine samples were prepared with a variation of cream cooling temperatures 6°C and 8°C and ripening times 3 hours and 10 hours used along with a variation in the addition of lactic acid permeate and starter culture. The control sample used was cooled at 10°C and ripened for 3 hours with the addition of a conventional starter culture. Table 3.1 outlines the breakdown of addition.

Sample Code	Cream Cooling/Crystallization Temperature (°C) and Time (hour/h)	Acidification Method and Ripening
Co (Control)	10 °C–3 h	Production by conventional method and ripening with starter culture
C6/10	6 °C–10 h	Starter culture injection/Cooling to 6 °C/10 h ripening
C6/15	6 °C–15 h	Starter culture injection/Cooling to 6 °C/15 h ripening
L6/10	6 °C–10 h	Lactic acid permeate injection/Cooling to 6 °C/10 h ripening
L6/15	6 °C–15 h	Lactic acid permeate injection/Cooling to 6 °C/15 h ripening
C8/10	8 °C–10 h	Starter culture injection/Cooling to 8 °C/10 h ripening
C8/15	8 °C–15 h	Starter culture injection/Cooling to 8 °C/15 h ripening
L8/10	8 °C–10 h	Lactic acid permeate injection/Cooling to 8 °C/10 h ripening
L8/15	8 °C–15 h	Lactic acid permeate injection/Cooling to 8 °C/15 h ripening

Table 3.1: Experimental design for butter samples production (taken from Ceylan and Ozcan, 2020).

Gas chromatography (GC) was used to determine the fatty acid profiles at the time of initial production. Milk fat was extracted, and fatty acid methyl esters (FAMEs) were analysed using an Agilent 6890N Series gas chromatograph from (Hewlett-Packard Co., in Avondale, Pennsylvania, USA) with a flame ionization detector and an (Agilent DB23 column; 60 m, 0.25 mm) in split mode. With the use of an HP computer integrator, the peak areas of triplicate injections were measured. Results were presented as a (%) of total fatty acid. Statistical analysis was undertaken using analysis of variance (ANOVA) and followed up with Fisher's LSD test.

Butter Samples	Milk Cream	Co	C6/10	C6/15	L6/10	L6/15	C8/10	C8/15	L8/10	L8/15
SCFA										
(C 4:0) Butyric acid	1.53	2.16	2.00	1.84	1.55	2.04	2.01	1.99	1.88	2.04
(C 6:0) Caproic asit	1.28	1.50	1.50	1.39	1.33	1.40	1.57	2.07	0.47	1.46
MCFA										
(C 8:0) Caprylic acid	0.78	0.98	0.97	0.93	1.60	0.97	0.96	0.93	0.94	0.98
(C 10:0) Capric acid	2.07	2.33	2.34	2.27	1.85	2.36	2.32	2.21	2.30	2.37
(C 11:0) Undecanoic acid	Non	0.14	0.04	0.03	Non	0.05	0.07	0.19	0.04	Non
(C 12:0) Lauric acid	2.69	2.89	2.89	2.83	2.26	2.92	2.87	2.71	2.87	2.94
(C 13:0) Tridecanoic acid	Non	Non	Non	Non	Non	Non	Non	Non	Non	Non
(C 14:0) Myristic acid	10.04	10.59	10.58	10.51	8.39	10.71	10.54	9.93	10.47	10.74
(C 14:1) Myristoleic acid	0.82	0.91	0.91	0.91	0.74	0.92	0.92	0.87	0.92	0.92
(C 15:0) Pentadecanoic acid	1.03	1.05	1.05	1.05	0.86	1.06	1.05	1.00	1.04	1.07
(C 15:1) *cis*-10-Pentadecanoic acid	Non	0.34	0.34	0.34	0.27	0.27	0.34	0.32	0.34	0.34
LCFA										
(C 16:0) Palmitic acid	28.54	30.08	29.89	30.13	25.9	30.18	29.93	28.47	29.59	30.11
(C 16:1) Palmitoleic acid	1.30	1.47	1.46	1.47	1.13	1.47	1.46	1.38	1.44	1.47
(C 17:0) Heptadecanoic acid	Non	0.64	0.64	0.64	0.49	0.64	0.64	0.59	0.63	0.64
(C 17:1) *cis*-10-Heptadecanoic acid	Non	0.26	0.26	0.26	0.33	0.27	0.26	0.25	0.26	0.26
(C 18:0) Stearic asit	13.44	11.67	11.84	11.98	11.14	11.71	11.64	11.62	11.54	11.75
(C 18:1) Oleic acid	22.38	27.92	28.8	28.36	23.24	28.52	28.14	26.73	27.86	27.95
(C 18:1 trans) Elaidic acid	Non	Non	Non	Non	Non	Non	Non	Non	Non	Non
(C 18:2) Linoleic acid	2.44	2.62	2.64	2.67	2.62	2.62	2.62	2.54	2.71	2.60
(C 18:2 trans) Linoleelaidicic acid	Non	0.12	0.19	Non	0.91	Non	0.23	0.12	0.08	0.15
(C 18:3) Linolenic acid	0.29	0.27	0.27	0.28	0.31	0.27	0.27	0.22	0.29	0.27
(C 18:3n3) Alfa Linolenic acid	Non	Non	Non	Non	Non	Non	Non	Non	Non	Non
(C 18:3n6) Gamma Linolenic acid	Non	0.06	Non	0.07	Non	Non	0.08	0.05	0.07	0.07
VLCFA										
(C 20:0) Arachidic acid	0.44	0.21	0.21	0.21	0.27	0.21	0.20	0.23	0.21	0.21
(C 20:1) *cis*-11-eicosenoic acid	1.59	0.34	0.21	0.30	0.69	0.20	0.36	1.05	0.55	0.29
(C 20:2) *cis*-11.14 eicosadienoic acid	0.41	0.17	0.17	0.17	Non	Non	0.18	0.07	0.18	0.18
(C 20:3) *cis*-8.11.14 eicosatrienoic acid	Non	Non	Non	Non	Non	Non	Non	Non	Non	Non
(C 20:3n3) *cis*-11.14.17 eicosatrienoic asit	Non	Non	Non	Non	Non	Non	Non	Non	Non	Non
(C 20:4n-6) Arachidonic acid	Non	0.06	Non	Non	0.39	Non	Non	0.12	Non	Non
(C20:5n-3) *cis*-5.8.11.14.17 eicosapentaenoic acid (EPA)	Non	Non	Non	Non	Non	Non	Non	Non	Non	Non
(C 21:0) Heneicosanoic acid	0.31	0.11	Non	0.11	Non	0.11	0.11	0.19	0.11	0.1
(C 22:0) Behenic acid	0.46	0.07	Non	0.09	Non	0.08	0.12	0.19	0.09	0.1
(C 22:1n-9) Erusic acid	Non	Non	Non	Non	Non	Non	Non	Non	Non	Non
(C 22:2) *cis*-13.16 docosadienoic acid	Non	Non	Non	0.03	0.54	Non	Non	0.23	Non	Non
(C 22:6n-3) *cis*-4.7.10.13.16.19 docosahexaenoic acid (DHA)	Non	Non	Non	Non	Non	Non	Non	Non	Non	Non
(C 23:0) Tricosanoic acid	1.11	1.00	0.63	1.00	1.16	0.59	1.09	1.64	1.98	0.88
(C 24:0) Lignoseric acid	Non	Non	Non	0.03	Non	0.13	Non	0.07	0.14	0.06
(C 24:1n-9) Nervonic acid	Non	Non	Non	Non	Non	Non	Non	Non	Non	Non
Omega 3 (EPA + DHA)	0.29	0.27	0.27	0.27	0.31	0.27	0.27	0.22	0.28	0.27
Omega 6 (EPA + DHA)	2.86	2.85	2.81	2.92	2.89	2.62	2.87	2.78	2.79	2.85

Table 3.2: Fatty acid composition of butter samples (g/100 g milk fat & %) (taken from Ceylan and Ozcan, 2020).

The most dominant saturated fatty acids (C4–C18) detected in butter samples were palmitic acid (25.90–30.18%), stearic acid (11.14–11.98%) and myristic acid (8.39–10.74%). The highest level of oleic acid was found in the cream which was cooled at 6°C and ripened for 10 hours. Oleic acid is a UFA which tends to promote softness and plasticity which may improve the spreadability of the butter (Jenkins and McGuire, 2006). Palmitic acid was highest in the cream which was cooled at 6°C and ripened for 15 hours. Palmitic acid is a SFA which is typically at high levels in winter butter

Fatty Acids	Cream	Co	C6/10	C6/15	L6/10	L6/15	C8/10	C8/15	L8/10	L8/15	*P-values*^{a}
SCFA	2.81^{h}	3.66^{b}	3.50^{d}	3.22^{f}	2.88^{g}	3.44^{e}	3.58^{c}	4.05^{a}	2.35^{i}	3.50^{d}	**
MCFA	17.43^{h}	19.23^{b}	19.12^{c}	18.87^{f}	15.97^{i}	19.26^{b}	19.07^{d}	18.15^{g}	18.92^{e}	19.35^{a}	**
LCFA	68.38^{h}	75.11^{e}	75.99^{a}	75.85^{b}	66.07^{i}	75.68^{c}	75.27^{d}	71.97^{g}	74.47^{f}	75.27^{d}	**
VLCFA	7.47^{a}	5.08^{d}	4.30^{f}	5.12^{d}	6.25^{bc}	4.21^{g}	5.15^{d}	6.19^{c}	6.32^{b}	4.94^{e}	**

Table 3.3: Fatty acid composition of butter samples according to carbon chain length (g/100 g milk fat & %). Abbreviations: Short-chain fatty acids (SCFA, C4:0 to C6:0); Medium-chain fatty acids (MCFA; C8:0 to C15:1); Long-chain fatty acids (LCFA; C16:0 to C18:3); Very long chain fatty acids (VLCFA, longer than 19 carbons). P values: Mean values in rows with different superscripts were significantly different. (*) $P < 0.05$; (**) $P < 0.01$; ns. non-significant (Ceylan and Ozcan, 2020).

Fatty acids are divided into groups as short (C4 – C6), medium (C8 –C14), long (C16 – C18) and very long chain fatty acids (longer than 19 carbons) by chain length (Bobe *et al.*, 2003). The classification of fatty acids in butter based on their carbon chain length is shown in table 3.3. The overall short chain fatty acid (SCFA) ratios of the butter samples ranged from 2.35 to 4.05%, and the medium chain fatty acid (MCFA) ratios ranged from 15.97 to 19.35%. The ratios of very long chain fatty acids (VLCFA) ranged between 4.21 and 7.47%, whereas those of long chain fatty acids (LCFA) ranged between 66.07 and 75.99%.

3.2 Free Fatty Acid (FFA)

Free fatty acid in butter can be determined using the following method. Around 2.0g of melted butter is weighed out and dissolved in 25ml of ether-alcohol solution and 1% phenolphthalein indicator in ethanol. This is then titrated against 0.1M sodium hydroxide solution until the sample begins to turn pink. The FFA content can then be calculated using the following equation where % FFA represents the percentage of free fatty acid, V is the volume of the solution, M represents the molarity of the NaOH solution while m corresponds to the mass of the butter sample. The results can be expressed oleic acid content(%m/m) (Medeiros Vicentini-Polette *et al.*, 2021).

$$\% \, FFA = \frac{(V.M.28.2)}{m}$$

Figure 3.1: Formula for % FFA expressed as oleic acid (taken from Medeiros Vicentini-Polette *et al.*, 2021)

3.2.1 The impact of milk cooling strategies on the FFA of milk.

The impact of milk cooling strategies on the FFA level of milk was investigated by (Wiking *et al.*, 2005). Cream is produced from the physical separation of milk as outlined in section 1.1.2 so understanding the how the FFA of milk can be managed is of interest to dairy manufacturers of butter. 8 samples were prepared for this study. Milk was collected from two groups of Holstein cows who were on differing diets as outlined in table 3.4. The first diet is the *High de novo* diet which is a low-fat diet while the second is the high saturated fat diet.

	High *de novo*	Saturated fat
Sugar beet pulp	453	555
Barley	329	
Soybean meal	206	312
Lipid supplement containing 80% Palmitic acid and 20% stearic acid		121
Mineral mixture	12	12
Total kg	1000	1000

Table 3.4: Composition of saturated fat diet and high de novo diet (kg) (taken from Wiking *et al.*, 2005).

After milking the milk was incubated at 31℃ for 90 minutes. The first set of milk was pumped at the incubation temperature and then later cooled to 4℃ in an ice water bath. A centrifugal pump was used to pump 7 litres of raw milk through the system for 450 s. The flow rate was regulated to 2274 l/h, corresponding to a wall shear rate of 565 s – 1. The next set of milk was cooled to 4℃ and pumped directly. Another two samples were segregated and were incubated at 4℃ for 15 minutes and 60 minutes respectively and then were pumped under the same conditions as outlined above. The FFA values of the 8 samples were analysed using the B.D.I method (Jellema *et al.*, 1991). Data from the pumping experiments were evaluated by a t-test between control and treatment.

FFA concentration in both milk types considerably increased after pumping at 31°C (Table 3.5). There was no increase in FFA levels in milk that had been incubated for 15 minutes or cooled to 4 °C right before pumping compared to control samples. However, both types of milk's FFA concentration significantly increased when milk was chilled and incubated for 1 hour prior to pumping. A significantly (P<0.05) higher level of FFA was found in milk from cows fed the saturated fat diet compared with milk obtained from cows on the *high de novo* diet when pumped after 1 hour incubation at 4℃. By pumping at 31°C, no significant variation in the content of FFA was discovered between the milk from cows fed either the high de novo diet or the saturated fat diet (Wiking *et al.*, 2005). The data obtained in this study is useful for cream processors as they can advise farmers on the optimal cooling conditions and feeding regimes to produce low FFA cream.

	Milk from High *de novo* diet		Milk from Saturated fat diet	
Temperature/time of incubation	Control	Pumped	Control	Pumped
31 °C	0·51±0·08	$1{\cdot}57^{P=0{\cdot}02}$±0·65	0·55±0·11	$0{\cdot}80^{P=0{\cdot}04}$±0·14
4 °C	0·44±0·09	0·54±0·18	0·55±0·09	0·62±0·15
4 °C/15 min	0·44±0·14	0·69±0·10	0·57±0·12	0·75±0·28
4 °C/60 min	0·50±0·10	$0{\cdot}78^{P=0{\cdot}03}$±0·15	0·69±0·15	$1{\cdot}59^{P=0{\cdot}01}$±0·47

Table 3.5: FFA content of the milk from cows fed the two different diets. The control is milk exposed to the temperature treatments but not subjected to pumping. The pumping duration was 450s and the shear rate 565 s – 1. Values are means ±SD for n= 4. Values without a common superscript indicates significant differences: P< 0.05. A, B between

control and pumped milk; a,b for pumped high de novo v. pumped saturated fat diet (taken from Wiking *et al.*, 2005).

3.3 Butter Hardness

Butter hardness can be measured in newtons(N).

3.3.1 Effect of cream aging temperature and agitation on butter texture

A study by (Lee and Martini, 2018) explored the combined effect of temperature at 5℃ & 10℃ and agitation rate 0, 40, 240RPM during the aging of cream on the physical properties of butter and cream in a model system. 100g of pasteurised cream with 40% fat content was transferred into a jar and set up to 1 of 2 aging temperatures (5℃ & 10℃). The cream was aged for 90 minutes while agitated with an overhead stirrer at 0 rpm (no agitation; NA), 40rpm (low agitation; LA) and 240 rpm (high agitation; HA). The aging time of 90 minutes was selected to ensure the complete crystallisation of the fat in the cream(Lee and Martini, 2018). Fresh butter was produced following a similar manufacturing process outlined in section (1.2.3).

The hardness of the samples was measured using the followed method. A penetrometry test was performed using a texture profile analyser with a spreadability rig. For each sample, five butter samples were placed into 5 cups. The samples were kept at room temperature (23℃) for 60 minutes before performing the test. The force (g) required for the probe to travel 23mm as a function of time (s) was plotted. The hardness of the butter sample was calculated using the peak force necessary to obtain the maximum penetration depth and then converted to Newtons(Lee and Martini, 2018). Tukey's multiple comparison was used for 1-way ANOVA for hardness while 2-way ANOVA was used to evaluate the effect of aging temperature and agitation level. Statistical differences were evaluated at $\alpha = 0.05$ level of significance(Lee and Martini, 2018).

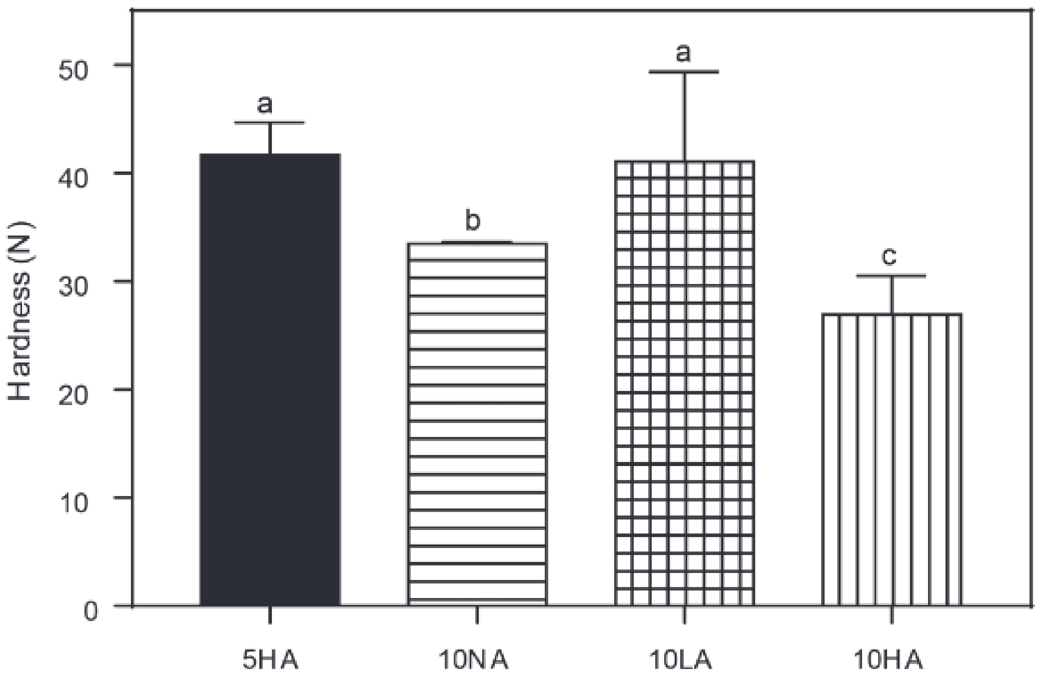

Table 3.6: Hardness (N) of butter stored at 5°C for 24 h. Butter was made with cream aged at 5 or 10°C with no agitation (NA), low agitation (40 rpm; LA), and high agitation (240 rpm; HA) and churned for 14.5 min at its aging temperature. The error bars represent the standard deviation of the mean (n = 2). Values sharing letters (a–c) are not significantly different (P > 0.05) (taken from Lee and Martini, 2018).

From Table 3.6 we can see that the hardest butter obtained or least spreadable was at 5℃ with 240 rpm (41N) and 10℃ with 40 rpm (40N) while the softest butter found was aged at 10℃ with 240 rpm (32N) (Lee and Martini, 2018). A study by (Herrera and Hartel, 2000) showed that a firmer material can be created by utilising a lot of small crystals. The number of crystals can be influenced by agitation, age, or churning temperature. High shear rates or agitation cause a lot of smaller crystals to form (Herrera and Hartel, 2000). The importance of this study is that it showed that hardness of butter can be controlled by the aging conditions of the cream. The dairy industry can benefit from this study's understanding of the connection between the aging processes of cream and the physical characteristics of butter (Lee and Martini, 2018). For instance, during the winter months butter hardness values tend to be higher than summer months. Applying the information found from this study can help butter manufactures produce a more desirable butter with a lower hardness which will be softer through controlling the aging and agitation of the cream.

3.3.2 Effect of modification of cream ripening and fatty acid composition on the consistency of butter

A study by (Schäffer, Szakály and Lőrinczy, 2001) compared how two cream ripening techniques can affect the butter's consistency. Cream obtained during the winter period was used in this study. The traditional (cold-warm-cold) ripening technique can increase the spreadability of winter butter. While the heat-step (warm-cold-cold) ripening techniques can be used to firm up the consistency of summer butters by selecting the ripening temperatures based on the melting and crystallization curves of milk fat. Both samples were enriched with LMP (Low melting point) fractions after the ripening and cooling of the cream preparation process. LMPs fractions are obtained from milk fat crystallised at different temperatures. The fraction that was used in this study was (LMP-20) and was created in a lab by crystallizing anhydrous milk fat at 20°C, followed by a filtration step to separate the liquid and the crystallized milk fat into low and high melting point fractions (Schäffer, Szakály and Lőrinczy, 2001).

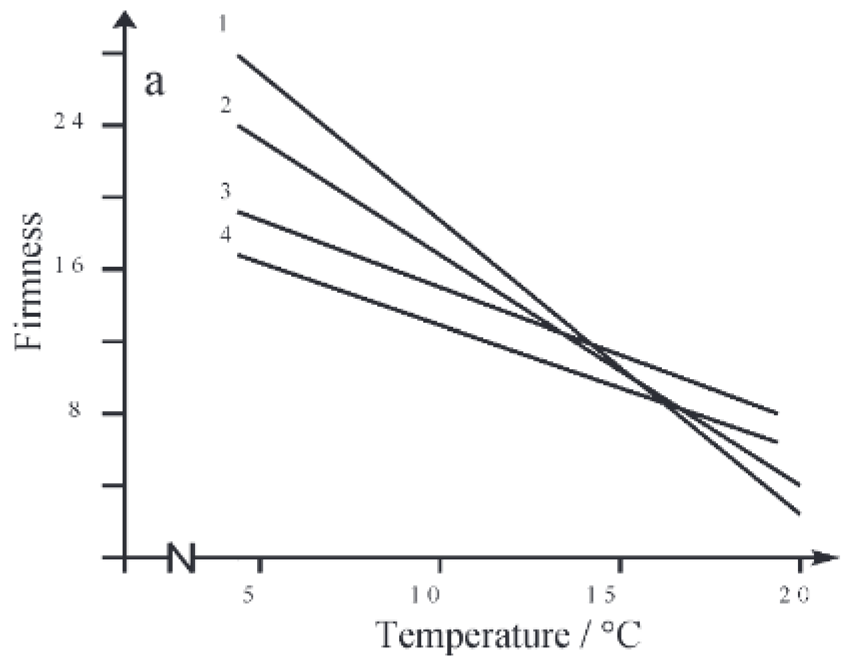

Figure 3.2: Consistency firmness of butters made of traditionally ripened cream containing 0% (1), 15% (2), 25% (3) and 30% (4) of LMP-20 milk fat fraction referred

to milk fat as a function of the temperature (taken from Schäffer, Szakály and Lőrinczy, 2001).

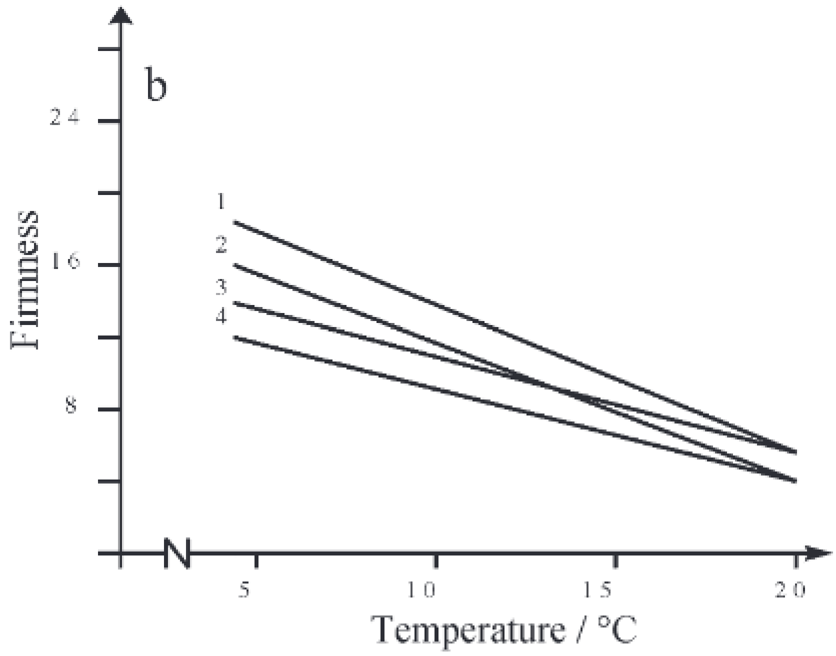

Figure 3.3: Consistency firmness of butters made of heat-step ripened cream containing 0% (1), 15% (2), 25% (3) and 30% (4) of LMP-20 milk fat fraction referred to milk fat as a function of the temperature (taken from Schäffer, Szakály and Lőrinczy, 2001).

Figures 3.2 and 3.3 illustrate how adding various amounts of a milk fat fraction with a 20°C melting point (LMP-20) affects the consistency and firmness of butters made from conventionally and heat-step ripened cream as a function of temperature. It is clear that, for both ripening techniques, adding milk fat fraction (LMP-20) to butter at a low temperature (below 10°C) reduces the firmness of the butter and increases its spreadability in proportion to its addition. The firmness values however, remain nearly the same at room temperature (20°C).

In comparison to butter made from normally ripened cream, butter made by the heat-step ripening and enrichment with an LMP milk fat fraction has a softer consistency at low temperatures (below 10 °C), which improves spreadability. For butter producers, this is crucial because adding an LMP milk fat fraction to winter cream will make the butter softer and more valuable to the business during the winter period.

3.3.3 Effect of cream cooling temperature and acidification method on the texture of butter

A study by (Ceylan and Ozcan, 2020) examined the effect of cream cooling temperature and acidification method on the hardness of butter. Nine samples were prepared with a variation of cream cooling temperatures 6℃ and 8℃ and ripening times 3 hours and 10 hours used along with a variation in the addition of lactic acid permeate and starter culture. The control sample used was cooled at 10℃ and ripened for 3 hours with the addition of a conventional starter culture. Table 3.7 outlines the breakdown of addition.

Sample Code	Cream Cooling/Crystallization Temperature (°C) and Time (hour/h)	Acidification Method and Ripening
Co (Control)	10 °C–3 h	Production by conventional method and ripening with starter culture
C6/10	6 °C–10 h	Starter culture injection/Cooling to 6 °C/10 h ripening
C6/15	6 °C–15 h	Starter culture injection/Cooling to 6 °C/15 h ripening
L6/10	6 °C–10 h	Lactic acid permeate injection/Cooling to 6 °C/10 h ripening
L6/15	6 °C–15 h	Lactic acid permeate injection/Cooling to 6 °C/15 h ripening
C8/10	8 °C–10 h	Starter culture injection/Cooling to 8 °C/10 h ripening
C8/15	8 °C–15 h	Starter culture injection/Cooling to 8 °C/15 h ripening
L8/10	8 °C–10 h	Lactic acid permeate injection/Cooling to 8 °C/10 h ripening
L8/15	8 °C–15 h	Lactic acid permeate injection/Cooling to 8 °C/15 h ripening

Table 3.7: Experimental design for butter samples production (taken from Ceylan and Ozcan, 2020).

The hardness values of the samples were measured using a texture analyser along with the wire cutting method outlined by (Rønholt *et al.*, 2014). Using a butter cutter probe that penetrated 35 mm/min from the sample surface at a speed of 1 mm/s, the cutting force (hardness) of butter was compared. The penetration force that was delivered to the sample was recorded as the butter's hardness. The measurements were done at 19± 1°C on one surface of the rectangular block of butter that measured 5 cm x 3 cm. Per treatment, six samples of each butter were examined. The hardness values during storage were also considered. On the first day, as well as the first, third, and sixth months of storage, analyses were carried out (Rønholt *et al.*, 2014).

Textural properties of butter samples.

Butter Samples	Hardness (g)
Co	1568.00[a]
C6/10	1431.29[c]
C6/15	1273.42[e]
L6/10	1497.03[b]
L6/15	1310.21[de]
C8/10	1463.27[bc]
C8/15	1318.31[de]
L8/10	1501.20[b]
L8/15	1351.50[d]
Storage	
1st day	1437.48[b]
1st month	1244.22[c]
3rd month	1502.39[a]
6th month	1466.67[ab]
ANOVA[a]	
Sample (S)	**
Storage Time (T)	**

[a] *P* values: Mean values in rows with different superscripts were significantly different. (*) $P < 0.05$; (**) $P < 0.01$; ns. non-significant.

Table 3.8: Hardness results in grams for the 9 samples with different cream/cooling temperatures and times. Hardness results during storage are also shown (taken from Ceylan and Ozcan, 2020).

The results of the texture analysis are given in table 3.8. The results are expressed in grams, these values can be converted into N using the following conversion rate: 1 gram = 0.0098 Newtons. Table 3.9 shows the conversion values. Depending on the type of butter and the amount of storage time, it was discovered that there were statistically significant differences between the textural qualities of butter samples at the level of $p < 0.01$. The control sample made using the traditional method had the highest firmness/hardness value, followed by L6/10 and L8/10. It was shown that the C6/15, L6/15, and C8/15 samples that were aged for fifteen hours were softer.

Butter Samples	**Hardness (g)**	**Hardness (N)**
Control	1568.00	15.37
C6/10	1431.29	14.03
C6/15	1273.42	12.48
L6/10	1497.03	14.68
L6/15	1310.21	12.84

C8/10	1463.27	14.34
C8/15	1318.31	12.92
L8/10	1501.20	14.72
L8/15	1351.50	13.25
Storage		
1st Day	1437.48	14.09
1st Month	1244.22	12.20
3rd Month	1502.39	14.73
6th Month	1466.67	14.38

Table 3.9: Hardness values converted from grams into Newtons: Conversion factor 1 gram = 0.0098 Newtons.

3.4 Milk Fat Crystallisation

3.4.1 Crystallisation mechanisms in cream during ripening and initial butter churning

A study by (Buldo, Kirkensgaard and Wiking, 2013) investigated polymorphism of fat crystals in the milk fat globule during the ripening and churning of the cream. Commercial winter cream with 38% fat was used for the ripening and churning of the cream. All data obtained was statistically analysed by 2-way ANOVA. By combining small- and wide-angle X-ray scattering measurements, the polymorphism of the fat crystals in the milk fat globules was examined during the ripening and churning of the cream. The X-ray scattering was performed using a small angle X-ray scattering (SAXS) instrument. While the churning step was replicated in a tabletop blender running at full speed, the ripening process was replicated by applying the same temperature (10°C) as utilized in the starch cell. After churning, the cream was aged at 10°C for about an hour. Samples were examined immediately following the ripening stage, after 2.14 and 3.4 minutes of churning, as well as on butter grains (Buldo, Kirkensgaard and Wiking, 2013). The polymorphism of oil droplets were classified into α, β', and β from the scattering patterns in accordance with (Lopez *et al.*, 2000) research.

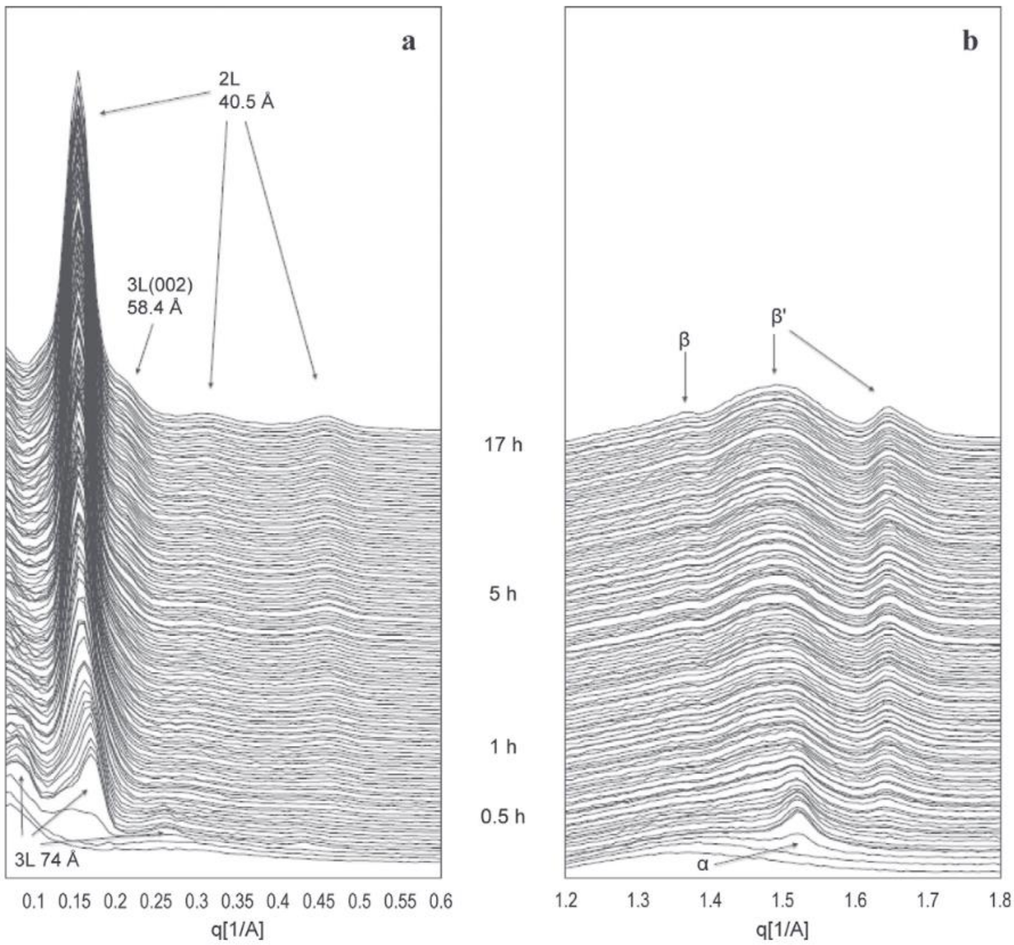

Figure 3.4 a&b: Small-angle X-ray scattering (a) and wide-angle X-ray scattering (b) spectra for cream ripened for 17 h at 10°C. 2L = double chain length structure; 3L = triple chain length structure; β = the polymorphic form of triacylglycerols (TAG) corresponding to the triclinic packing of the sub-cells; β' = the polymorphic form of TAG corresponding to the orthorhombic packing of the sub-cells; q = scattering vector [$q = 4\pi/\lambda \sin(\theta)$, where $\lambda = 1.54$ Å is the X-ray wavelength and θ is half of the scattering angle] (taken from Buldo, Kirkensgaard and Wiking, 2013).

After 10 minutes of ripening at 10°C, the first scattering was seen, and three peaks with a long spacing of 74 Å, corresponding to 3L packing, were visible (Figure 3.4a). This structure changed into a 2L packing with lengthy spacing of 40.5 Å in the ensuing 20 minutes. The initial packing was hexagonal lateral chain packing (4.15 Å), which corresponds to the unstable form of TAG, as indicated by the wide-angle scattering time evolution (Figure 3.4b;). After 33 minutes of ripening, the form peak lost some of its intensity, and two additional peaks (3.8 and 4.2 Å respectively) representing the orthorhombic sub-cell of the β'form of TAG developed. Peaks from the form of TAG finally began to accumulate after around an hour, displaying a 58.4 Å 3L packing and a weak peak at 4.6 Å. For the remainder of the ripening, these 3 crystals coexisted.

This is quite important for industry as it can help butter manufacturers choose the optimal ripening time for cream to create β' crystals as they lead to the production of softer butter which is outlined in section (1.3.4 milk fat crystallisation)(O'Brien, 2012).

3.4.2 Effect of cream cooling rate and water content on butter microstructure during storage

A study from (Rønholt *et al.*, 2014) explored the impact of cream cooling rate and water content on butter microstructure during four weeks of storage. 38% fat cream was used. The butter samples were prepared in lab scale and all used in triplicate. 6 samples were prepared through two different parameters. A moisture content of 20%, 26% & 32% was used while each of these were subjected to a fast cream cooling rate at (7.5°C/min) and a slow cooling rate of (0.4°C/min). The cream samples were kept at 65°C for 10 minutes to erase all the crystal memory and were subjected to either slow (0.4°C/min) or fast (7.5°C/min) cooling to reach a churning temperature of 10°C. The period of time between the beginning of churning and phase inversion was called the churning time. When butter grains and a liquid phase, buttermilk, developed, the churning was deemed to be finished. The necessary amount of water was then squeezed out of the butter to reach the desired moisture content. In order to prevent moisture loss during storage, the butter was finally packed in plastic containers designed for butter and kept at 5°C in a refrigerator (Rønholt *et al.*, 2014).

Sample	Churning time (min:sec)
Fast cooled cream	3:40 ± 0:12
Slow cooled cream	2:00 ± 0:10

Table 3.10: Churning times for fast and slow cooled cream taken from (Rønholt *et al.*, 2014).

Table 3.10 shows that the churning time for fast cooled cream is higher than slow cooled cream. The existence of bigger crystals among oil droplets in slowly cooled cream as opposed to quickly cooled cream can be used to explain why churning takes less time (Boode, Walstra and de Groot-Mostert, 1993).

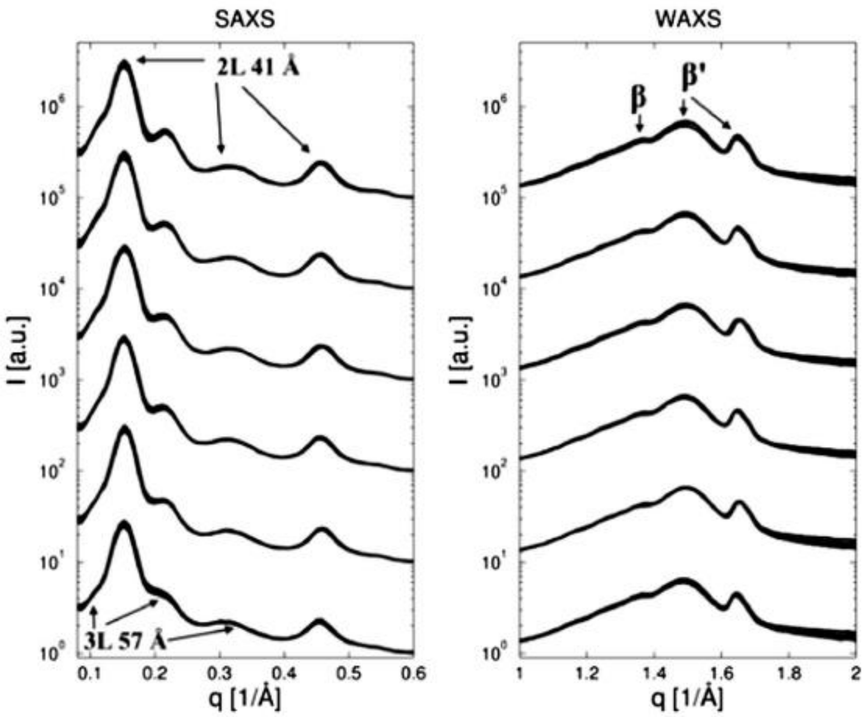

Figure 3.5: (SAXS) Small-angle X-ray scattering (left) and (WAXS) wide-angle X-ray scattering (right) spectra from all samples from day 1 (bottom curve) to day 28 (top curve) after production. Long spacings (1st, 2nd and 3rd order peaks are indicated): 41 Å 2L packing and 57 Å 3L packing (1st, 2nd and 3rd order peaks are indicated). Short spacings: β-4.6 Å and β' - 3.81 Å and 4.2 Å (taken from Rønholt *et al.*, 2014).

Milk fat can crystallise in either α, β or β' form in increasing order of stability. The time progression of small and wide-angle X-ray scattering (SAXS and WAXS), as determined at days 1, 4, 7, 14, 21 and 28 post production, is summarized in Figure 3.5. Similar spectra are shown by all samples in the SAXS and WAXS data. Wide angles reveal two significant peaks at 4.2Å and 3.81Å, which are consistent with the β' polymorph as shown in (Figure 1.8). Additionally, a minor peak at 4.6Å is seen and is consistent with remnants of β as shown in (Figure 1.8). A peak at 41Å, corresponding to a double layer (2L) packing of the triacylglycerols, as well as a peak at 57 Å, corresponding to a triple layer (3L) packing, are both visible at small angles. There was no changes to the WAXS pattern from days 1 through 28. In the SAXS spectra, an increase in the 3L peak (57 Å) is observed during storage (Rønholt *et al.*, 2014).

3.4.3 Effect of cream aging temperature and agitation on butter structure

A study by (Lee and Martini, 2018) explored the combined effect of temperature at 5℃ 10℃ & 15℃ and agitation rate 0, 40, 240RPM during the aging of cream on the physical properties of butter and cream in a model system. 100g of pasteurised cream with 40% fat content was transferred into a jar and set up to 1 of 3 aging temperatures (5℃, 10℃ & 15℃). The cream was aged for 90 minutes while agitated with an overhead stirrer at 0 rpm (no agitation; NA), 40rpm (low agitation; LA) and 240 rpm (high agitation; HA). The aging time of 90 minutes was selected to ensure the complete crystallisation of the fat in the cream(Lee and Martini, 2018). Fresh butter was produced following a similar manufacturing process outlined in section (1.2.3).

Firstly, the solid fat content (SFC) of the butter at various temperatures and agitation rates were examined. SFC is a good indicator of the rate of fat crystallisation. Figure 3.6 depicts the increase in SFC in cream aged at 5, 10, and 15°C with various levels of agitation (NA, LA, and HA) over the course of 90 minutes. Under all of the experimental conditions, the increase in SFC decreased and eventually reached a plateau after 90 minutes. The SFC values were highest at 5°C, then at 10°C and 15°C. After 90 min of cream aging at 5°C for NA, LA, and HA, respectively, the SFC values were 18.0, 18.6, and 19.2%, and these values were not substantially different from one another ($P > 0.05$). After 90 minutes at 10°C, the SFC values for the cream samples were 12.5, 13.5, and 13.6% for LA, NA, and HA, respectively. SFC values obtained under LA conditions were significantly lower than those obtained under HA conditions ($P < 0.05$), but samples aged under NA and LA or NA and HA conditions showed no difference in SFC values. SFC of samples aged with NA and LA at 15°C showed no difference ($P > 0.05$), while after 90 min of aging with HA, a considerably increased SFC ($P < 0.0001$) was seen. After 90 minutes at 15°C, the SFC values for NA, LA, and HA were 5.0, 5.0, and 6.4%, respectively. At all three aging temperatures, the SFC in cream samples aged with HA grew more quickly than in samples aged with NA and LA(Lee and Martini, 2018)

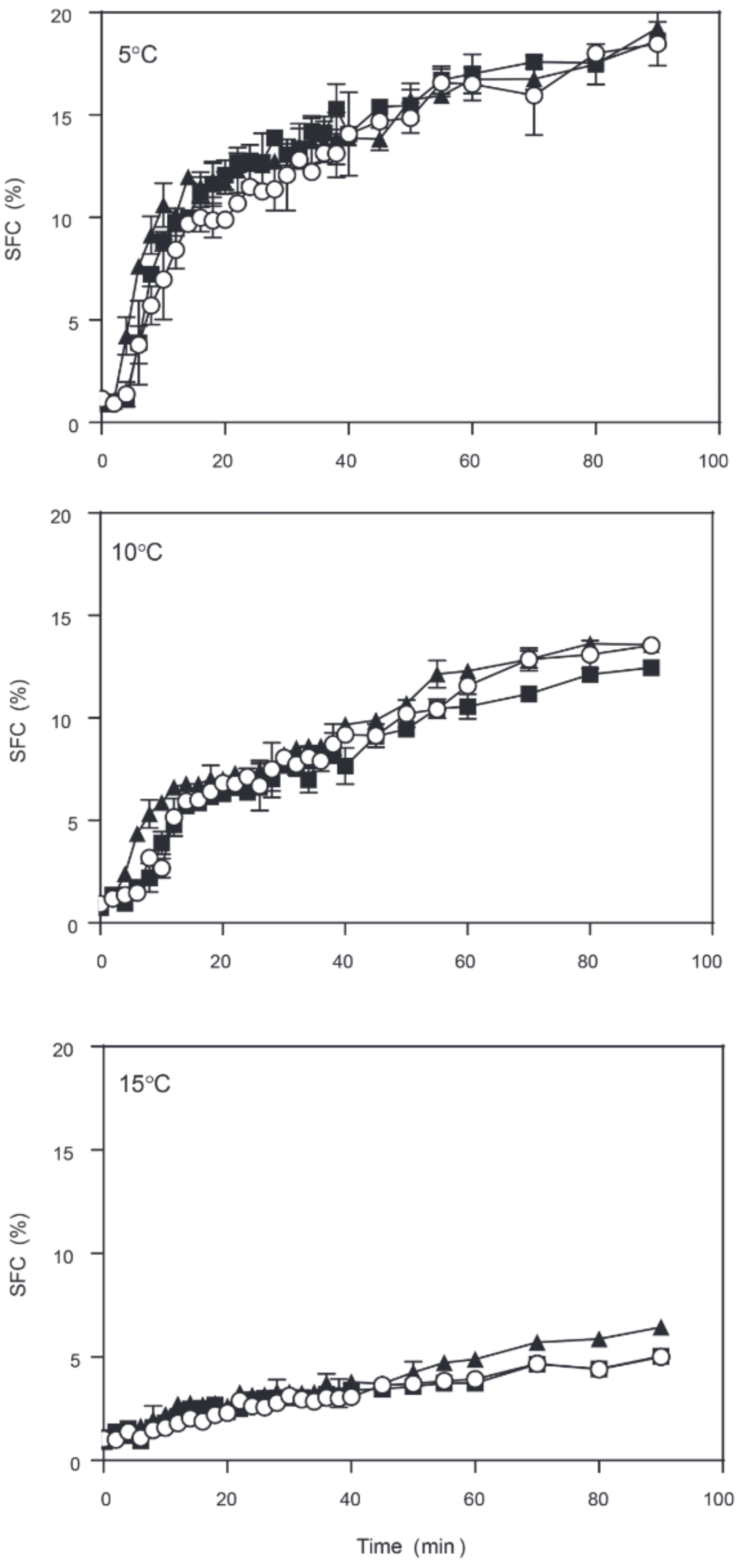
5°C
10°C
15°C
SFC (%)
SFC (%)
SFC (%)
0
5
10
15
20
0
20
40
60
80
100
Time (min)

Figure 3.6: Solid fat content (SFC) in cream aged at 5, 10, or 15°C with no agitation (NA, ○), low agitation (40 rpm; LA, ■), and high agitation (240 rpm; HA, ▲) for 90 min. The error bars represent the SD of the mean (n = 2) (taken from Lee and Martini, 2018).

The next parameter of interest that this study examined was the effect of the aforementioned parameters on cream droplet size. The amount of coalescence in an emulsion can be determined by the droplet size; the larger the droplet size, the more coalescence in the emulsion. Coalescence, which happens when two droplets combine to produce one large droplet, is an indication of cream instability. Emulsion instability or stability can be brought on by shear or agitation. Figure 3.7 displays the cream droplet size distributions that were measured after aging. The cream samples aged at various temperatures and stirred with LA showed a minor variation, whereas the cream samples stirred with NA and HA at 5, 10, and 15°C showed no difference. In contrast to cream aged at 5 and 10°C with LA, the cream aged at 15°C with LA had a higher quantity of bigger droplets (Lee and Martini, 2018). This is useful information for manufacturers of winter butter as they can apply the most suitable parameter here for instance LA with cream aged at 10°C which helps to reduce levels of cream instability during processing.

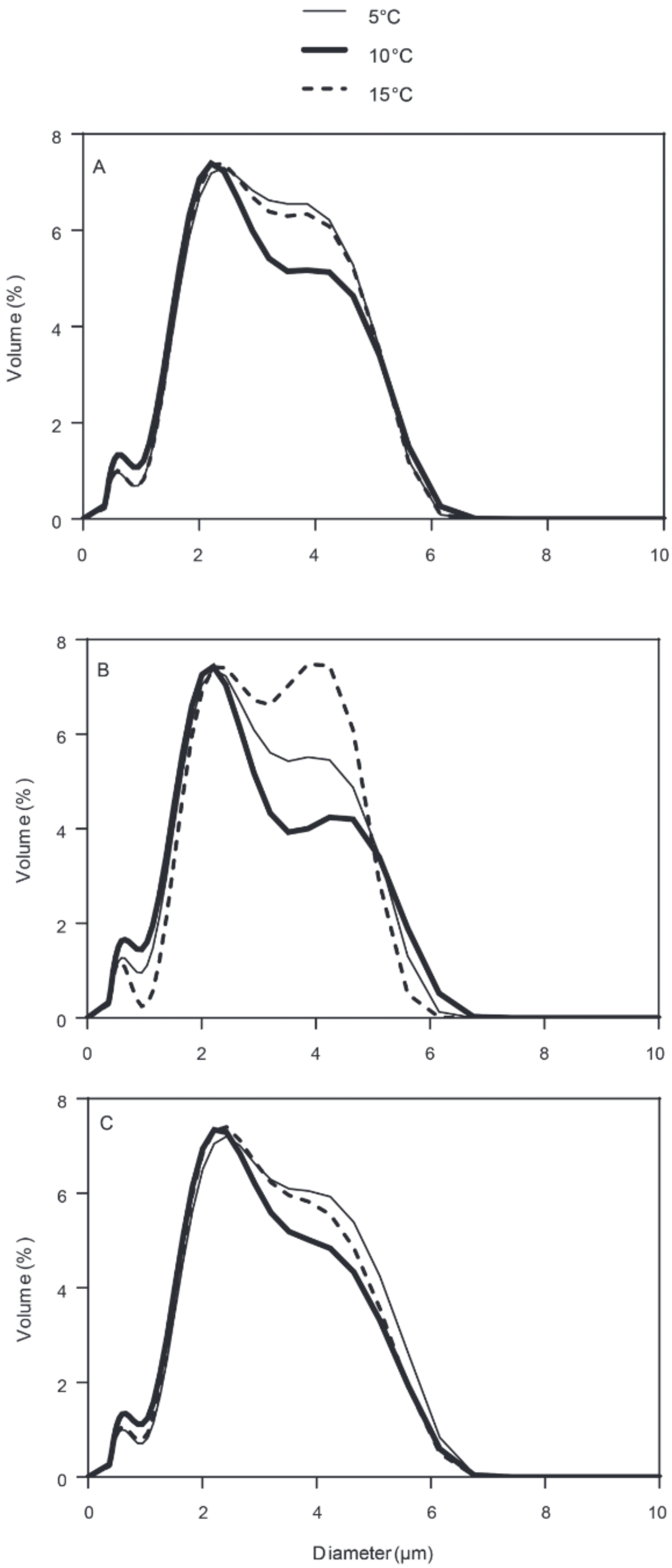

Figure 3.7: Droplet size distribution of fat droplets in cream aged at 5, 10, or 15°C with (A) no agitation, (B) low agitation (40 rpm), and (C) high agitation (240 rpm) for 90 min (Lee and Martini, 2018).

3.4.4 Effect of cream heat treatment on the polymorphism, microstructure and rheology of butter

A study by (Rønholt *et al.,* 2012) explored the effect of the heat treatment of cream on the polymorphism, microstructure and rheology of butter. The effect of the heat treatment on the polymorphism of the butter is most relevant to this section. For the first part of this study, cream with 38% fat was used. The cream was heated to 65℃ for 10 minutes to erase all the crystal memory and was subjected to first fast cooling (7.5℃/min) and slow cooling (0.4℃/min) to reach the required churning temperature of (10℃). From here for each cooling method a sample was stored at 5℃ for 48 hours which was considered the matured samples while further cream from each cooling method was prepared immediately after reaching the churning temperature (10℃) and was identified at the non-mature sample. Table 3.11 outlines the various samples which were created and analysed.

Identification of Cream	**Cooling Temperature**	**Maturity Status**
CS	0.4℃/min (Slow Cooling)	Not matured
CF	7.5℃/min (Fast Cooling)	Not matured
CMS	0.4℃/min (Slow Cooling)	Matured at 5℃ for 48 hours
CMF	7.5℃/min (Fast Cooling)	Matured at 5℃ for 48 hours

Table 3.11: Cooling temperatures and maturity status of samples analysed in figure 3.7.

X-ray scattering measurements were performed with a pin-hole collimated beam with the detector positioned asymmetrically to yield a single measurement q-range of 0.05–2.8 Å -1 with the magnitude of the scattering vector defined by q =4π/λsinΘ, where λ = 1.54 Å is the X-ray wavelength and Θ is half of the scattering angle. To gather all relevant peak data for both short and long spacings in a single test, SAXS and WAXS were measured simultaneously in this setup. The formula for calculating the d-spacings is d = 2π/q*, where q is the location of the Bragg peak. The samples were placed in cooled sample holders at 5 °C and sealed with mica windows that ranged in thickness from 5 to 7 μm while the background scattering from the mica was subtracted from the sample spectra (Rønholt *et al.*, 2012).

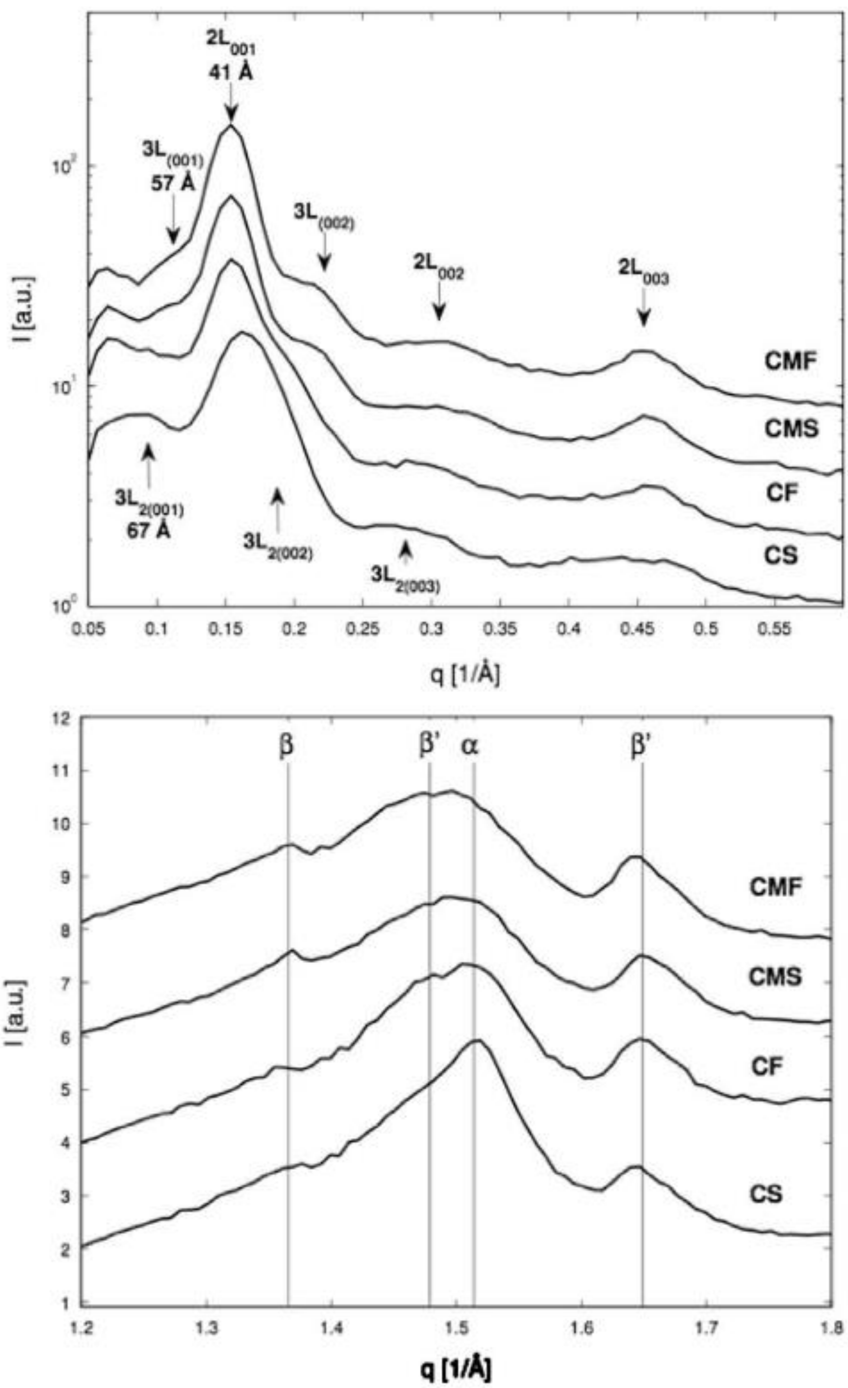

Figure 3.8: SAXS (Top) and WAXS (Bottom) spectra from cream at 5 °C subject to different temperature treatments. CS: slow cooled cream, CF: fast cooled cream, CMS: slow cooled and matured cream and CMF: fast cooled and matured cream. Vertical lines indicate the positions of the characteristic peaks from the polymorphs forms: a: 4.15 Å, b0: 3.81 Å, 4.2 Å, b: 4.6 Å (taken from Rønholt *et al.*, 2012).

From the SAXS and WAXS data in figure 3.8, the polymorphic forms of the four cream samples can be identified: CS: slow cooled cream, CF: fast cooled cream, CMS: slow cooled and matured cream and CMF: fast cooled and matured cream. The WAXS data shows that the non-matured cream samples (CS & CF) form predominately α and β' crystals with smaller traces of β crystals found. The transition of from α to β' and β crystals typical happens in maturing cream samples with the same conclusion can be drawn from the SAXS where the non-matured samples showing an α-related 3L structure around 67 Å combined with the typical β' 2L lamellae around 41 Å. As the crystals mature, the 3L arrangement transforms into a 57 Å stacking pattern, suggesting a crystal rearrangement from α to β' form crystals. This information may be quite useful for manufacturers of winter butter as introducing as introducing a maturing time of 5°C for 48 hours can lead to the promotion of β' crystals which have been shown to produce a more desirable softer final butter as outlined by (O'Brien, 2012).

To summarise the milk fat crystallisation section it was found that from (Buldo, Kirkensgaard and Wiking, 2013) study on cream ripening showed that the crystallisation state that promotes partial coalescence is obtained during the first hour of cream ripening. (Rønholt *et al.*, 2014) study on the effect of cream cooling rate on the microstructure of butter showed a faster cream cooling time increased the total churning time. (Lee and Martini, 2018) showed that in their study regarding the effect of cream aging time and agitation on butter properties showed cream droplet size which was treated with LA and aged at 10°C was the most likely to stay stable during processing. Lastly, (Rønholt *et al.*, 2012) study on the effects of cream heat treatment highlighted that a maturing time of 5°C for 48 hours can lead to the development of desirable β'crystals which can lead to the development of a softer butter.

3.5 Key Findings

The key findings throughout this chapter showed that there was a relationship between the altering of cream processing parameters and the final results of the key characteristics of butter. Various alterations to the cream cooling temperature, ripening times, agitation rates, acidification method and fatty acid composition saw different results which were noted under each of the headings in this chapter.

Fatty acid composition noted that a shorter cream ripening time resulted in higher levels of oleic acid which is a UFA while the longer ripening time resulted in higher levels of palmitic acid which is an SFA. High levels of UFA are associated with the development of a softer butter. With regards to FFA in milk, it was discovered that lowest FFA values were found in milk cooled in a plate heat exchanger to 4°C and pumped directly without an incubation time after cooling.

For butter hardness, the combined effect of a cream ripening time at 10°C with agitation at 240rpm was seen to produce the softest butter with the introduction of a high shear rate and agitation producing a higher number of smaller crystals. The addition of an LMP-20 milk fat fraction along with the usage of the heat-step cream ripening method can lead to the development of a softer butter. For cream cooling temperature and ripening, the best cooling temperature was found to be 6°C along with a ripening time of 15 hours was found to produce the softest butter.

Lastly, in the milk fat crystallisation section, it was found that the crystalline state that promotes the development of β' milk fat crystals can be found during the first hour of cream ripening. Slow cooling of cream was found to reduce churning time which favours the formation of larger crystals with fewer contact points which in turn produces a softer butter. A cream aging temperature of 5°C along with an agitation rate of 240 rpm was shown to produce the highest amount of SFC which is an indicator of the rate of milk fat crystallisation. Slow cooled cream which was matured at 5°C for 48 hours was found to produce the highest level of the desirable β' milk fat crystals.

Chapter 4: Discussion

The focus of this thesis was to explore the potential to improve the quality of winter cream, for the purposes of producing higher quality butter during the winter period. This chapter will present an overview of the introduction chapter and an analysis of the results chapter. The aim is to compare desk-based research studies, noting similarities and dissimilarities. The results will be discussed in relation to the research question.

In section 1.1.1 cream is defined in order to develop an understanding of the key ingredient in butter along with why bovine derived cream is typically chosen due to its high availability and popularity worldwide. Section 1.1.2 outlines the typical cream production process which happens through a centrifugal separator which results in the creation of cream and skim milk. While section 1.1.3 highlights the importance of the quality of raw cream towards the overall quality of the final butter product. For instance, during the summer months FFA values of cream which is an indicator of rancidity tend to be below 0.30% while they increase towards the winter months with values of >0.30% expected.

The definition and main constituents of butter are explored in section 1.2.1 &1.2.2 with the chemical values of butter outlined in table 1.2. Butter typically has a fat value of around 80-82% with a moisture of <16%. The remaining components are curd at 1.90% and salt at 1.8% if required. If moisture values exceed the 16% threshold, the butter produced can either be reworked to reduce the moisture or can be reclassified as downgrade product and sent for AMF production as outlined in section 1.4.4. Butter produced by Irish manufacturers can typically be classified into two types. Firstly, sweet cream butter which can be either salted or unsalted depending on customer requirements and secondly cultured butter which included the addition of a starter culture. There is a high demand globally for Irish butter particularly in Germany where it's the number one butter brand ('Ornua | Our Brands | Meet the Ornua Family of Brands', 2022). This increased demand for butter products illustrates the need for increase production with the valorisation of winter cream seen as a method of achieving increased output during off peak months.

In order for the reader to gain a better understanding of butter, the production process was outlined in section 1.2.3. Figure 1.6 illustrates the process flow for butter. Cream is first produced through the separation of whole milk while the skim milk that remains can be dried into skim milk powder which can be sold to customers for use in infant formula manufacture. The cream is pasteurised and starter cultures can be added if required. The cream is then transferred to a ripening tank where it's subjected to a temperature programme which will help a desirable crystalline structure develop when the final butter is chilled during storage. The majority of milk fat around 97-98% is made up of TAG crystals (Lopez, 2018). A desirable crystalline structure would entail the inclusion of a high quantity of β′ crystals as they produce butter which is softer, better aerated and is more creamy compared to butter which a crystalline structure that is high in α or γ form crystals (O'Brien, 2012).

After ripening is complete the cream is transferred to the churn where vigorous agitation results in the development of two fractions: butter grains and buttermilk. The buttermilk is continuously drained where similar to skim milk can be dried into powder and sold to customers across the world. The moisture of the butter grains is then reduced to a desirable level <16%. Once this moisture is obtained the butter can be sent to the packaging unit and is be stored at <4°C (*Butter and Dairy Spreads*, 2015).

Section 1.2.4 detailed the differences between butter produced in Ireland compared to the rest of the world. Butter produced in Ireland is predominately produced using milk sources from cows on a pasture-based diet. From the months of March to October, cows are typically on a grass-based diet due to the high availability of grass during this period. Irelands climate which consists of high rainfall and mild conditions is a key driver of this growth. During the late autumn and into winter as grass growth decreases concentrated supplements and grass-fed silage are introduced into the cow's diet. These combining factors results in the composition of the milk changing during this period with notable alterations in the fatty acid composition and concentration of fat were seen (O'Callaghan *et al.*, 2019). Due to a lack of grazing infrastructure and shorter growing seasons many regions such as the United States, middle east and central Europe commonly implement a TMR feeding regime. TMR feeding regimes have been shown to increase the total milk yield but contain a lower fat content compared to pasture-based diets (Gulati *et al.*, 2018). This gives Irish dairy producers an advantage over their worldwide competitors as they can produce higher quantities of butter due to the relatively higher fat contents that can be seen in the raw milk.

The history of butter was examined in section 1.2.5 in order to gain insight into the product in connection to how it was discovered and the justification for why it has evolved into a staple of many western diets. Although it was initially processed using a relatively straightforward process, it has greatly advanced since its initial discovery.

Section 1.3 detailed the key characterising factors of butter with reference to the contribution of each towards the overall quality of the final butter. The objective of this section was to help the reader understand how butter is classified and how these characterising factors are primarily driven by the quality of the milk and cream used in the butter production process. Section 1.3.1 looked at the fatty acid composition of butter with TAG considered the primary fatty acid in milk fat at 98%. During the winter months from October to March when milk fats tend to be higher there is significantly higher level of SFAs present in milk such as palmitic acid. This is linked to the high level of concentrate that cows consume during this period. As the grazing season begins in March the levels of UFAs increase with oleic and linolenic acid being the two prominent fatty acids here. UFAs are of interest to dairy processors as they have lower melting points compared to SFAs. Butter with high levels of UFA tend to produce a softer butter which is quite desirable for manufacturers.

The next characterising factor examined was FFA in section 1.3.2. FFAs are lipid species that are released during the lipolysis from adipose tissue. The more FFA in milk results in the development of a sour, bitter and unpleasant flavour. FFA of shorter chain length (C4-C12) have been shown to play a key role in the development of a rancid flavour, The level of these shorter chain FFA are typically higher in the winter months which means finding ways to decrease these levels during the winter months could be quite valuable for butter manufacturers.

Section 1.3.3 & 1.3.4 explore the importance of butter hardness and the milk fat crystalline structure. Butter produced in early lactation tends to have a lower hardness due to the availability of high quantities of fresh pasture. Hardness values tend to significantly increase during the winter months as cows move into an indoor feeding regime which consists of silage and concentrates. With regard to the milk fat crystalline structure, the quantity and kind of milk fat crystals present can have a significant impact on the functional qualities of milk fat. The presence of high levels of β' crystals which have a low melting point in milk fat can lead to the development of a softer final butter which is more attractive for consumers. α & γ crystals can also be found in butter but high levels of these tend to lead to the development of a harder butter.

Section 1.4 examined the state of the economy in regard to butter and its intended use. It informed the reader on the size of the butter market and how much growth is anticipated for it over the coming years. This section served to provide the reader with information about the major producers and consumers of dairy products around the world. Lastly, product is downgraded when there may be microbial or pathogenic problems occurring within the plant such as the introduction of high levels microorganism or pathogen. This product is typically destroyed while with butter produced with a high FFA which is >0.40%, this can be processed further through oiling as described in figure 1.11.

The objective of Chapter 3 was to outline the results and findings relative to the impact of altering cream processing parameters on the overall quality of butter. With reference to the research title, it examined the impact of cream processing parameters on the fatty acid composition, free fatty acid levels, butter hardness and milk fat crystallisation structure in butter. The purpose of this thesis was to explore the potential to improve the quality of winter cream for the purposes of producing higher quality butter during the winter period.

The determination of the fatty acid composition and the relative amounts of each fatty acid in cream can be considered a valuable indicator of final butter quality. A study from (Ceylan and Ozcan, 2020) illustrated the effect of exposure to a variety of cream cooling temperatures and acidification methods on the final fatty acid composition of butter. The experimental design is outlined in table 3.1. Table 3.2 outlines the relative amounts of in each of the nine butter samples divided into groups as short (C4 – C6), medium (C8 – C14), long (C16 –C18) and very long chain fatty acids (longer than 19 carbons) by chain length. The most prominent SFA found in the butter samples was palmitic acid with values ranging from 25.90-30.18% with the peak of 30.18% seen in cream that was matured at 6°C with a ripening time of 15 hours. Oleic acid was found in the butter sample with values ranging from 23.24% to 28.8%. The highest value of 28.8% was found in cream that was matured at 6°C with a ripening time of 10 hours.

From these results we can see that a lower cream maturing temperature and shorter ripening time can lead to the promotion of higher levels of oleic acid in butter. The relative levels of oleic acid are important in butter as they are seen to promote softness and plasticity in butter which may enhance the spread-ability of butter(Jenkins and McGuire, 2006). This data is useful for producers of winter butter as they can alter the cream ripening time and maturing temperature to enhance the development of oleic acid in winter cream. This statement is supported from analysis undertaken by (Hillbrick and Augustin, 2002) which stated that the proportion of unsaturated fatty acids (UFAs) in the milk fat content positively correlates with the butter's softness and spread-ability (Hillbrick and Augustin, 2002).

A higher ripening time of 15 hours has been shown to increase the levels of palmitic acid across all samples. Higher levels of palmitic acid in cream tends to lead to the development of a harder butter. This is supported by a study from (Marangoni and Ghazani, 2021) which stated that high levels of saturated fatty acids (SFA) such as palmitic acid should produce a harder fat, whereas high levels of unsaturated fatty acids (UFA) like oleic acid should produce a softer fat. However, during the assembly of triglyceride molecules, which contain combinations of 3 fatty acids each, allows SFA and UFA to combine, resulting in a wide range of melting points. (Marangoni and Ghazani, 2021). This indicates that further research may be needed to be undertaken to analysis the role of both SFA and UFA in triglyceride molecules when they combine.

A study by (Wiking *et al.*, 2005) examined the effect of differing milk cooling strategies and feeding regimes on the FFA of milk. Cream is produced from the physical separation of milk so it of interest to butter manufacturers to understand how the FFA can be controlled during the storage of milk. Milk was subjected to a variety of incubation times and cooled at 4℃ in an ice water bath. The combined impact of a high saturated fat diet and low-fat diet were also explored. The results are illustrated in table 3.5. These results showed that the FFA concentration increased significantly after pumping at 31℃ with values of 1.57% for the low-fat diet and 0.80% from the saturated fat diet. The level of FFA increased when milk was chilled and incubated 1 hour prior to pumping with values of 0.78% for the low-fat diet and 1.59% for the saturated fat diet. The lowest level of FFA was found for milk that was produced from the low-fat diet and cooled in the plate heat exchanger at 4℃ and pumped.

While understanding how cream processing parameters can be altered to produce a higher quality butter during the winter period, it's also important to consider how milk can be altered to produce a more desirable final product. The results from (Wiking *et al.*, 2005) study show that the lowest FFA milk was obtained from samples that were incubated at 31℃ for 90 minutes, then were cooled in an plate heat exchanger to 4℃ and pumped directly. This information is useful for cream processors as they can advise farmers on the optimal cooling conditions and feeding regimes available in order to produce lower FFA milk. Manufacturers can then receive this lower FFA milk and process it to produce cream. This could be particularly beneficial during the winter period as lower quality milk can be improved to produce a more desirable butter during this time.

The effect of cream aging temperature and agitation on butter hardness was examined by (Lee and Martini, 2018). The results obtained in table 3.6 showed the hardness value(N) of samples obtained with reference to whether the cream was aged at 5 or 10°C with no agitation (NA), low agitation (40 rpm; LA), and high agitation (240 rpm; HA). From the results it can be determined that the hardest butter was with cream aged at 5°C with 240 rpm and 10°C with 40 rpm while the softest butter obtained was with cream aged at 10°C with 240 rpm.

With reviewing the data in table 3.6 it can be said that softest butter was produced with cream aged at 10°C with 240 rpm (HA) at 25N while 5°C with 240 rpm at 41N and 10°C with 40 rpm at 40N. These results show the impact of the combined effect of both the cream aging temperature and agitation speed on the hardness of butter. Taking the title of the thesis into consideration, the impact of the changing of the cream processing parameters to produce a more desirable butter can be shown. A conclusion can be drawn from the above results that a combination of higher ripening temperature and higher shear agitation can lead to the development of a softer butter. A study from (Herrera and Hartel, 2000) supports these finding with agitation and aging of the cream seen as an important factor that control the number of crystals formed with the introduction of a high shear rate and agitation producing a higher number of smaller crystals (Herrera and Hartel, 2000). A subsequent study revealed that low aging or churning temperature lengthens the churning time due to high supercooling which further supports these findings (Rønholt *et al.*, 2014). These results provide valuable information for the dairy industry in order to understand the relationship between cream aging conditions and agitation on some of the key properties of butter.

A study by (Schäffer, Szakály and Lőrinczy, 2001) compared how two cream ripening techniques can affect the hardness of butter. Figure 3.2 & 3.3 show the firmness of butter made with traditional ripened cream versus butter made with heat-step ripened cream. The figures also illustrate how the addition of various concentrations of LMP-20 milk fraction can help to reduce the overall hardness of butter. It is clear that, for both ripening techniques, adding milk fat fraction (LMP-20) to butter at a low temperature (below 10°C) reduces the firmness of the butter and increases its spreadability in proportion to its addition. The firmness values however, remain nearly the same at room temperature (20°C). Butter produced by the heat-step ripening and enrichment with an LMP milk fat fraction has a softer consistency at low temperatures (below 10 °C) compared to butter manufactured from regularly ripened cream.

When comparing the traditionally ripened cream in figure 3.2 to the heat-step ripened cream in figure 3.3 we can see for both methods across the various LMP-20 percentage additions a gradual decrease in the overall hardness in N. At 5℃ for both method's, we can see the hardness values for the 30% addition of LMP-20 to be 17N for the traditionally ripened method while lower at 12N for the heat-step method. As the temperature increase to 20℃ it can be seen that the hardness for both methods and all concentrations become nearly the same with values ranging from 2N-5N.

This information can be quite valuable for manufacturers of butter as the addition of an LMP milk fat fraction could lead to the development of a softer butter. This could be particularly useful during the winter period when the hardness of butter tends to increase. LMP milk fat fractions could be added to winter cream during processing in order to develop a softer more desirable butter during the winter period. The addition of an LMP-20 milk fat fraction along with the usage of the heat-step cream ripening method can lead to the development of a softer butter at 5℃. This could be a potential way that for butter manufacturers to produce a more desirable butter with lower quality cream.

The modification of cream processing parameters for purpose of producing a softer butter was explored in the following study. The effect of altering the cream cooling conditions and acidification method on the texture of butter was explored by (Ceylan and Ozcan, 2020). The experimental design is outlined in table 3.7. Depending on the type of butter and the amount of storage time, it was discovered that the differences in the hardness values of the butter samples compared to the control were statistically significant at the level of $p < 0.01$. The control sample used was cooled at 10℃ and ripened for 3 hours with the addition of a conventional starter culture which had a hardness of 15.37N. The results obtained in table 3.9 showed that the softest butters produced were from cream that had a starter culture injection which was cooled at 6 ℃ with a ripening time of 15 hours at 12.48N. The cream which had the addition of a lactic acid permeate injection which was cooled at 6 °C with a ripening time of 15 hours showed a slightly higher hardness value of 12.84N. The hardest butter produced were from creams which were injected with lactic acid permeate, ripened for 10 hours and cooled at 6°C (14.68N) and at 8°C (14.72N).

From the above results we can see that butter produced with cream that was matured by crystalising at 6°C combined with a ripening time of 15 hours was found to produce the softest butter. This information can be quite useful for butter manufacturers as it can help them add value to winter cream by altering both the crystallising temperature and the ripening time to produce a softer butter which will be more appealing to the final customer during the winter period.

A further study by (Staniewski *et al.*, 2020) showed how temperature can play a role in the rate of crystallisation and the overall microstructure of butter. This study claimed that claimed that the desired microstructure and textural qualities in butter were achieved by heat treatment application at 6/20.5/14°C (Staniewski *et al.*, 2020). Further analysis by (Vithanage, Grimson and Smith, 2009) showed how the temperature, cooling speed, crystallisation method, emulsified oil, acidity, and solid/liquid ratio can all affect the microstructure of an oil crystal network. The microstructure can, however, differ significantly even at the same solid/liquid level depending on the size of the crystals and crystal clusters as well as the quantity and type of bonds connecting them (Vithanage, Grimson and Smith, 2009).

The hardness of butter can be seen to be reduced through a variety of cream processing parameters ranging from (Lee and Martini, 2018) study on cream aging temperature and agitation rate along with the cream ripening conditions and fatty acid composition as outlined by (Schäffer, Szakály and Lőrinczy, 2001). Similarly, the work undertaken by (Ceylan and Ozcan, 2020) illustrated how the alteration of the cream cooling temperature and acidification can help to produce a softer butter with poorer quality cream.

(Lee and Martini, 2018) study showed that a cream ripening temperature of 10°C with agitation at 240rpm produced the softest butter which is slightly higher than (Ceylan and Ozcan, 2020) study which found that a ripening temperature of 6°C with a ripening time of 15 hours produced the softest butter. The outcome of these differences could be attributed to the differing agitation rates and ripening times seen in each study.

Section 3.4 explored how the alteration of a variety of cream processing parameters can be used to create an optimal milk fat crystalline profile. A study from (Buldo, Kirkensgaard and Wiking, 2013) analysed the polymorphism of fat crystals in cream during ripening for 17 hours at 10℃ and initial churning. Figure 3.4b shows through the time development of wide-angle scattering, the initial packing was hexagonal lateral chain packing (4.15 Å), which corresponds to the unstable α form of TAG. Then after 33 minutes of ripening the α form peak decreases significantly in intensity with the development of two new peaks with correspond to the β' form of TAG (3.8 and 4.2 Å, respectively). After around an hour of ripening, peaks from the β form of TAG finally began to accumulate, displaying a 58.4Å 3L packing and a faint peak at 4.6 Å. These 3 crystal forms coexisted for the remaining stages of ripening.

These results align with the findings from (Lopez *et al.*, 2000) where it was demonstrated that the α and β' forms could coexist in the temperature range of 5 to 17°C when the cream was heated at a rate of 2°C/min from -8 to 50°C. A further study from (Lopez *et al.*, 2002) discovered that β and β' coexisted with the same long spacing signatures as those observed in (Buldo, Kirkensgaard and Wiking, 2013) study (3L 58.4 Å + 2L 40.5 Å) after cream had been stored at 4°C for more than 100 hours (Lopez *et al.*, 2002).

With reference to the thesis title, it can be said that the development of β' milk fat crystals begin to occur 33 minutes into ripening which are considered to play an important role in the development of a soft butter. (O'Brien, 2012). This data can be quite useful for butter manufacturers looking to improve the quality of winter cream as they can process the cream in correlation with the above-mentioned parameters to produce a softer butter during the winter period.

Another way which was found to help find a desirable crystalline structure in butter is through the altering the cream cooling rate as outlined by (Rønholt *et al.*, 2014). 38% fat cream was used with the cream being cooled at a fast-cooling rate at (7.5℃/min) and a slow cooling rate of (0.4℃/min) they reached the desired churning temperature of 10℃, with the final moisture contents in the butter varying from 20%, 26% and 32%. Table 3.10 outlines the churning times for both the fast cooled and slow cooled cream. The churning time can be defined as the time taken from the start of churning to phase inversion which is when butter grains begin to appear in the liquid phase. The churning time for fast cooled cream was seen to be 3.40 (min:sec) compared to 2.00 (min:sec) for the slow cooled cream. Why churning takes less time can be attributed to the presence of larger crystals among oil droplets in slowly cooled cream compared to the swiftly cooled cream. The crystals penetrate the milk fat globule membrane and act as eroding agents during churning. More milk fat globule membrane breakage will be made possible by larger crystals, which will also make it easier to transition from an oil-in-water emulsion to a water-in-oil emulsion at a later stage. (Boode, Walstra and de Groot-Mostert, 1993). The importance of these findings for butter manufacturers is that fast cooling is believed to encourage the development of small crystals, leading to a harder crystal network, as opposed to slow cooling, which favours the formation of larger crystals with fewer contact points, producing a softer crystal network (Wiking *et al.*, 2009). Butter manufacturers could utilise a slow cream cooling procedure during the winter months in order to produce a softer butter during this period.

Figure 3.5 analysed the crystalline structure of the samples during days 1, 4, 7, 14, 21 and 28 post production. The x-ray data showed that in all samples the formation of β' crystals occurred along with minor traces of β crystals. This is consistent with research that reported the presence of β' crystals and traces of β in anhydrous milk fat and cream after four days of storage at 4°C. This study observed a change in milk fat during storage with the development of more stable crystals seen (Lopez *et al.*, 2005, p. 200). The importance of this information for butter manufacturers is that after one day of storage at 5°C no α crystals are present which from section 1.3.4 we can see is the least stable of the three polymorphs (ten Grotenhuis *et al.*, 1999). This illustrates that the transition from α to β' occurs sometime between when the cream reached 10°C during preparation until day 1 after it was produced. Manufacturers can then apply this information to the processing parameters of cream to process cream to produce high level of β' crystals.

Along with its reduction in hardness values, the effect cream aging temperature and agitation during processing can be seen to have an impact on the milk fat crystalline structure. The combined effects of aging temperature at 5°C, 10°C, and 15°C and agitation rate at 0, 40, and 240RPM during the aging of cream for 90 minutes were investigated in (Lee and Martini, 2018) study using a model system. The SFC content was first looked at in figure 3.6. The SFC is known to be a good indicator of the rate of fat crystallisation. From the results in figure 3.6 we can see that the highest SFC content was found at 5°C with values of 18.0% NA, 18.6% LA and 19.2% for HA. Next highest was at 10°C with values of 12.5, 13.5, and 13.6% for LA, NA, and HA seen respectively. The lowest SFC content came from cream aged at 15°C with values of 5.0, 5.0, and 6.4% shown for NA, LA and HA respectively.

When cream was crystallised at 5 and 10°C, the SFC values rose over time in a sigmoidal form, but at 15°C, a non-sigmoidal increase in SFC was seen. In comparison to high crystallization temperature, nucleation is more effective at low crystallization temperature (high supercooling). As a result, at lower temperatures and with increased viscosity, SFC grows more quickly which can be seen in the results as cream which was crystallised at 5°C with high agitation at 240 rpm showed the highest SFC content of 19.2%. This can be implemented into industry through the introduction of these methods into the cream processing process. This is of particular importance with regard to lower quality cream which is available during the winter. The cream processing process can be altered to produce a softer butter during this timeframe which may result in increased sales and profit for dairy manufacturers.

As viscosity rises, molecular mobility decreases, the rate of nucleation slows, and SFC hits a plateau. This can be seen in cream that was aged at 15°C where the supercooling was too low for the cream and as a result, the increase in SFC happened gradually and never reached a plateau. When the aging temperature is low, the onset period of crystallization is independent of the agitation rate (Lee and Martini, 2018). A study from (Dhonsi and Stapley, 2006) showed shear decreased the induction time of cocoa butter crystallization at high temperatures (20 and 23°C), whereas shear had no effect on the induction time at lower temperatures (13 and 17°C).

The results on figure 3.7 highlight the effect of the above mentioned parameters set out by (Lee and Martini, 2018) on the cream droplet size. The size of the droplet can influence how much coalescence is present in an emulsion; the more coalescence present, the greater the droplet size. Cream instability is indicated by coalescence, which occurs when two droplets unite to form one big droplet. The results on figure 3.7 showed that sample LA (40 rpm) which was aged at 10°C had the smallest droplet size. Irrespective of agitation rate cream aged at 15°C produced the highest quantity of big droplets. This aligns with (Hinrichs and Kessler, 1997) study which discovered that at higher temperatures, fat globules are more susceptible to shear stress because their stability is improved by a higher SFC than it is at lower temperatures (Hinrichs and Kessler, 1997).

This information is helpful for producers of winter butter because it allows them to utilize the best parameter, such as LA with cream matured at 10°C, which can lower the levels of cream instability during processing.

Another study by (Rønholt *et al.*, 2012) explored the effect of cream heat treatment on the polymorphism of the milk fat crystals of butter. Four samples were prepared as outlined in table 3.11 CS, CF, CMS and CMF with a range of slow and fast cooling along with matured and non-matured cream used in the tests. The WAXS data from figure 3.8 showed that the non-matured cream samples (CS & CF) formed mostly α and β' crystals with smaller traces of β crystals found. A change from α to β' and β results from the cream maturing. The SAXS data, which indicate an α-related 3L structure around 67 Å paired with the normal β' 2L lamellae around 41 Å in the non-matured samples, support the same conclusion (Lopez *et al.*, 2005). The observations (Rønholt *et al.*, 2012) study in the matured cream are confirmed by the fact that milk fat tends to form β'-crystals and occasionally also β-crystals after a suitably extended crystallization time.

From the above we can see that heat treatment prior to butter manufacture can alter the microstructure of the butter. While the fragility of the butter is greatly reduced when butter is matured using fast-cooled cream, the hardness of butter is significantly increased when butter is matured using slow-cooled milk. The promotion of β'crystals, which have been found to generate a more desired, softer final butter as described by (O'Brien, 2012), can be promoted by introducing a maturing time of 5°C for 48 hours. This information could be very beneficial for manufacturers of winter butter.

Both (Lee and Martini, 2018) and (Rønholt *et al.*, 2012) showed that a cream ripening temperature of 5°C produced the highest levels of levels of desirable β' crystals. With regard to cream ripening time (Buldo, Kirkensgaard and Wiking, 2013) study showed the development of high levels of β' crystals to be found in the first hour of cream ripening while this is shorter compared to (Rønholt *et al.*, 2012) study which found that the highest levels of crystals were produced during ripening for 48 hours.

The main outcomes in this chapter demonstrated a connection between the final outcomes of the essential properties of butter and the alteration of cream processing parameters. The results varied depending on the changes made to the cream chilling temperature, ripening times, agitation rates, acidification procedure, and fatty acid makeup. For the fatty acid composition, shorter cream ripening times produced higher quantities of oleic acid, a UFA, whereas longer times produced higher levels of palmitic acid, an SFA. A softer butter is thought to emerge when UFA levels are high. In terms of FFA in milk, it was found that milk that had been cooled to 4°C in a plate heat exchanger and pumped immediately after cooling had the lowest FFA values. The introduction of a high shear rate and agitation was observed to produce a higher number of smaller crystals, whilst a combination of a cream ripening period at 10°C and agitation at 240rpm was seen to yield the softest butter. A softer butter may result from the addition of an LMP-20 milk fat fraction and the use of the heat-step cream ripening process. The ideal cooling temperature and ripening time for cream were found to be 6°C and 15 hours, respectively. These conditions produced the softest butter. The crystalline state that encourages the creation of β' milk fat crystals which can be detected during the first hour of cream ripening, was discovered in the milk fat crystallisation section. It has been discovered that slow chilling of cream shortens the time required for churning, favouring the creation of bigger crystals with fewer contact points, which results in softer butter. The most SFC, a measure of the rate of milk fat crystallisation, was found to be produced at a cream aging temperature of 5°C and an agitation rate of 240 rpm. The maximum concentration of the desired β' milk fat crystals were discovered to be produced by slowly cooling cream that was matured at 5°C for 48 hours.

Chapter 5: Conclusion & Future Work

5.1 Conclusion

The objective of this thesis was to explore the potential to improve the quality of winter cream for the purposes of producing a higher quality butter during the winter period. This was done by reviewing studies relating to the fatty acid composition, FFA level, hardness and milk fat crystalline structure within butter and cream. This led to the development of the research question: Exploring the Influence of Cream Processing Parameters on Butter Quality.

From the results and discussion, Chapter 3 and Chapter 4, it can be confirmed that there is a relationship between the altering of cream processing parameters and the final results of the key characteristics of butter of fatty acid composition, FFA, hardness and milk fat crystalline structure. For fatty acid composition, a shorter cream ripening time led to higher levels of oleic acid, a UFA, whereas a longer ripening time led to higher levels of palmitic acid, an SFA. The creation of a softer butter is linked to high levels of UFA. This can be useful for producers of winter butter as they can shorten their ripening times to enhance the value of this winter cream and produce a softer butter.

For FFA in milk, the cooling of milk to 4℃ followed by instant pumping results in the lower levels of FFA. This can be useful for manufacturers of winter butter as they can advise farmers about the optimal cooling conditions needed to produce milk with a more desirable FFA value during the winter months, which can then be further processed to make cream.

In relation to the hardness of butter, the introduction of a high shear rate of agitation which helps to produce a higher number of smaller crystals along with a ripening temperature varying from 6-10℃ can lead to the development of a softer final butter. The addition of an LMP-20 milk fat fraction also plays a role in the reduction of hardness in butter. Combining and applying these cream processing parameters will help manufacturers add value to lower quality cream particularly that which is produced during the winter period.

To conclude for milk fat crystallisation, it was found that β' crystals begin to develop within the first hour a cream ripening while a cream aging temperature of 5°C was optimal for the development of β' milk fat crystals while further growth can be seen through the addition of a high rate of agitation during processing along with a maturing time of 48 hours seen as pertinent. These processing measures along with the aforementioned can be applied to butter manufacturing plants across Ireland with particular value to those with high stocks of winter cream who can enhance its overall quality during this period to maximise revenue.

5.2 Future Work

The dairy industry may use the above findings to gain a better understanding of how the processing parameters of cream can be altered to develop a more desirable softer butter using lower quality cream during the winter period. Currently as outlined in the above findings the cream chilling temperatures, ripening times, agitation rates, acidification process and fatty acid makeup are used to improve the quality of winter cream. There is however scope for other methods which could improve the overall quality of cream.

One such is the use of a spinning cone column which has been used in other industries to remove volatile compounds. Using steam and a vacuum, the spinning cone column distillation method separates volatile chemicals from liquids at low temperatures. The column is made up of a vertical stainless-steel vessel with alternating spinning cones attached to a central rotating shaft and stationary cones affixed to the inner wall of the column. Gravity causes liquid injected to the column's top to flow down the first stationary cone and into the base of the first spinning cone, where it produces a thin film. The liquid then moves as a thin film across the surface of the spinning cone due to centrifugal force before it becomes airborne and falls onto the next stationary cone. The liquid flows downward as a result of the repetition of this cycle. A counter-current (upward) flow is produced at the same time by the addition of steam at the base of the column. As the steam passes over the surface of the thin films and interacts with airborne liquid droplets, volatile chemicals are "stripped" into the vapor phase. While the remaining "stripped" liquid is collected from the bottom of the column, the volatile-enriched vapor that exits the top of the column is passed through a condensing system and recovered in a concentrated liquid state (Puglisi *et al.*, 2022).

While there are limited studies on this type of technology within the dairy industry, its effectiveness at removing volatile compounds has been proven in other industries such as juice and wine manufacture. A spinning cone column can be used in the dairy industry during cream processing to remove volatile FFA compounds in the cream. This could be of particular benefit to cream manufactures during the winter months as they could implement this technology on their lower quality cream which would reduce the total

FFA levels which in turn would lead to the development of butter with a lower risk of oxidation.

The use of a spinning cone column along with the findings mentioned in Chapter 3 can help dairy manufacturers reconsider their processing parameters to help produce a softer, low FFA butter all year round which will be more attractive to customers worldwide.

Chapter 6: References

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