THESIS

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INVESTIGATION OF THE EFFECT OF FREEZING AND THAWING DURING MEAT CURING

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1. INTRODUCTION

Curing as a method of meat treatment involves addition of salt on the meat pieces in order to preserve them for a long period of time, as well as to develop its organoleptic parameters such as flavour and texture. A key part of this process is how salt penetrates and spreads within the meat. When salt either in a form of crystals or diluted in water reaches the meat, two processes take place: diffusion and osmosis. Diffusion promotes the salt crystals in the meat matrix, where the salt concentration is significantly lower, whereas osmosis moves water from the meat towards the high salt concentration to dilute it. Under normal conditions speed of the salt penetration and diffusion into meat is a very slow process.

Salt curing is represented by two main curing methods: dry curing and wet curing. Dry curing requires addition of curing salts on the surface of the meat piece, whereas wet curing is immersion of the meat pieces under saturated salt solution. Wet curing advanced technologies allow to inject the brine to accelerate the diffusion of salt in the meat tissues. Brine injection is usually followed by tumbling process, which provides more homogeneous brine distribution.

Recent innovations, like freezing and thawing, newest non-thermal processing, and food preservation methods such High Hydrostatic Pressure (HHP), Pulsed Electric Fields (PEF), as well as ultrasound treatment, have the potential to speed up salt penetration and improve the flavour and texture of cured meats. In this work freezing-thawing process prior to meat salting is going to be discussed on the example of the example of pork loin (M. Longissumus dorsi.) muscle as a muscle with good structure homogeneity as well as high demand on the market.

OBJECTIVES

This thesis aims to investigate how freezing and thawing during the brining process impact salt and moisture transport as well as diffusion in meat. A comparison will be made between brining during thawing, brining after thawing, and regular brining without freezing. Study will also involve the measurement of salt and moisture levels and analysis of their movement within the meat. Two empirical mathematical models (Peleg, 1988; Zugarramurdi & Lupín, 1980) and one diffusion model (Telis et al., 2003) were used for the prediction and evaluation of the salt and water mass transfer and diffusion. Through this research, a deeper understanding of meat curing, and potential enhancements will be achieved. These findings have a potential to enhance the quality of meat products and make contributions to the field of food science and technology.

2. LITERATURE REVIEW

2.1. History of curing

From the ancient times question of collecting and preserving food was standing in front of humanity. Meat was always one of the most important components of the human diet together with crops and vegetables, for many cultures it remains the main source of energy and essential animal proteins. People living in warmer climates were more exposed to the meat conservation issue, as of temperature that accelerates the processes of the meat microbiological spoilage. For the meat preservation salt curing appeared to be the best and most reliable technique that protect the meat from microbiological spoilage, make the meat piece more favorable, and pleasant for the consumption. Practically what we call "salt" was a rock or sea salt that was the main raw ingredient used for the salt-curing of the fresh meat pieces (Toldrá. F., 2002). It's process simplicity allows it to be used practically by everyone increase the amount of stored meat both in quantity and quality aspects. However, salt alone was not used. Spices and herbs as well as sesame oil was part of Sumerian diet (Internet source 1). They not only cured meat that way but also fish and poultry.

Beginning from the culture animal breeding and domestication introduces a brand-new story of the social interactions and ways of making business. The Semites on the Euphrates and the Tigris, and the Aryans in India were the initial pastoral tribes, as first people domesticating animals on the planet.

In Golden Age most of the population mindset changes. Indians consuming milk and dairy products refuse eating meat (especially beef) in order to keep purity of the body and the soul. Christianity in the Middle Age especially in Europe made it compulsory to fast, by reducing amount of meat on certain days, maintaining meat only in very few amounts which made the tradition of meat consumption as a part of the high-class minority of people. Such attitude traced back from the Roman and Byzantine empires when meat, specifically pork and beef was served only for the governing establishments and royalty.

Therefore, butchers' meat consumption has always had a very important value in the human diet which ultimately led its storage and preservation techniques to become more developed and advanced. Best meat as a primary necessity with simple salting and curing techniques made its way to one of the most precious and luxury food commodities available for human diet *(Maguelonne T., 2009)*. History of the curing is briefly represented on Figure 1.

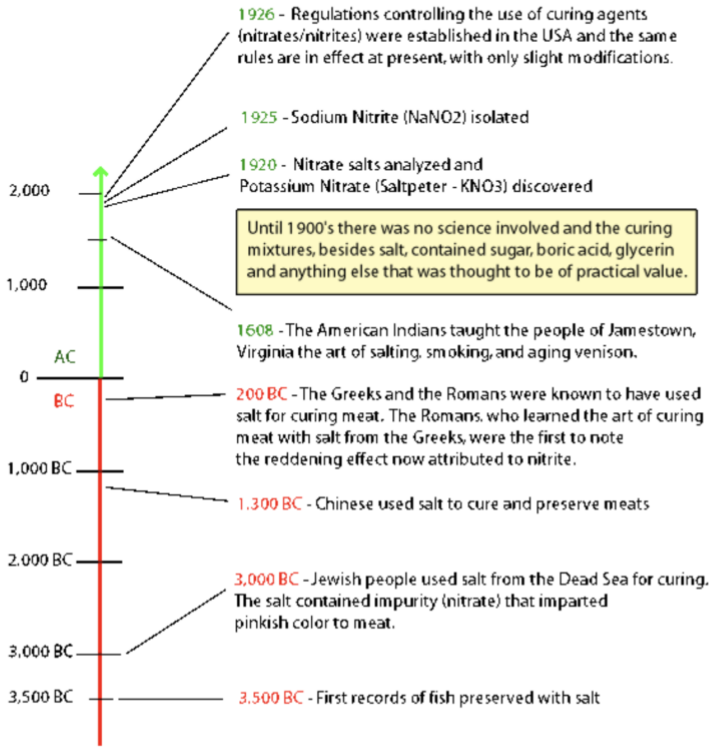

Figure 1. History of meat curing (Meats and Sausages ©, 2022a)

2.2. Definition and aim of the curing

Meat curing is a process of application of the curing salts such to the meat to improve its flavor and shelf life. There are several methods of the meat curing including dry curing, wet curing, and injection curing. Curing method mainly depends on the type of the product that is going to be produced and its characteristics. Main propose of the curing is to improve microbiological stability and inhibit spoilage bacteria, increase the shelf life of the product, develop the flavor, taste, and appearance. On one hand sodium hydroxide (NaCl) is responsible for the flavor and taste formation as well as acts as a texture forming agent and preservative. On the other hand, nitrites and nitrates are responsible for the color formation, microbes inhibition and antioxidant effect, as well as contribution to the flavor and taste formation. Curing is a very effective preservation technique to produce a high-quality food product with an extended shelf-life such as raw cured beef and ham, cooked beef and ham, bacon, and reconstructed products. (Toldrá Fidel, 2002). Figure 2 represents the types of the cured meat products currently provided on the global market.

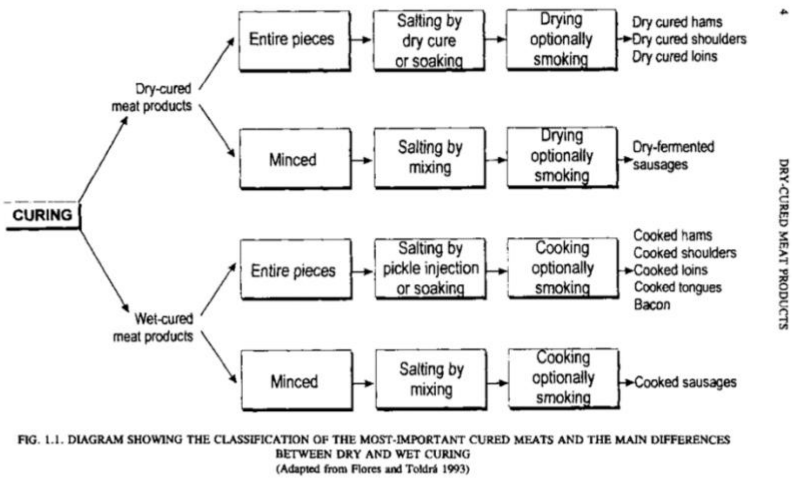

Figure 2. Types of the cured meat products (Toldrá Fidel, 2002)

2.3. Curing methods presenting

Today four main curing methods are used nowadays on the meat processing factories and private households. These are dry curing, wet curing and injection curing or pumping as an advanced wet curing method. Wet cuing it is applicable in three different modes such as immersion curing (or soaking), stitch pumping and spray pumping. In certain cases, combination of these methods is applied such as dry and immersion curing and spray cutting with immersion curing. Figure 3 represents curing types by three main categories.

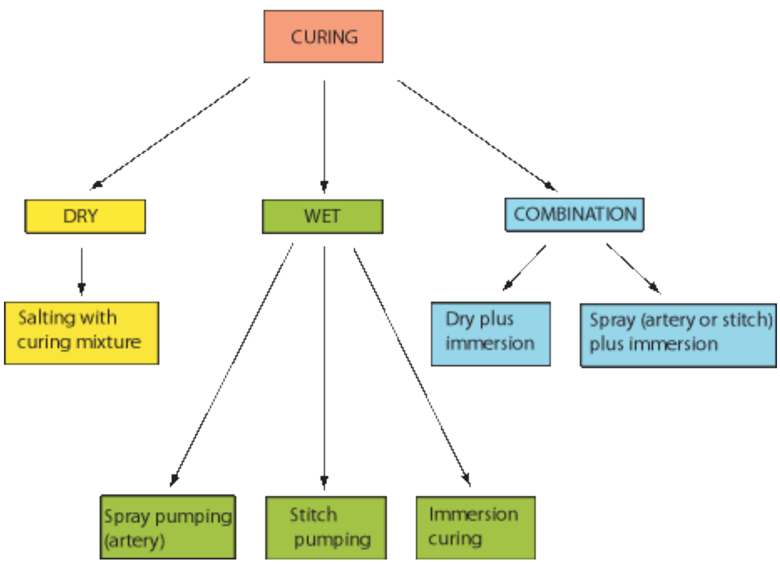

Figure 3. Curing methods (Meats and Sausages ©, 2022b)

Dry curing is a curing method that is used an introduction of the curing salts into meat tissues simply applying it on the surface of the meat pieces. It's one of the simplest and more convenient ways of curing. Normally curing is performed under 2-4ºC and at 90-95% for relative humidity (Toldrá Fidel, 2002). Temperature that is higher than 10ºC will cause bacterial spoilage. Therefore, keeping temperature below 10ºC it is possible to protect product from undesirable bacterial growth (Toldrá Fidel, 2002). Dry curing is usually performed in the curing tanks, or any other suitable container or vat, by putting meat pieces in the curing salts and covering it again with the curing salts every layer, to make it more efficient. After certain time wet salts can be refreshed by adding new portion of the fresh curing salts as soon as water is going out from the meat tissues — water loss occurs as well as change the position of the meat pieces for better coverage of the meat cur surfaces. Rearrangement of the meat pieces in the tank is called overhauling (Meats and Sausages ©, 2022b). Salt introduction happens due to the gradient difference on the surface of the meat piece and its inner parts. Depending on the size and duration of curing meat will absorb according to amount of salt. Dry curing is mainly applied for the production of the cured pork pieces mainly thighs traditionally called Jamón and dry-cured sausages. Figure below represents dry curing process in the curing tanks.

Figure 4. Dry-curing vat with meat pieces (Meats and Sausages ©, 2022b)

Wet curing or soaking is meat curing method that applies brine as media for the salt introduction in the meat cut. Brine is prepared by dilution of the curing salts in the water. Salt concentration of the brine is usually 8-10%, in comparison to saturated salt solution that is 26.3% of salt which is not efficient in mass production scale. Normally this percentage is applied for most of the brine curing methods as well as for injection curing and tumbling. First seven days of soaking will cause a meat cut to lose significant amount of water due to the rapid salt diffusion in the meat tissues. Next step will be swallowing of the meat proteins and slow absorption of the water, due to the damage of the meat cells by salt crystals from the brine. Figure 5 represents wet curing salt diffusion dynamics (Internet source 1).

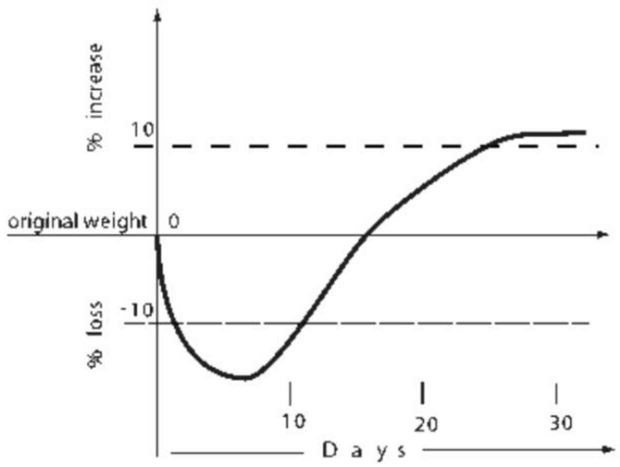

Figure 5. Wet curing dynamics

Wet curing is quite primitive as dry curing and does not require any specific environmental conditions suggesting that meat piece can be placed in the brine for as long as it is needed to achieve desired salt content of the meat cut. Wet curing is performed in the curing tanks.

Injection curing is one of the most advanced methods of the meat curing. Its main operating system is based on the injection of the brine by the needles directly to the meat pieces (Figure 6). Injection curing is applied on most of the meat processing plants due to its operating speed and reliability. Injection curing is performed by automatic brine injector. Needles put in rows are penetrating meat cut several times to achieve most homogeneous spreading of the brine. This technique is used mainly for the boneless meat cuts. However whole chicken or any whole poultry carcass can still be injected with brine injector as the construction of the machine allows it to introduce brine safely throughout the carcass. Some production cites also apply coloured brine — brine with the natural meat colorant. After cooking of such coloured brine injected meat product will have a nice pink color which is desirable for most of the consumers.

There is another injection method that are slowly going out of usage but still can be found in some private households such as artery pumping, which is used for the curing of the pig thighs (jámon) (Meats and Sausages ©, 2022b).

Figure 6. Injection curing of the pork loin (Meats and Sausages ©, 2022b)

Tumbling is a curing method that applies meat curing with brine in the container with rotational paddles under low pressure to achieve most homogeneous brine introduction into meat tissues. Production of the meat with the usage of the tumbling method includes placement of the meat pieces in the tumbling machine. Tumbling process significantly contributes to the protein size increasing. Tumbling causes meat protein to swell, therefore absorb more water and increase process of meat ripening such as color and flavour development. Tumbling can also greatly enhance rheological and sensory features of meat such as palatability and chew of meat.

Tumbling is performed under vacuum to avoid foaming of the meat proteins after certain time of cooking. Protein foam is formed as a result of the meat protein denaturation. If action is performed under normal external pressure conditions air is going to be trapped during the mixing process and form a solid foam. This protein foam is undesirable during the meat curing process as it makes the meat pieces "cook" and stick together despite continuous mixing. Therefore, while producing meat product that includes tumbling and injection as a necessary step raw materials should be considered cold. Temperature of the brine and raw materials below +4ºC will ensure best microbiological stability of the ready product, so that during the massaging process meat pieces will not heat.

Meat massaging time is calculated according to the type of raw material and parameters of the tumbler. Such parameters of the tumbler are considered as size of the tumbler (effective diameter of the chamber and length) as well as equipment with climate control system, maintaining low temperature throughout production time. Tumblers bigger and size and equipped with fridge will be more expensive. If tumbler has no additional cooling agent, it should be installed in a cooled place with low ambient temperature. Number of cycles and time need for adequate treatment of the meat piece varies on the type of meat. For instance, beef takes longer time for achieving required tenderness and condition than pork. Pork however takes longer ripening time than chicken.

Tumbling is normally used in the production together with brine injector to achieve best salt distribution through the meat piece. Injection together with tumbling is used to produce cooked meat products such as cooked ham and reconstructed meat products. Meat tumbling is applied from several hour to several days according to the product type and quality. Tumbling is usually performed in the factory scale rotational tumblers presented on the Figure 7 below.

Figure 7. Meat tumbler (cross section) (Internet source 2)

3. PHYSICAL AND CHEMICAL REACTIONS DURING CURING

3.1. Colour reactions

According to the by S. Banón normal colour of dry-cured meats depends on three factors which are the pigment concentration in the tissue, the degree of nitrosated pigment conversion and the condition of the proteins in the meat (Bañón et al., 1999). Another study suggests such factors as freshness and type of meat as well as color forming reactions taking place during manufacturing of the meat product. Fresh meat has only two main colours: bright red (oxymyoglobin) and purple (myoglobin), which later are going to be stabilised and transformed into dark red color (typical color of dry-cured sausage) with application of curing salts (Chr. Hansen ©, 2009).

Main salt types used for curing are sodium chloride (NaCl), sodium nitrite ($NaNO_2$), and very rarely sodium or potassium nitrate ($NaNO_3$ or KNO_3). Additionally, sodium ascorbate or erythrobate can be applied for meat color intensification and stabilization. As a substitute of the sodium chloride recent interest was pointed on potassium chloride (KCL) (Chr. Hansen ©, 2009).

As the meat tissues composition is not homogeneous proteins that are present in the meat are different as well. Proteins responsible for the blood transportation to the oxygen to the meat cells and storing them are called globins. There are two main types of globins that are important to discuss when it comes to the color formation of the meat. These are myoglobin, which is present in the meat tissues, and hemoglobins that are present in the blood cells.

Myoglobins store oxygen that is transferred by hemoglobins from lungs to the blood and from blood to muscle tissues. Prefix "myo" suggests that globin protein is related with the muscle whereas hemoglobin is a protein that can be found in the red blood cells (erythrocytes). Difference in oxygen affinity of hemo- and myoglobins plays determines how they will react with the oxygen. Myoglobin has higher oxygen affinity therefore it can store oxygen better. On the other hand, hemoglobin with its lower oxygen affinity suggests better properties for transporting oxygen to the tissues. Once oxygen reaches the tissue (for instance, muscle tissue), myoglobin attaches oxygen and lets carbon hemoglobin to attach carbon dioxide and go back to the lungs. (Encyclopedia Britannica ©, 2017; Wikibooks ©, 2017)

Hemoglobin contains heme group — an iron ion attached to a porphyrin ring. Heme groups account only 4% of the total mass of the hemoproteins whereas the rest 96% are the globin groups. Heme that is bind to the oxygen from the lungs produces the bright red color which later appears in the muscle tissues. Such iron oxidation causes myoglobin turn to oxymyoglobin (as well as hemoglobin turns into oxyhemoglobin. (Encyclopedia Britannica ©, 2023)

Oxygen provided by hemoglobins and stored by myoglobins has to be fixed. Once animal is slaughtered and no more oxygen will appear in the tissue's meat will start to change its color. First it will turn to light purple color due to effect of deoxygenation and with the accumulation of the deoxymyoglobin then to purple color. Presence of oxygen in the environment will start the process of reoxygenation which will turn the surface of the meat to cherry-red color, while remaining purple inside (formation of myoglobin). Longer exposure to the oxygen will finally turn to brownish coloured meat due to the formation of the metmyoglobin (Shakil et al., 2022). Unpleasant color of the meat will however be still safe for the consumption.

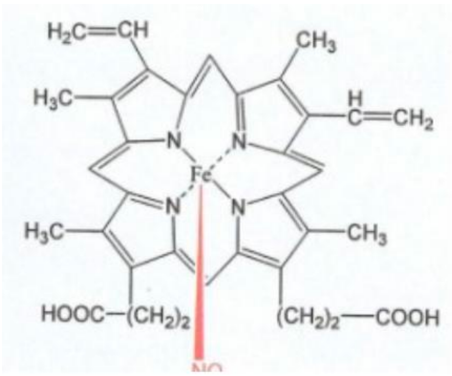

Figure 8. Structure of the nitroso-myoglobin (NOMb)

Knowing the right conditions for the best meat appearance and its properties it is then necessary to stabilise for extended amount of time. One option available for the fixation of the original red color that is present only for a few days after cut meat is separated from the slaughtered animal. Addition of nitrite as a very reactive oxidant rapidly reduces into nitric oxide (NO). At the same time the oxidative formation of metmyoglobin takes place. The iron atom in the hem group of the molecule is oxidized from the ferrous (Fe^{2+}) to the ferric state (Fe^{3+}). This results in an turns the meat or mince into greyish colourless form. Afterwards nitric oxide reacts with metmyoglobin and myoglobin and results with nitrosylmyoglobin, immediately converting the greyish color to reddish (Chr. Hansen ©, 2009).

Different oxidation reaction can still take place after NOMb was formed. For instance, after heat treatment nitrosomyoglobin will turn to nitrosomyochromogen which is pink in color — typical for the cooked sausages. It is enough to add 3-5 ppm of nitrites to achieve stable pink touch of meat piece (Feiner, 2016). Oxidated form of nitrosomyochromogen will be called metmyochromogen which is brown in color. At the same time the same compound can be formed from metmyoglobin with the heat treatment as well as be reduced with addition of the nitric oxide back to nitrosomyochromogen. Both nitrosomyochromogen and metmyochromogen can convert into oxidized porphyrins which are greenish or yellowish in color which are nitrihemins (Shakil et al., 2022).

Amount of nitrite needed for the production of the typical dark red color of the dry-cured hams is 120 – 150 mg/kg. Indicated amount of curing salt is sufficient for adequate nitrosomyoglobin formation (Toldrá & Aristoy, 2010). This amount will greatly vary on the type of meat product and the technology of the production however color formation of the meat, which appears to be one of the most important parameters after safety can be achieved by addition of 30 to 50 ppm of nitrates per kilogram of meat (Feiner, 2016).

Lee and his colleagues bring to the discussion that how much nitrates human daily consume from non-meat food products. (Lee et al., 2018). This study suggests that the number of nitrates consumed from processed meat is significantly lower than that from the vegetable sources. This way, there is overestimated attention on the number of nitrates added to the meat products and highly emotional approach toward added nitrites from the meat food products consumers.

From the microbiological point of view nitrous compounds can take over such critical foodborne pathogens as *Clostridium botulinum*, *Clostridium perfringens* as well as *Listeria monocytogenes*, and *Bacillus cereus* with the suggested dose of 80-140 ppm of nitrate per kilogram of meat (Feiner, 2016). Therefore, it is important to consider proper number of nitrous salts added to the meat. Nitrites can be of synthetic or natural plant origin as for example from celery, lettuce, cress, spinach, rucola providing up to 2500 milligram of nitrates per kilogram (Shakil et al., 2022). Such attitude will protect consumers from undesired food born disease consequences or even death. Low or nitrate-fee meat processing will require special hygienic attention on microbiological conditions and safety of the production as well as nitrate substitutes (such as sorbates, parabens, and biological acidulants) being constantly applied (Pierson & Smoot, 1982). On the other hand, too many nitrites apply will cause so-called nitrite burn effect. Nitrite burn appears as green coloured meat due to formation of green-brown compound called nitrihemin. Nitrite burn takes place when more than 600 ppm of nitrites per kilogram of meat are added together with low pH of the meat. To ensure good quality of the product and avoid undesired consequences it is advised addition of extra 10-15 ppm of nitrites (Shakil et al., 2022). Figure 9 shows the alternative nitrite options.

Application of the nitrates will also contribute to the antioxidant activity and preservation effect against pathogens based on the reaction that takes place between the nitrate oxidized to nitrite and free ferrous ions available in the meat proteins: myoglobin and hemoglobin. (Morrissey & Tichivangana, 1985). Such reaction blocks potential of oxygen to contact with the meat components and delays rancidity period, thus causes indirect antioxidant effect. To ensure antioxidant effect for the meat, it is advice to apply 20-60 ppm of nitrites per kilogram of meat (Feiner, 2016).

Last thing to mention about nitrites is that it also contributes to the flavour formation. Nice flavour of meat appears when nitric oxide reacts with the components that are originally present in the meat. These components can be aldehydes, alcohols, inosine, as well as several important sulfuric components. Appearing flavour is a result can be achieved by addition of 30 – 50 ppm of nitrated per kilogram of meat as in case of color formation. Figures 10 and 11 represent red color formation and myoglobin forms changing.

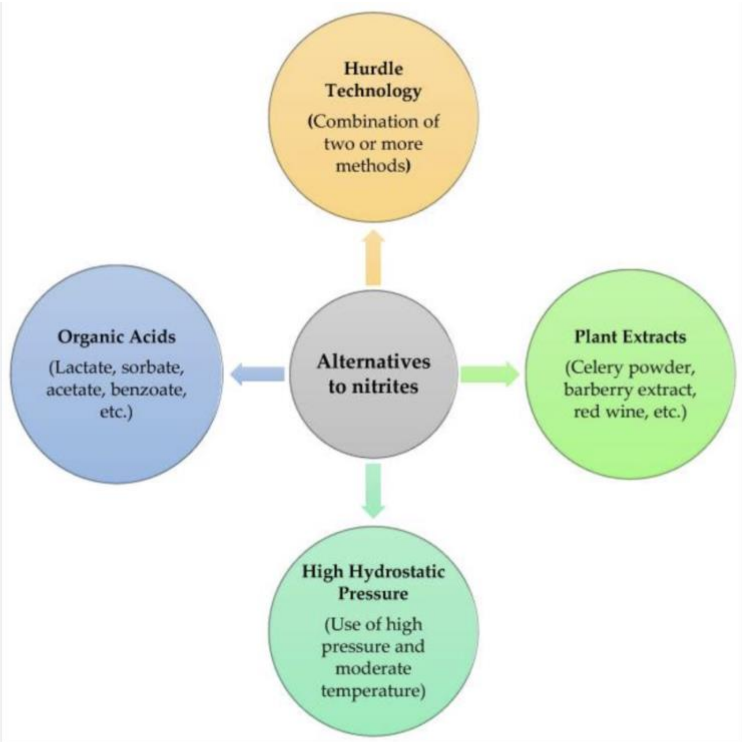

Figure 9. Alternatives to nitrite in processed meat (Shakil et al., 2022)

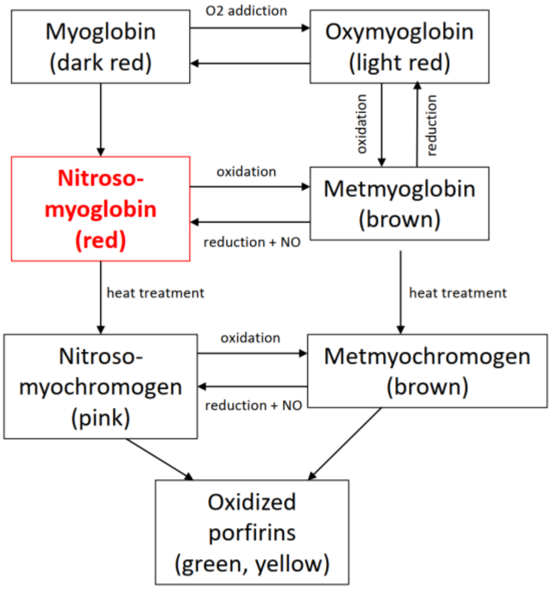

Figure 10. Reactions responsible for color formation

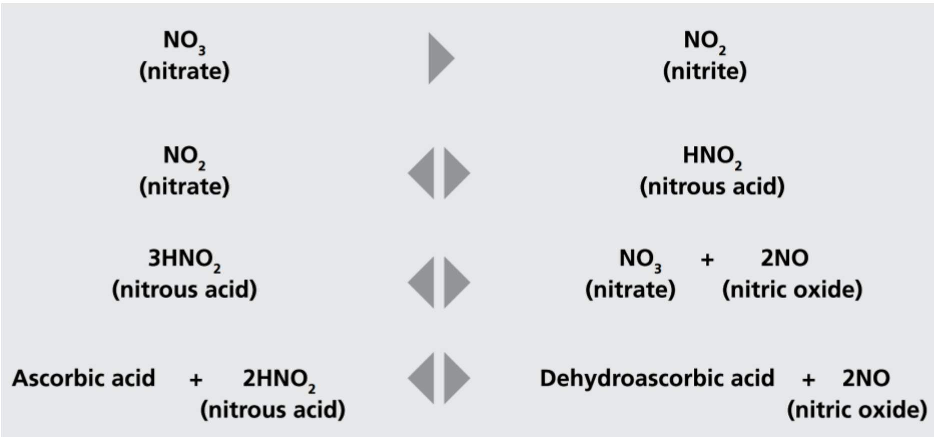

Figure 11. Color reactions (non-balanced) (Chr. Hansen ©, 2009)

3.2. Effect of the salt on meat

As already discussed, for the curing salts are used which are sodium chloride (NaCl) and sodium nitrate ($NaNO_2$) in certain proportion. Both sodium chloride and nitrate greatly contribute to the taste and flavour formation and enhancement. Taste and flavour are the main reasons why the salt is added to the meat.

Another reason why the salt is added to the meat is the salt ability to preserve. Preservation of the meat happens due to immobilization of the pathogenic bacteria by reducing amount of free water to bare minimum, hence reducing water activity in the meat.

Salt greatly affect the water holding capacity of the meat. Due to the salt's hydrophilic properties, water which is bind by the salt is going to remain there in a stronger an much more stable connection.

In the sausages and cured hams production practice around 2% salt concentration presalting is applied before processing of the meat into forced meat. This is done to ensure meat proteins to **swell**, absorb more water as well as to retain more meat juice in the cells. This provides higher quality product with better organoleptic characteristics as well as enhances safety features by reduction of water activity (Toldrá et al., 2010).

On the other hand, higher concentration of salt applied on the meat will cause opposite effect of protein coagulation or denaturation due to increased pH and acidity which is favorable in the production of other product types. Studies show that salt addition can increase meat protein digestibility which is important for human consuming meat on normal basis. This makes salt curing more important when it comes to human diet and meat consumption. (Zhao et al., 2020)

Another similar consequence of elevated salt concentration in the meat is the so-called effect of salting out. Salting out takes place in the meat tissues as a drawback of too much salt ions present in the system. Dissolved in brine or crystalline form salt competes with meat proteins for water ions. Excess amount of salt ions causes proteins to change structure and force proteins to bind with each other forming hydrophobic connection (to desaturate) which causes water from the system. This interaction explains reduction of the water binding capacity of the meat tissues and meat dehydration during salt curing with high salt concentration. Salting out however is very beneficial in the production of the dry-cured meat products, where water content should be reduced as much as possible in short amount of time (Visy et al., 2021).

3.3. Salt diffusion (physical background of diffusion)

To determine the speed of the curing it is very important to understand the process of the salt diffusion. Diffusion is one of the ways that mass transfer phenomena can occur. Mass transfer is a process of moving substances from one place to another, as for example salt moves from more concentrated solution towards less concentrated one. It has an opposite direction to the osmosis effect, when salt distributed in the water is mixing with the water from the meat, which contains less salt, so the water flows towards more concentrated solution (Genuine Ideas ©, 2020). Salt diffusion is subjected to the Fick’s law of diffusion (Equation 1):

$$(X - X_0) = D * (C - C_0) \quad \text{(Equation 1)}$$

where X is distance (m), C the moisture content (Kg/m^3) and D is the diffusivity coefficient (m^2/s). Diffusivity coefficient describes how the diffusion process happens in the media. Meat has heterogeneous composition which makes salts and any other substances to travel non-directionally, in some way unpredicted. In addition, salt penetration in the meat causes compositional changes such as osmotic dehydration as well as protein denaturation and which may affect the diffusion rate already during the measurement (Visy et al., 2021). This way, diffusivity coefficient number is not a constant number but depends on many factors such a composition of the meat tissues, especially the direction of the fibers according to water flow as well as the processing parameters such as type of curing: dry or wet. Practically D value is not used in the calculation, but De value which is apparent (effective) diffusivity number. It is normally determined in the scientific literature and can be found in the calculation part of the experimental research (Tolrdrá F., 2002).

3.4. Factors affecting salt diffusion

There are several known factors affecting salt diffusion in the meat pieces during the meat curing. Among the main factors there are geometry and size of the meat pieces, concentration of the salt in the brine, ratio of the meat against brine, diffusion constant (D), chemical reactions between meat and additives, constant boundary layer on the surface of the meat in brine, temperature, and the curing salts distribution in the meat pieces.

Geometry and the size on the meat piece play major role in the introduction of the brine in the meat. Bigger meat cut requires longer time for the salt to reach the center of the piece. Meat cuts are not always homogeneous in shape; therefore, number of connective tissues and fats may greatly affect the speed of salt in introduction. Fat is hydrophobic and connective tissues are very hard, therefore salt introduction is delayed. It is one of the reasons why factories opt for a lean meat for curing and processing. There are special mathematical rule present expressing the relationship between the geometry of the meat piece and the salt introduction speed (Equation 2):

$$\frac{t_1}{t_2} = \frac{a_1^2}{a_2^2} \qquad \text{(Equation 2)}$$

Another important parameter of the curing is the concentration of the brine. The higher is the concentration of the salt in the brine faster will be the process of curing, due to the greater difference between the salt content in the meat and salt content in the brine (greater gradient of the salt concentrations). In the scientific literature brine concentration is usually mentioned as "d_0".

Ratio between the amount of meat and the amount of brine also affects the salt diffusion to the meat. More brine is present according to the amount of meat, more effective and faster will be the curing. In the scientific literature ratio of the meat to the brin is stated as "p".

Homogeneity of the meat pieces in the production cannot always be ensured. That is why every separate piece of meat has its own specific properties that affect the salt diffusion such as diffusion constant (usually referred as "D"). Diffusion constant is "the quantity of a substance that in diffusing from one region to another passes through each unit of cross section per unit of time when the volume-concentration gradient is unity". (Merriam-Webster Dictionary ©, 2023). Diffusion constant may be greatly affected by the composition of the meat piece. Greater the amount and thickness of the fat will be, longer will be salt take time to reach the salting core. Salting core is a special point where the salt takes longest time and effort to reach to. As fat is hydrophobic curing salt as well as brine will take much longer to get to the most distant point in terms of curing speed. This way presence of fat shifts the curing center towards the fatty side as salt migration in fat is much slower than that in the meat tissues. Therefore, meat curing process always consider amount of fat, its location on the meat pieces and its distribution through the meat piece.

Chemical reactions that are taking place in the meat tissues during the curing process should be considered as well. Previously mentioned properties of sodium nitrate indicate that alongside with the simple salt introduction into meat pieces, increasing pH changes the structure of the proteins. Denaturation of the proteins opens "gates" for the salt crystals, or salt in the brine to introduce physically faster, not only due to the osmosis and mass transfer force, in other word: changing water holding capacity of the meat.

Boundary layer on the surface of the meat is another important parameter that affects the diffusion. boundary layer is formed on the surface of the cured meat during the brining process. Boundary layer naturally forms due to the flow of the liquid phase through the solid one. It affects the mass transfer and heat transfer, therefore affecting the adhesion of the salt into meat. That layer has different composition creating a barrier resisting the salt to introduce in the muscle tissues. In the context of fluid flow over a solid surface, as the Reynolds number increases, the flow is more likely to transition from laminar to turbulent. This transition can occur due to increased fluid velocity, larger surface roughness, or larger objects. Boundary layer that resists introduction of the salt has to be managed. In case of brine curing steering of the brine solution must be applied. Constant movement of the solution disturbs the established layer, weakens the resisting force, and allows more salt to form the brine to brake throw and introduce to the meat.

Temperature as an important and basic physical parameter that suggests faster curing is speed and affects salt introduction in the meat has certain features. With the increased by one-degree Celsius temperature diffusion rate will increase by approximately 2%. However too high curing temperatures will eventually lead to the mild protein denaturation as well as more problematic handling of the undesired microbial growth. Therefore, it is not recommended to perform curing at the temperatures that exceeds fifty degrees Celsius and stick to the lower and safer standards.

Uneven distribution of the salt in and through the meat pieces also determine the way diffusion will happen. It is important to consider higher concentration of salt towards the edges of the meat piece and lower concentration in the middle or center of the meat piece due to the presence of the previously discussed boundary layer as well as inhomogeneous structure of the meat tissues, amount of intramuscular fat and connective tissues present. This way it is not possible to reach fully homogenous curing with the same amount of salt throughout all the meat cut, but reaching desired concentration of the salt in the middle of the piece can be considered as an end point of curing.

Discussed points are crucial to understand the way salt appears in meat pieces. This information is very helpful in effective managing of the dried meat commodities as well as cured ham pieces manufacturing.

3.5. Possibilities of salt diffusion accelerating

Acceleration of the production process steps of food commodities today becomes one of the most necessary and important objectives of the scientist researches and more advanced and innovative engineering solutions which allow food industry to achieve better results in manufacturing of high-quality products with considerably reduced amount of time spent on the production of goods as well as significant reduction on production costs in long run. Meat curing as one important part of the food production industry and as an essential part of human daily consumption diet also comes under scientists' investigation.

Previously discussed injection curing is one of the most widely available and successfully applied wet curing techniques. Injection curing has several advantages compared to the traditional dry curing or static brining methods. Injection curing has faster rate of brine introduction as well as improved slat distribution homogeneity of the brine in the meat piece. Likewise brine injection is beneficial in terms of decreasing moisture losses in the frozen and thawed meat due to the effect of salts high capacity to bind and retain water in the system (Leygonie et al., 2012). As trustworthy technology injection brine curing together with meat tumbler has already been applied worldwide in the meat processing plants.

Another advanced technique of salt curing introduction speed accelerate is ultrasound treatment of the meat during curing process. According to number of researches ultrasound applied to salt curing can significantly increase the curing rate due to its ability to decrease water binding capacity of the meat (Visy et al., 2021). Experiment performed by Visy A. and Jónás G. suggests that ultrasound can have a significant effect on the salting kinetics increasing amount of the salt introduction in the meat piece by decreasing the water binding capacity of the meat tissue. Decrease in water binding capacity happens due to the of salting out effect. Same experiment suggests even higher degree of salt introduction with application of microbubbles together with ultrasound treatment. Microbubbles create small pores in the meat proteins which allows more brine to be absorbed by as well as significantly increasing curing speed and highest protein swelling compared to static brining and ultrasound brining (Visy et al., 2021). This way application of ultrasonic treatment during brining can significantly increase salt introduction speed compared to static brining method (Siró et al., 2009).

Pulsed Electric Fields (PEF) is one of the newest non-thermal processing and food preservation methods. Pulsed electric field is based on application of short bursts of electric fields to a food product or any other substance which then causes pores to form in cell membranes. Such pores opening influences speed of the diffusion of ions like salt. Recent studies suggest of with the use of PEF it is possible to achieve acceleration of the salt intake during pork curing (McDonnell et al., 2014), however few years later pulsed electric field treatment was found to be much more effective in the production of dry-cured Spanish sausages mince resulting in almost fifty percent time reduction efficiency (Astráin-Redín et al., 2019).

Similarly High Hydrostatic Pressure (HHP) as one another advanced non-thermal food processing and preservation techniques that can impact the structure of food potentially influence diffusion processes, including those involving salts and other similar substances. High hydrostatic pressure treatment is also known as "minimal processing technology" as it can preserve native quality features of the food. Such technique is widely applied worldwide since 90's became one of the common techniques for inactivation of pathogenic microorganisms and increasing the shelf-life of meat products (Keerthi et al., 2017).

Thawing in meat curing is a convenient method of salt curing acceleration. There are several techniques applied for meat thawing such as traditional methods which are room temperature and still water thawing, as well as physical field thawing methods which are microwave thawing, ultrasonic thawing, and infrared thawing. Among them ultrasonic thawing was found to be the best in terms of protection of muscle tissues as well as overall reduction of the thawing consequences (Gan et al., 2022). Studies suggest that brine thawing with salting has a significant time reduction compared with the traditional salting method of the dry-cured hams (Barat et al., 2006). Another similar study proved previously proposed results suggesting even more benefit from pre-freezing and thawing by registering advancement in sensory features of dry-cured hams (Flores et al., 2006).

Tumbling is another effective method of the meat curing that is widely applied on the modern production sites. Researchers performed by Gao and his colleagues suggests that tumbling paired with marination can initiate loosening of the muscle structures, disruption of the muscle cells and destruction of the connections between the myofibers and the connective tissues of the boneless pork chops (Gao et al., 2015). This stimulates the sarcomere degradation of I-filaments and Z-lines, and by extracting salt soluble proteins (SSP) marinade introduction into meat pieces is accelerated. This contributes to the development of the physical and sensory paraments of the ham such as color stabilization and improvement in product yield. Therefore, vacuum tumbling has been recognized as an effective method of acceleration of marinade transfer into meat tissues and is proved to improve the overall quality and sensory parameters of the marinated meat products compared to other treatment methods such as static marination.

3.6. Scientific results of freezing and thawing on curing

Several studies have already revealed the positive effect of freezing and thawing on the salt curing process of different types of food commodities. Among these studies several researches on beef, pork carcasses and dry-cured ham are significant to understand the potential of the applied methods.

According to the research performed by Ahmet Akköse et al. on the effect of freezing and thawing process on salting kinetics and thermal properties of beef, it was found out that the process of thawing and freezing significantly increased the salt content of the meat cut during the salting process in compare with the fresh meat piece salt content after salting. Difference between the results was by 50%. This means that the thawing and freezing process has a great impact on the salting kinetics increasing amount of salt intake in given amount of time. (Akköse, 2017).

Similarly, Picouet et al. applied the thawing and freezing treatment before the salting period of the pork carcasses. One of the carcasses was subjected to the thawing and freezing treatment and another piece was not. Resulting salt content of the treated pork carcass was 30% higher than that of the non-treated sample (Picouet et al., 2013). This way thawing and freezing significantly affects the curing speed by increasing amount of salt intake in given amount of time as previous experiment suggests.

According to the research on how pre-cure freezing affects proteolysis in dry-cured hams author suggests that pre-cure freezing operations has a significant increase of the proteolysis levels ($p<0.05$) in the zones of the ham where water losses and absorption of salt was slowest, however pre-cure freezing and thawing does not significantly affect meat sensory parameters (Bañón et al., 1999).

On the other hand, Kemp J. and his colleagues have different opinion in this regard. Research suggests that the ham pieces that were not frozen and thawed before curing had lower initial bacterial as well as for yeast and mold counts as well as had less weight loss lower peroxide numbers, while having similar sensory scores. Thus, author concludes that for the production of high-quality cured hams it is not necessary to apply freezing and thawing as it does not significantly change the quality of the final product (Kemp et al., 1982).

Freezing and thawing therefore overall has a considerable effect on the curing process increasing salt diffusion rate and producing greater water loss. Yet, freezing and thawing does not really affect the sensory parameters and palatability of the ready product.

3.7. How thawing affects the ham properties

Due to the globalization meat and meat products are transported more intensively around the world. To preserve properties of high-quality meat, there is yet no better way to preserve meat pieces and carcasses than freezing them. There are several reports on the effect of freezing and thawing on properties of meat which are important to look at.

Researchers from Nanjing Agricultural University studied how different freezing and thawing rates affect pork properties. In the research two pairs of M. Longissimus dorsi muscles under 2 freezing speeds and 6 thawing speeds were investigated. Results presented that slower freezing rates cause intercellular ice crystals formation, whereas quick freezing rates followed by formation of intracellular ice crystals. Freezing and thawing processing showed some negative effects on the structure of meat, as for instance, reduction in the density of the Z-disks, and the overall integrity of the myofibril was lost after meat was thawed. Disruption of the myofibril was quicker and more emphasized together with the increasing thawing rates (Yu et al., 2010).

Researchers from Jiangnan University performed an experiment describing different thawing techniques and their effect on meat (including pork) suggest that thawing has some negative effects on meat which should be properly handled to conserve as much original quality of the meat as possible. Such negative effects on meat can be During the thawing process, meat is often accompanied by protein degradation, fat oxidation, color deterioration and reduced water holding capacity due to the melting of ice crystals (Gan et al., 2022).

According to James and his colleagues, there is no significant difference in the freezing method of the meat as it does not influence quality characteristics or final eating quality of meat (James & James, 2010). As for thawing process, there is not much evidence on how thawing can affect the meat quality. Only few studies suggest that cooking directly from the frozen state produced less juicy lamb rib – loins and less tender beef rolled rib joints compared to the meat that was thawed before cooking.

4. MATERIALS AND METHODS

4.1. Raw materials applied in the experiments:

Best material due to homogeneous structure. Homogeneous structure of the pork loin (M. Longissimus dorsi) is ensured with absence of bones and very low number of connective tissues. Only fresh and meat without any possible defects such as PSE, DFD or any off-odors and color and textural changes meat was used in the experiment. Measured pH of the meat was on the level of 5,60 ± 0,03 which corresponds to a normal pH of this type of meat muscle in normal conditions. Meat was purchased from the biggest and Hungarian food supplier.

4.2. Description of the experiment

Experiment was carried out using meat pieces that were previously frozen in the Nortech deep freezer under -30ºC for about 70 minutes. To protect meat from freezing crust and one-sided ice formation it is necessary to flip meat pieces in the freezer periodically, preferably each 20 minutes (Figure 12). The aim of the meat pieces freezing is to ensure straight cut and uniform sample shape as well as to preserve original quality of the meat. Deep freezing provides homogeneous crystal formation which is important to protect raw material from unnecessary structural damage and excessive water losses. Sample cut was performed using cylindrical knife which was introduced into meat with rotational movement (Figure 13).

Figure 12. Frozen meat pieces — raw material

Figure 13. Sample preparation: frozen meat and cylindrical knife

To ensure homogeneous meat cut structure it is important to avoid fat and connective tissues. Such approach will provide clarity to the experiment, as connective and fat tissues are bad in salt intake. Cylindrical shape cuts were made along the meat tissues to minimize structural damage of the meat piece and to retain as much meat as possible. Form the same meat piece it is possible to extract around 6–7 cylindrical shape samples.

To conduct the experiment, it is necessary to determine 3 groups of wet brining modes, number of samples and its treatment time. For the following experiment wet brining was applied. To provide a tracible and representative approach 15, 30, 60, 90, 120, 150, 180 minutes brining time frames were chosen. For each time frame 3 cylindrical shape samples were used resulting in 21 samples. Raw materials were treated differently prior to the brining, therefore can be classified in three treatment groups.

4.2.1. Curing methods description

Three wet curing methods were applied in this experiment. First wet curing method is control group, mentioned as “C” (Control), where previously prepared cylindrical shape samples were stored under -3–5ºC prior to curing. Once samples were removed, they were placed in the plastic flasks with brine of room temperature for curing under specified time frames (15, 30, 60, 90, 120, 150, 180 minutes).

Second wet curing method group is wet curing after sample thawing. This group is mentioned later as “BAT” (Brining After Thawing), where samples of these curing group were stored in the deep freezer under -30ºC for 12 hours prior to curing. Once samples are removed from the deep freezer, they should be thawed for 1.5 hour to make sure thawing process was finished. After thawing cylindrical shape samples were transferred to the curing flasks for curing under room temperature with determined time frames.

Third group is wet curing during sample thawing. This group is mentioned later as "BDT" (Brining During Thawing). To perform curing of this group of samples it is required to store cylindrical shape samples under -30ºC for 12 hours in deep freezer. Once the samples were removed from the freezer, they were put into plastic flask to start brining process under specified time frames.

Number of samples necessary to carry out the experiment was 63 in total, which is curing methods (3) x curing time (7) x parallel samples (3). Prior to the brining mass of each sample individually was recorded. Materials used for wet curing or brining are described in the following section.

4.2.2. Brine preparation and curing materials

To perform wet curing of the samples brine first must be prepared. For the preparation of the brine 3 cylindrical plastic flasks were used with the volume of 2000 milliliters each (Figure 14). Saturated brine solution was prepared using commercial curing salts containing 0.4 – 0.5% of nitrites of "GUSTOSAL" brand (357 g/L; 26.3 m/m%). Each sample was placed in the separate cell of the holder. Samples were placed in plastic grid structure to avoid the floating of meat samples in the brine (Figure 14). Meat sample weight ration to brine weight was 1:10. Each curing group was named and marked by paper below the name of the group respectively. Once samples were introduced into brine stopwatch start running to trace the determined time frames. With the end of each curing period respective sample group was gently removed from the curing tank and dried up using paper tissues until the surface is free from extra moisture.

Figure 14. Meat samples under wet curing

4.2.3. Determination of the dry matter and moisture content

For determination of the dry matter content (DMC) of the samples they were dried in a heating chamber at 105ºC for 24 hours. To calculate the dry matter content final weight of the sample after drying must be divided by the initial weight of the sample and multiplied by 100 (expressed in %):

$$DMC\ (\%) = \text{dry sample weight (g)} * 100 / \text{initial sample weight (g)}$$

Moisture content (X) calculation is performed by deduction of the dry matter content from 100:

$$X\ (\%) = 100 – DMC\ (\%).$$

4.2.4. Determination of the salt content (NaCl)

Determination of the salt content was performed using Morh argentometric method. For the salt content determination only central part of the samples were used, therefore cutting the edges of the cylindrical shape samples approximately for 10 millimeters was necessary for the determination of the radial salt penetration. Central parts of the sample were chopped into small pieces with approximate size of 3x3 mm and weight of 5 g placed into volumetric (Stift) flask. Mass of meat samples was accurately measured and registered. Volumetric flasks were half-filled with distilled water, properly mixed and placed into steam bath at 85ºC for 25 minutes. Once heat treatment is over, volumetric flasks are placed into ice, to cool down for 5 minutes. Cooled down volumetric flasks were filled with the distilled water up to 100 ml mark and shaken again. The extracts were filtered.

For each brined sample 10 ml of extract was titrated. Titration was performed with 0.1 N standardized $AgNO_3$ solution in presence of 2-3 drops of K_2CrO_4 indicator. Titration followed until stable red–brown color was reached (Figure 15). Chemical reactions that underwent during titration are following:

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

$$AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3$$

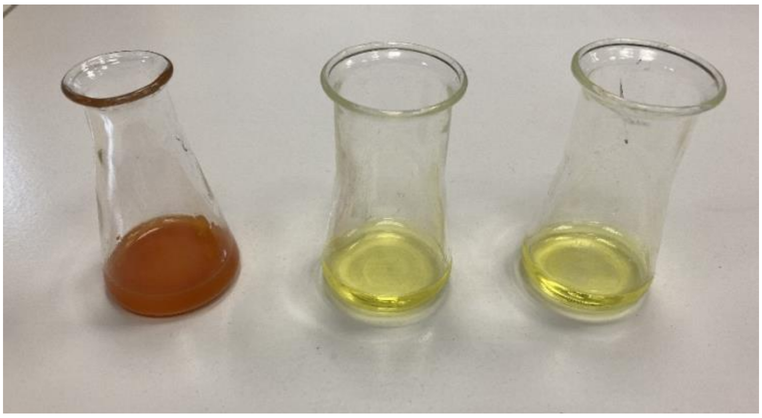

Figure 15. Titration color transition
from initial lemon-yellow to reddish-brown

Calculation of the salt content was performed using the following formula (Equation 3):

$$\text{Salt content } [\text{m/m\%}] = \frac{V_f \times f \times E \times V_{st}}{V_t \times m} \quad \text{(Equation 3)}$$

Where:

V_f – consumed volume of $AgNO_3$ titer (ml)

f – titer factor

E – salt equivalent (0.00585 g)

V_{st} - volumetric flask volume (ml)

V_t – titrated volume (ml)

m – measured meat weight (g)

4.2.5. Determination of salt and moisture content equalization

To determine the equilibrium salt (C_{eq}, m/m%) and moisture (X_{eq}, %) content it is necessary to make an experimental group of samples which are slated for infinite long amount of time. Three cylindrical shape samples were placed into saturated brine solution for 48 hours. Determination of the salt and moisture content was performed according to 3.5 and 3.6 subchapter.

4.2.6. Mathematical modeling of salt and water content kinetics

Calculation of the diffusion rate of the salt and water in salt solutions for non-classical geometrical objects such as cubes, sphere etc., and providing necessary numerical coefficients is not an easy task (Sanches et al., 2023). Therefore, two empirical mathematical models (Peleg, 1988; Zugarramurdi & Lupín, 1980) and a diffusion model (Telis et al., 2003) were used to prediction and evaluation of the salt and water mass transfer and diffusion.

a) Peleg model

Peleg's (1988) model containing two parameters (*k*) describes the kinetics of material transfer up to the equilibrium state (Equation 4):

$$WC = WC_0 - \frac{t}{k_{w1} + k_{w2}t} \qquad \text{(Equation 4)}$$

$$SC = SC_0 + \frac{t}{k_{s1} + k_{s2}t}$$

where:

WC - moisture content (g/100g sample)

SC – salt content (g/100g sample)

WC_0 – moisture content at time t=0

SC_0 – salt content at time t=0

t – time

k_w and k_s – moisture and salt material transport constants

b) Zugarramurdi and Lupín model

Model equations describing the material transport of salt and water (Equation 5):

$$WC = WC_0 exp(-k_w t) + WC^{\infty}(1 - exp(-k_w t))$$

$$SC = SC_0\ exp(-k_s t) + SC^{\infty}(1 - exp(-k_s t))$$

(Equation 5)

where:

WC - moisture content (g/100g sample)

SC – salt content (g/100g sample)

WC0 – moisture content at time t=0

SC0 – salt content at time t=0

t – time

WC^{∞} – equilibrium moisture content (g/100g sample)

SC^{∞} – equilibrium salt content (g/100g sample)

k_w and k_s – moisture and salt material transport constants

a) Telis model

Telis et al. (2003) provide information on material transport in the form of a diffusion factor (*D)* (Telis et al., 2003). Equation 6 is provided in this method:

$$\frac{C_t - C_0}{C_\infty - C_0} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} exp\left(\frac{-D(2n+1)^2\pi^2 t}{R^2}\right) \qquad \text{(Equation 5)}$$

where:

C_0	the salt content of the meat at time *t*=0 (initial salt content) (g/100g)
C_t	the salt content of the meat at time *t* (g/100g)
C_∞	equilibrium salt content of the meat (g/100g)
D	diffusion factor (m^2/s)
t	time (s)
R	radius (m)

This model suggests calculation of the diffusion coefficient (D_v) by substitution of moisture content (X) with salt content (C). Drastic decrease of the exponential term value, with increasing n, being equal to infinity ($n=\infty$) can be well approximated by the sum of the first 50 terms ($n=0…50$).

Peleg and Telis models values of the material transport parameters (k_w and k_s) as well as diffusion factor (D) were computed by MS Excel Solver software using non-linear GRG. In such way minimal difference between measured and calculated salt and water content root square values — RMSE (Root Mean Square of Error) — was obtained, providing information about how well the model fits to the measured data. Further calculation of R^2 value (coefficient of determination) represents which model describes the salt diffusion in the most proper way. Therefore, Equation 8 equation is used for determination of R^2 value:

$$R^2 = \frac{\sum(Y_p - \bar{Y}_p)^2}{\sum(Y_p - Y)^2 + \sum(Y_p - \bar{Y}_p)^2} \qquad \text{(Equation 6)}$$

where:

Y_p predicate value of the Y variable

$\bar{Y}_p$ predicated value of the Y variable

5. RESULTS AND DISCUSSION

Results of the performed experiments are going to be discussed in this chapter. According to the experiments absolute salt and moisture content, kinetic constants and diffusion coefficients were determined and calculated.

5.1. Salt content

Salt content determination was performed according to the Materials and Methods chapter (chapter 3). Figure 16 represents the average salt content changing in time in the case of three bring methods (Control, BDT and BAT).

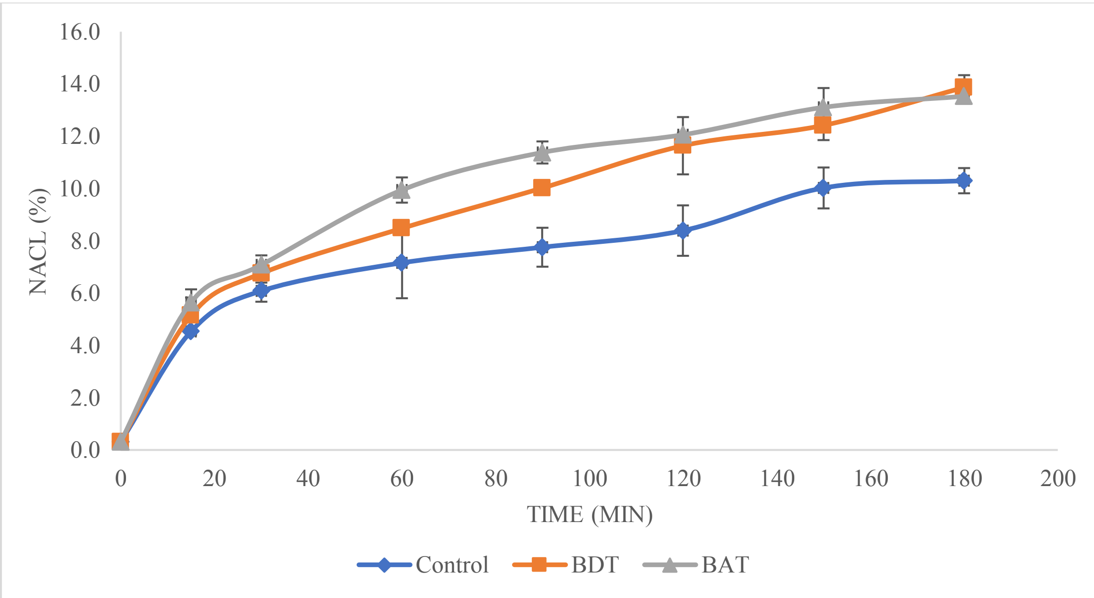

Figure 16. Pork meat samples salt content changing in time in the case of different brining-thawing methods (C – control, BDT – Brining during thawing, BAT – Brining after thawing). Data points show average salt content and standard deviations.

At the beginning of the brining higher rate of the salt content intake can be observed for all sample groups. Control group can be clearly seen to uptake the lowest amount of salt among the 3 curing groups. Both BDT and BAT presented much higher salt content values compared to the control group at all stages of the curing process also considering standard deviation.

However, BAT compared to BDT showed larger amount of salt content at all stages of brining except the last stage of 180 min., where both curing groups' salt intake was merely the same. This way, brining of the meat samples after the thawing process represents most amount of salt intake compared to the brining during the thawing process as well as brining without prior sample treatment.

5.1.1. Peleg model for salt diffusion

Peleg model was used for the prediction of the salt content intake. Calculation of the diffusion factor was performed according to the Materials and Methods chapter (p. 3.8 a)). Following figures (Figure 17, 18 and 19) represent the measured and model calculated salt content.

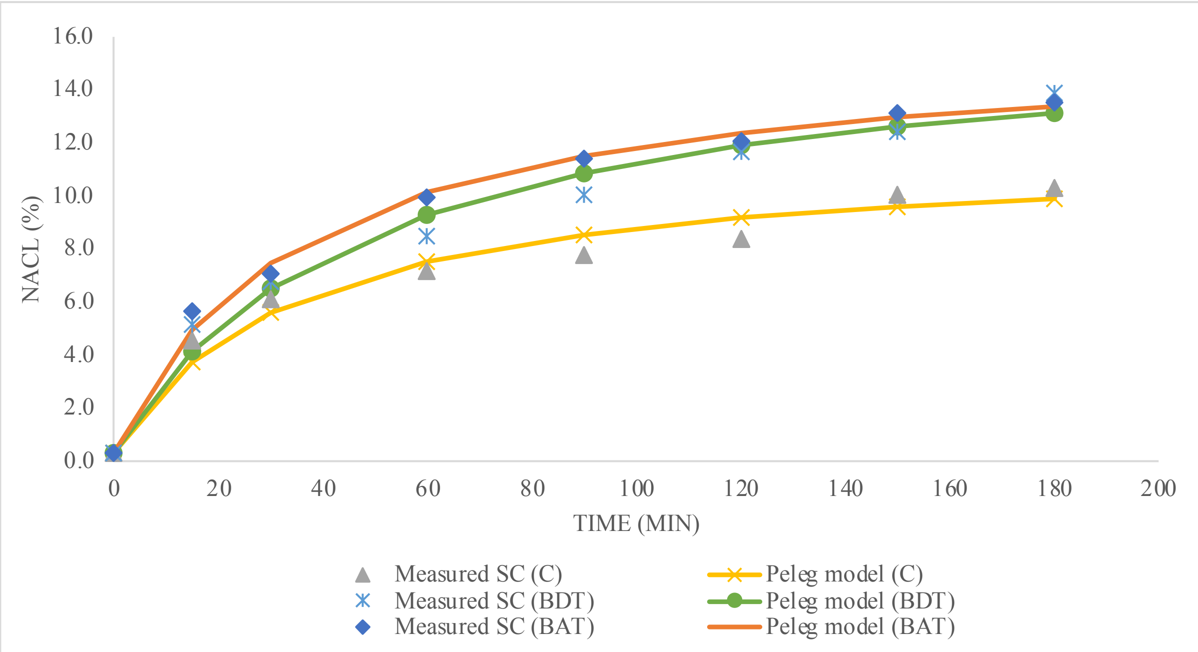

Figure 17. Peleg model calculated salt content (SC) values represented together with the measured values for C, BDT and BAT groups.

BAT sample group presented fastest diffusion rate, following by the BDT and control groups. Although BAT in the first steps of the brining presented higher diffusion rate compared to the BDT, in the last brining period both methods showed similar values. All the sample groups followed the same pattern. Both measured and calculated parameters provide similar results showing good fit to the calculation model.

5.1.2. Zugarramurdi and Lupín model for salt diffusion

Zugarramurdi and Lupín method of salt diffusion rate calculation provide a similar approach as the previous method defining the salt content kinetics having comparable results. Figure 18 represents calculated data using Zugarramurdi and Lupín method of salt diffusion rate.

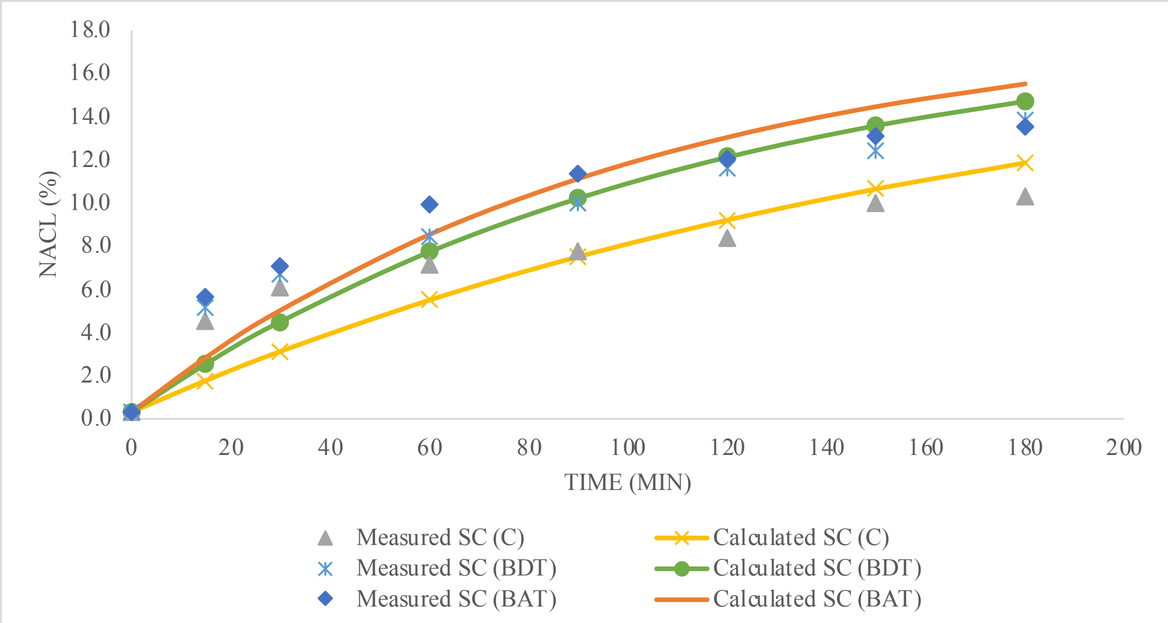

Figure 18. Zugarramurdi model calculated valued for SC represented together with the measured values for three sample groups.

BAT again appears to be having the highest diffusion rate followed by BDT and control sample groups. In this scenario, however, model fitting appears to be less. Measured results, despite having a good correlation among each other, are not well fitting the calculated salt content lines in all cases. Providing similar tendency as in case of Peleg's model, results cannot be considered as a good fit that are important to describe the salt content kinetics.

5.1.3. Telis model for salt diffusion

Provided calculations using Telis model of salt diffusion rate are represented on the Figure 19.

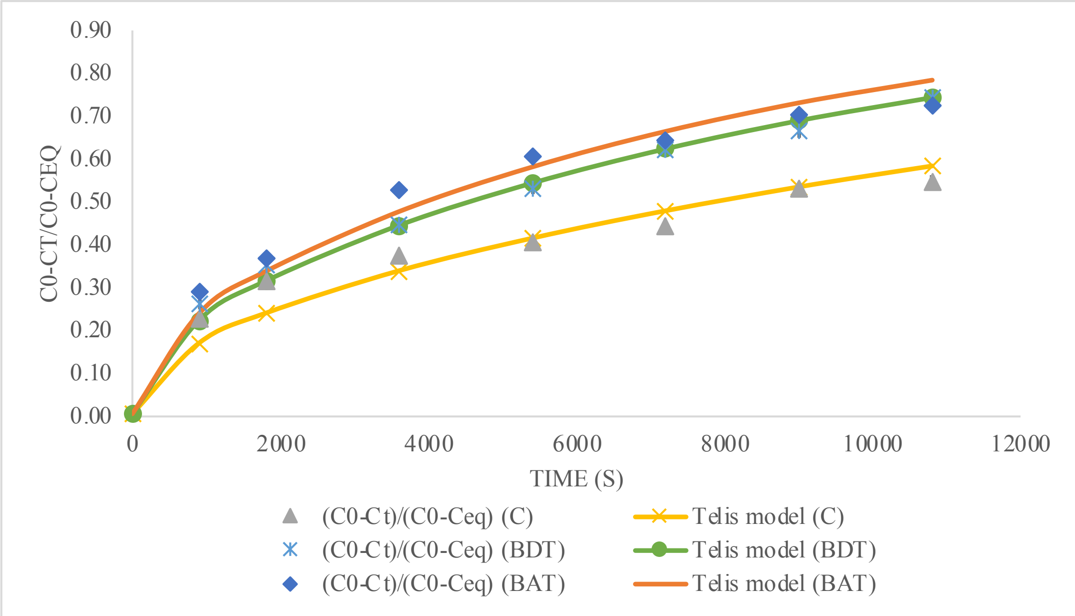

Figure 19. Telis model calculated values for SC represented together with the measured values for three sample groups.

Following the same pattern as the previous methods BAT again showed highest kinetics compared to BDT and control sample groups following the same ranking in salt intake speed. Measured and calculated values are very well fit and represent BAT and BDT to have higher diffusion rate equally compared to control group at all determined time frames.

5.1.4. Evaluation of salt mass transfer and diffusion

Provided table (Table 1) introduces the values calculated coefficients, R^2 and RMSE for Peleg, Zugarramurdi and Telis models for three sample group's salt content.

Table 1. Summarized table for salt content

Model	Parameter	Control	BDT	BAT
Peleg	k1	3.072	3.007	2.283
	k2	0.088	0.061	0.064
	R^2	0.9683	0.9792	0.9944
	RMSE	0.5697	0.6225	0.3239
Zugarramurdi	ks	5.61E-03	8.77E-03	1.00E-02
	R^2	0.8488	0.9401	0.9301
	RMSE	1.681	1.3573	1.609
Telis	Ds	3.50E-10	6.05E-10	6.95E-10
	R^2	0.9540	0.9930	0.9822
	RMSE	0.0405	0.0218	0.0381

Even though all the models provide good results and represent the experiment with very nice precision not all of them do it equally good. R^2 value more than 0.85 can be considered as a good fit. This way Peleg model is outstanding, showing biggest number for all three brining groups at the same time, meaning it can be considered as the best fit for the measured data. Therefore, Peleg model can be used to compare the brine–thawing methods to each other from the salt mass transfer perspective. Peleg model suggest that the coefficient k1 with the decreasing tendency describes increasing salt mass transfer. The k1 model parameter shows already familiar pattern of mass transfer, where BAT sample group has largest mass transfer, followed by BDT group and resulting with the Control group with the lowest salt mass transfer. Although other model fit to lesser extent same relation can be seen for ks in Zugarramurdi model as well as for diffusion coefficient (D) in Telis model. In the diffusion model however the higher D value is, higher is the salt diffusion.

5.2. Moisture content

Moisture content highly depends on the amount of salt content: osmosis versus diffusion. While osmosis is responsible for the movement of the water towards the higher concentration of the salt (brine), diffusion makes salt to move toward the area of low salt concentration (meat water). This way the moisture content of the meat samples is going to be decreasing by the time, presenting opposite tendency on the plot. Following figure (Figure 20) represents the absolute moisture content of the sample groups measured form the experiment.

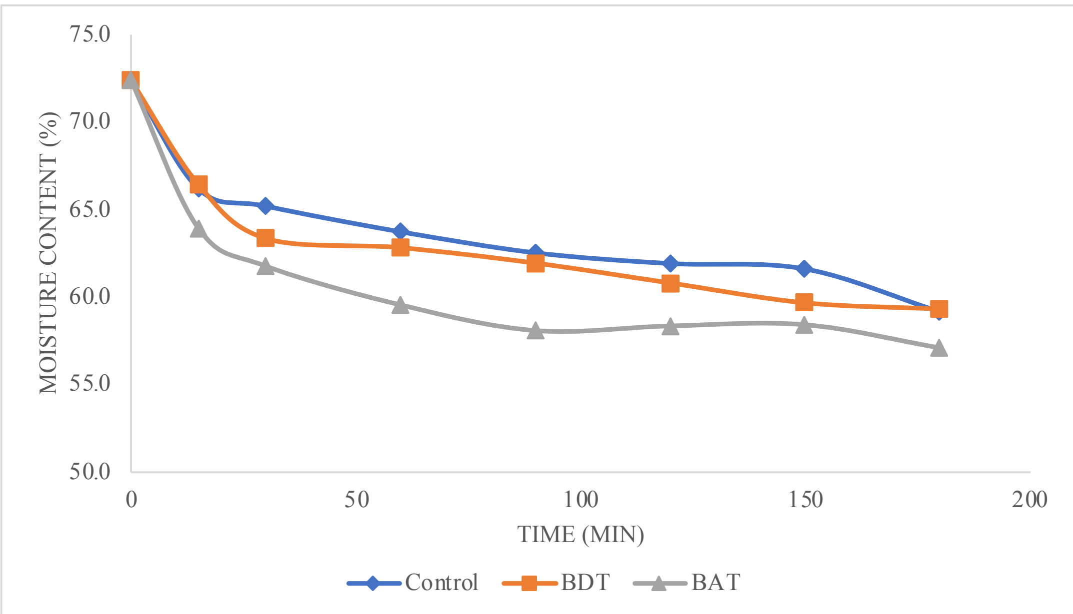

Figure 20. Pork meat samples moisture content changing for different brining-thawing methods. Data points show average moisture content.

Moisture content reduction of the control group appears to be the smallest among the sample groups followed by BDT and BAT. BDT moisture content loss after 15 min. time frame reduces with the rate but differs in quantity however equalizing after 180 minutes. BAT however shows drastic moisture content drop from 15 min. time frame and keep decreasing reaching lower than 60% of moisture.

5.2.1. Peleg model for moisture content

Peleg model for the moisture content was used as in case of salt content. Result of the modeling are provided in the following figure (Figure 21)

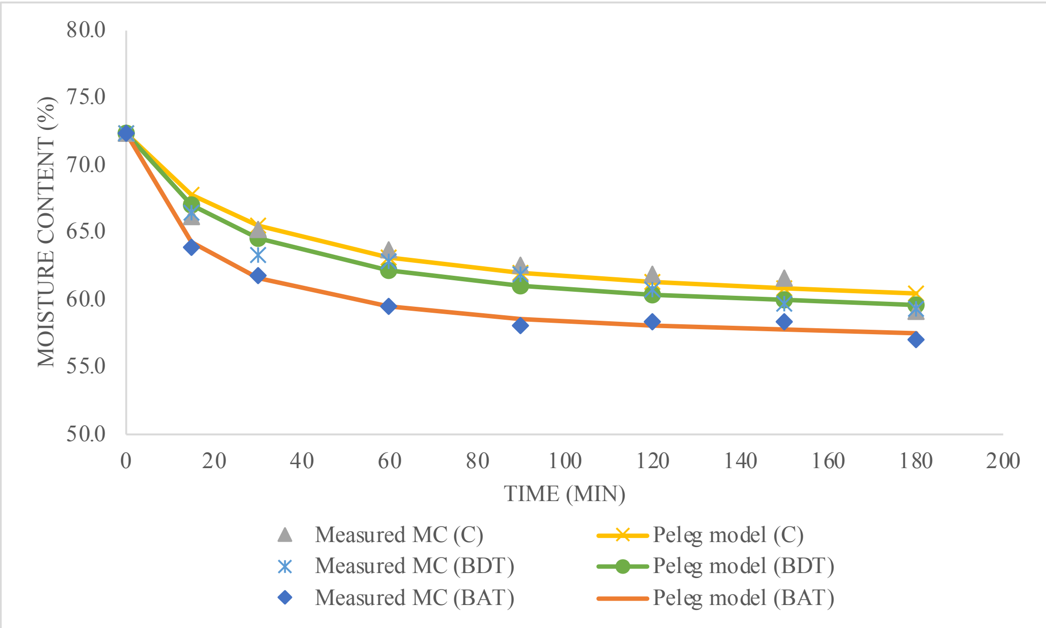

Figure 21. Peleg model calculated moisture content (MC) values represented together with the measured values for C, BDT and BAT groups.

Control group appears to have the least amount of moisture by the end of the brining, followed by BDT and BAT sample groups. Similar tendency can be traced on the Figure 20, where the moisture content reduction for both BDT and the control group comes with very mild differences, as well as BAT having a big gap compared to the other two groups. It is noticeable as in case of salt content how well does the Peleg model fit the measured values.

5.2.2. Zugarramurdi and Lupín model for moisture content

Zugarramurdi and Lupín model for calculation of the moisture content is represented in the Figure 22.

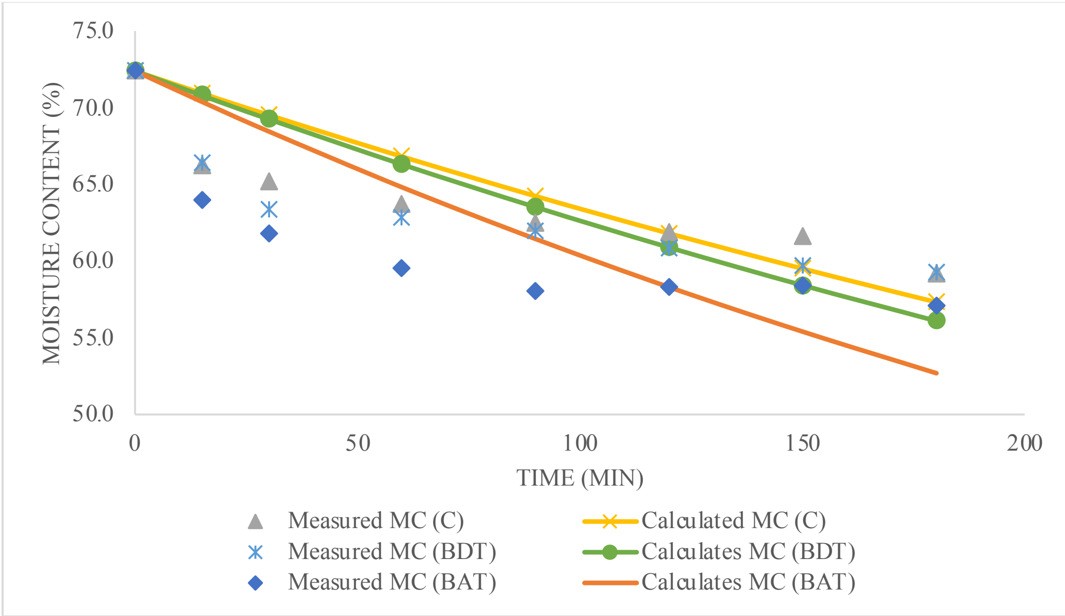

Figure 22. Zugarramurdi model calculated valued for MC represented together with the measured values for three sample groups.

As in case of Peleg model it clear that calculated MC for BAT is lower compared to both BDT and C sample groups throughout the whole time of the experiment. Zugarramurdi model does not provide a perfect fit, however, still represents the same pattern, where BAT group has lowest MC after brining and C group has highest MC.

5.2.3. Telis model for moisture content

Telis model using diffusion coefficient is represented on the following figure (Figure 23).

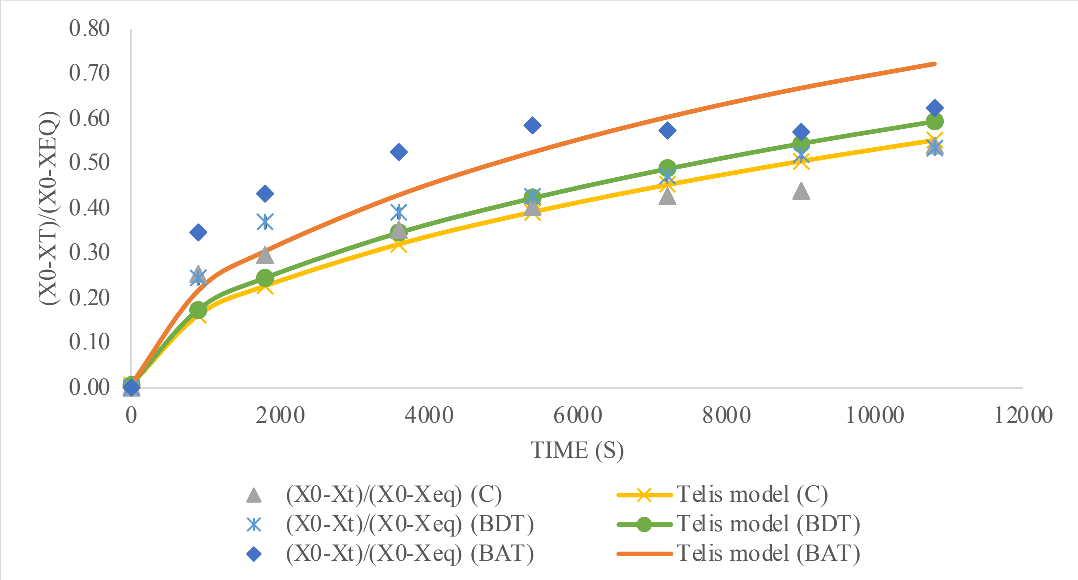

Figure 23. Telis model calculated values for MC represented together with the measured values for three sample groups.

As previously mentioned, diffusion coefficient (D) provides an opposite to k1 and ks tendency. Increasing value of the D shows decreasing MC. This way Telis model provides a good picture, where BAT group MC is decrease appears to be the highest, followed by BDT and C groups respectively with relatively small difference in MC decrease.

5.2.4. Evaluation of moisture content

Provided table (Table 2) introduces the values calculated coefficients, R^2 and RMSE for Peleg, Zugarramurdi and Telis models for three sample group's moisture content.

Table 2. Summary table for moisture content

Model	Parameter	Control	BDT	BAT
Peleg	k1	-2.177	-1.754	-0.902
	k2	-0.072	-0.069	-0.062
	R^2	0.9528	0.9767	0.9940
	RMSE	0.8673	0.6401	0.3690
Zugarramurdi	ks	1.82E-03	2.00E-03	2.52E-03
	R^2	0.7759	0.7582	0.7242
	RMSE	2.775	3.174	4.392
Telis	Ds	3.13E-10	3.65E-10	5.65E-10
	R^2	0.9264	0.9142	0.8861
	RMSE	0.0492	0.0582	0.0911

For the moisture content table similar results as for salt content are to be expected. The quality of the modeling for the experiment can be discussed considering the R^2 values for each sample group separately, to see how well it fits the specific group, as well as together, to decide on the model that appears the best for the MC determination in general. Peleg model in this case clearly provides the best fit on individual sample group level as well as considering all sample groups together, considered the most precise for the MC modeling.

CONCLUSION

Considering both calculated and measured data, it can be clearly stated that salt and moisture content are greatly affected by the method of brining. Brining of the pork after thawing provides higher salt content and greater mass transfer compared to the brining during thawing. Brining without preliminary treatment has the lowest number of salt content as well as lowest mass transfer. Similarly, moisture content depends on the brining method. Sample group brined after thawing were having lowest moisture content (highest water losses) compared to the sample group brined during thawing. Sample group without preliminary to brining treatment had highest moisture content (lowest water losses).

Experiment results can be applied for the further development of brining technology. It can be significant for the meat processing plants that looking for rapid increase of the salt content (or fast decrease of the moisture content) within a short period of time, which will significantly increase production capacity.

SUMMARY

From the ancient times meat curing was an important part of human diet. Main reasons why do people salt meat is to preserve its original quality as well as to improve its sensory parameters. Preservation of the meat through time developed significantly as knowledge about salt curing methods find its scientific approach.

Salt curing nowadays is represented by two main techniques such as dry curing which performed by simple addition of the salt on the meat pieces, and wet curing or brining which is curing of the meat in the saturated salt solution. More advanced version of the wet curing which is nowadays widely applied on the modern meat processing plants is injection curing, where meat tissues are penetrated with the brine directly. Injection curing is usually subjected to further vacuum tumbling process, which ensures homogeneous distribution of the brine.

Salt influences flavor, preservation, and water holding capacity in meat. Factors affecting salt diffusion include meat piece geometry, brine concentration, meat-to-brine ratio, diffusion constant, chemical reactions, boundary layer, temperature, and salt distribution. Accelerating salt diffusion methods, such as injection curing and ultrasound treatment, enhance salt distribution, reduce curing time, and improve meat product quality. Freezing and thawing processes significantly increase salt intake during curing, improving curing kinetics, but the impact on sensory parameters varies based on specific conditions.

In this study, the choice of raw materials involved using pork loin (M. Longissimus dorsi) with a homogeneous structure, free from bones and connective tissues, and ensuring the meat is fresh and free from defects such as PSE, DFD, or off-odors. The meat was purchased from a reputable Hungarian food supplier and had a normal pH level. The experiment involved freezing the meat to -30ºC to maintain its quality and enable uniform sample preparation. Samples were cut into cylindrical shapes, avoiding fat and connective tissues. The experiment encompassed three wet brining methods, involving various curing times (15, 30, 60, 90, 120, 150, 180 minutes), and the samples were categorized into three treatment groups. The wet curing methods included a control group stored at -3–5ºC before curing, a group brined after thawing (BAT) following 12 hours of freezing at -30ºC, and a group brined during thawing (BDT). A total of 63 samples were used in the experiment. The brine was prepared using commercial curing salts, and salt and moisture content were determined. The study also employed mathematical models to evaluate salt and water mass transfer and diffusion, with parameters (kw, ks, D) determined through software optimization and evaluated using RMSE and R^2 values.

The salt content was assessed for three brining methods: Control, BDT (Brining during Thawing), and BAT (Brining after Thawing). Figure 16 illustrates how salt content changes over time for these methods. Notably, BAT showed the highest salt intake, followed by BDT and Control, indicating that brining after thawing results in the most significant salt absorption.

We employed the Peleg model for salt diffusion, and Figure 17 presents the calculated and measured salt content values. BAT displayed the fastest diffusion rate, followed by BDT and Control, with the model fitting well for all groups. Zugarramurdi and Lupín model provided similar results (Figure 18), with BAT again having the highest diffusion rate but less satisfactory model fitting. Telis model for salt diffusion (Figure 19) confirmed BAT's faster kinetics and excellent model fit. A summarized table presented a Peleg model being the most accurate.

Moisture content was also investigated, and Figure 20 shows the absolute moisture content over time for the same sample groups. Control exhibited the smallest moisture loss, followed by BDT and BAT. The Peleg model for moisture content (Figure 21) showed that Control had the least moisture by the end of brining, with excellent model fitting. Zugarramurdi and Lupín model (Figure 22) confirmed that BAT had the lowest moisture content, although the model fit was not perfect. Telis model (Figure 23) also demonstrated that BAT had the highest moisture content decrease, with good model fitting. The summarized table for moisture content evaluation revealed that Peleg's model was the most accurate.

In conclusion, our experiments clearly indicate that the brining method significantly affects salt and moisture content. Brining after thawing results in higher salt content and more substantial mass transfer compared to brining during thawing. Brining without prior treatment has the lowest salt content and mass transfer. Moisture content follows a similar trend, with samples brined after thawing experiencing the highest water losses. These results have implications for the development of brining technology and can benefit meat processing plants looking to increase salt content or reduce moisture content rapidly, thereby enhancing production capacity.

DECLARATION

on authenticity and public assess of thesis

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Student's Neptun ID:	C00M44
Title of the document:	Investigation of the Effect of Freezing and Thawing During Meat Curing
Year of publication:	2023
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