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DETERMINATION OF MOISTURE CONTENT AND CRYSTALLINITY OF HARD CANDIES BY TD-NMR

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

SENA KUZU

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DETERMINATION OF MOISTURE CONTENT AND CRYSTALLINITY OF HARD CANDIES BY TD-NMR

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ABSTRACT

DETERMINATION OF MOISTURE CONTENT AND CRYSTALLINITY OF HARD CANDIES BY TD-NMR

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Hard candies are perfect amorphous food materials prepared by minimal ingredients. Crystallization process in a hard candy is not desirable since it has a negative effect on the quality of the product. Crystallization of a hard candy can be determined by different techniques such as Differential Scanning Calorimetry (DSC) and X-ray Diffraction (XRD). Another quality parameter of the hard candies is the moisture content which should normally be around 2-3% and determined by highly chemical intensive method of Karl-Fischer titration.

Low field Time Domain Nuclear Magnetic Resonance (TD-NMR) technique is widely employed in assessing changes in foods, commonly relying on T_1 (spin-lattice) and T_2 (spin-spin) relaxation times. Recently, it has been shown that TD-NMR can also be used to assess the crystallinity of different products through the use of *Solid Echo* (SE) pulse sequence. TD-NMR can also be a great tool to determine the moisture content of candies as well. In this thesis, two types of hard candies were studied for assessing crystallinity and moisture content by TD-NMR. The first one is the regular hard candies made of sucrose, glucose syrup, and water. The second one is the traditional akide candy which is made of sucrose, water, and citric acid. In the first part of the study, hard candies were cooked and stored at different temperatures. Moisture content, total soluble solids, and XRD analysis were also made as complementary methods to TD-NMR experiments of T_1 and Solid Echo. T_1 relaxation times and SE results significantly changed at different cooking and storage temperatures ($p \leq 0.05$).

In the 2nd part of the study, akide candies were formulated, and T_1 and SE experiments were conducted. Akide candies were prepared by using different citric acid concentrations and cooked different temperatures. Likely, moisture content, total soluble solids, and XRD analysis were made as complementary methods to TD-NMR. T_1 results showed significant differences at different citric acid concentrations and cooking temperatures ($p \leq 0.05$) corroborated by SE outcomes ($p \leq 0.05$).

Overall, it can be seen that TD-NMR method is an appropriate and easy method for determination of moisture content and crystallinity in hard candies.

Keywords: Hard candy, akide candy, TD-NMR, crystallinity, moisture content

ÖZ

ZAMANSAL ALANDA NMR YAKLAŞIMI İLE SERT ŞEKERLERİN SU İÇERİĞİ VE KRİSTALLİK TAYİNİ

Kuzu, Sena
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Sert şekerler minimum miktarda malzeme ile hazırlanan mükemmel amorf gıda malzemeleridir. Sert şekerde kristalizasyon işlemi ürünün kalitesine olumsuz etki ettiğinden tercih edilmemektedir.Sert şekerin kristalleşmesi, Diferansiyel Taramalı Kalorimetri ve X-ışını Kırınımı gibi farklı yöntemlerle belirlenebilir. Sert şekerlerin bir diğer kalite parametresi, normalde %2-3 civarında olması gereken nem içeriğidir. Karl-Fischer titrasyonunun yöntemiyle belirlenir ve bu yöntem yüksek kimyasal yoğunlukludur.

Düşük alanlı zamansal alanda NMR tekniği, genellikle T_1 (spin-latis) ve T_2 (spin-spin) relaksasyon sürelerine dayanan, gıdalardaki değişiklikleri değerlendirmede yaygın olarak kullanılan bir yöntemdir. Son zamanlarda düşük alanlı zamansal alanda NMR'ın Katı Hal Ekosu yaklaşımı kullanılarak farklı ürünlerin kristalliğini değerlendirmek için de kullanılabileceği gösterilmiştir. Düşük alanlı zamansal alanda NMR aynı zamanda şekerlerin nem içeriğini belirlemek için de harika bir araç olabilir. Bu tezde kristallik ve nem içeriğinin düşük alanlı zamansal alanda NMR ile değerlendirilmesi için iki tip sert şeker üretildi. Bunlardan ilki sakaroz, glikoz şurubu ve su ile yapılan normal sert şekerlerdir. İkincisi sakaroz, su ve sitrik asitten yapılan geleneksel akide şekeridir. İlk bölümde sert şekerler farklı sıcaklıklarda pişirilip saklandı. Nem içeriği, toplam çözünebilir katı ve XRD analizleri zamansal alanda NMR yöntemini tamamlayıcı yöntemler olarak yapılmıştır. T_1 relaksasyon süreleri ve Katı Hal Ekosu sonuçları farklı pişirme ve saklama sıcaklıklarında önemli ölçüde değişmiştir ($p \leq 0.05$).

Çalışmanın ikinci bölümünde akide şekerleri formüle edilmiştir. T_1 ve Katı Hal Ekosu deneyleri yapılmıştır. Akide şekerleri farklı sitrik asit konsantrasyonlarında ve farklı sıcaklıklarda pişirilmiştir. Zamansal alanda NMR yönteminin tamamlayıcısı olarak nem içeriği, toplam çözünebilir katı ve XRD analizi yöntemleri kullanılmıştır. T_1 relaksasyon süreleri farklı sitrik asit konsantrasyonlarında ve pişirme sıcaklıklarında önemli farklılıklar göstermiştir ($p \leq 0.05$). Katı Hal Ekosu ölçümleri yoluyla elde edilen kristallik değerleri de geleneksel (T_1) zamansal alanda NMR ölçümleriyle ilişkili olarak önemli farklılıklar göstermiştir ($p \leq 0.05$).

Genel olarak bakıldığında zamansal alanda NMR yönteminin sert şekerlerde nem oranı ve kristallik belirlemek için uygun ve kolay bir yöntem olduğu görülmektedir.

Anahtar Kelimeler: Sert şeker, akide şekeri, zamansal alanda NMR, kristallik, nem içeriği

Dedicated to my family, especially to my niece Asya Meva.

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TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

LIST OF ABBREVIATIONS

CPMG : Carr-Purcell-Meiboom-Gill

FID : Free induction decay

M_2 : Second moment

M.C. : Moisture content

MSE : Magic sandwich echo

RF : Radiofrequency

SE : Solid echo

TD-NMR : Time domain nuclear magnetic resonance

T_g : Glass transition temperature

TSS : Total soluble solids

XRD : X-ray diffraction

CHAPTERS

CHAPTER 1

INTRODUCTION

1.1 Hard Candies

Hard candies are the simplest confectionery products. They mainly include water and sucrose. Hard candies are obtained by cooking the mixture of sucrose and corn syrup to very high temperatures (Sabbagh & Fagerson, 1979). The sugar and water mixture are boiled to high temperatures to reduce the water content. The boiled sugar mass is cooled down to room temperature. The final product has a glossy appearance and hard texture (Hartel et al., 2011). Hard candies are in a glassy state, and they have low moisture content such that 2-3% because of the applied processing conditions (Ergun et al., 2010). The main mechanism behind the cooling of hard candy is to produce a product in a glassy amorphous state below its glass transition temperature (T_g). In the glassy state, the system is kinetically stable, and molecular mobility is severely blocked (Sherwin & Labuza, 2006a). This restriction of molecular mobility provides provisional stability during the storage time. Nevertheless, changes in storage temperature and relative humidity (RH) may immensely cause destabilization of the products (Roos & Karel, 1991).

Excessive moisture absorption during the storage of hard candies causes two main problems which are sucrose recrystallization (graining) and stickiness (McFetridge et al., 2004). Moreover, the composition of hard candy plays an important role in storage stability. Hard candies containing a high amount of sucrose can have high T_g

values, but they may be more likely to graining based on the storage conditions. The sticky texture is an undesired property because of the difficulties in wrapping parts and the reduction in consumer acceptance. Thus, it is critical to control the composition, process, production, and storage conditions of hard candies (Hartel, 2002).

Hard candy production is not a complex process. However, even small changes related to composition and production may harshly affect product quality. Moisture content, temperature, pH, color, rheological and textural properties are the main quality parameters for hard candy. Each of these parameters can have various effects on the quality of the final product. For example, temperature is a very crucial parameter for both production and storage periods. An increase in temperature during the production stage results in a more concentrated low moisture product. Nonetheless, extreme levels of temperatures may lead to some unacceptable changes such as caramelization, etc. in the hard candy structure (Hartel et al., 2011). Temperature is also important for storage conditions. When the storage temperature is higher than T_g of hard candies, a transition from a glassy to a rubbery state occurs which causes an increase in molecular mobility. Under these kinds of conditions, hard candies may encounter stickiness or graining (Balasubramanian et al., 2016).

Akide candy is a traditional type of hard candy. The formulation of akide candy differs from common hard candy. It is produced by mixing water, sucrose, and citric acid. Boiling temperatures for akide candy are higher than the boiling temperatures for hard candy. The final product of akide candy is similar to common hard candy. It has also a glassy structure and hard texture. The quality parameters are also the same for akide candy as well (Kürşat Demir et al., 2010).

1.2 Moisture Content

Hard candies have a moisture content range of 2-3% (Sharma & Ghoshal, 2021). This low moisture content generates a low water activity that provides physical, flavor, and microbial stability. If the moisture content of hard candy becomes higher than 5% which is an unacceptable level, water in the hard candy acts as a plasticizer and reduces the T_g. This decrease in T_g causes disruption of the glassy structure (Raudonus et al., 2000). The existence of excess water is the main reason behind sucrose graining (Bund & Hartel, 2010). Therefore, to obtain a longer shelf-life, low moisture content is desired. High moisture content levels also alter the textural and physicochemical features of hard candies.

Karl Fischer titration method can be used to determine the initial and final moisture contents of hard candies (Spanemberg et al., 2019). Control of the initial moisture content is really important since extreme levels of moisture in the formulation may prevent the hardening of the mixture during the production process (Shukla & Kandra, 2015). Materials in the formulation are very effective on the final moisture content of hard candies. For instance, if a gum is added at a high concentration to the formulation, very high moisture content levels would be obtained (Dinesh Kumar et al., 2022). Another parameter related to moisture content is flavor retention. A low moisture content causes delaying in the release of flavor by minimizing the loss of flavor during the high-heat treatment process (Reineccius et al., 2004).

1.3 pH

Hard candies have a pH interval of 3-4 due to the presence of food acids. Generaly sour taste of hard candy is provided with citric acid. pH is impactful on many hard candy quality parameters such as color, taste, sucrose inversion and pigment stability (Hubbermann, 2016). pH of the hard candy mixture affects the color shade of the candy. Some color pigments are susceptible to acidic pH values and such pigments may present a variation in their colour in hard candies. Thus, acid-stable color pigments should be selected. pH also plays an important role in sucrose inversion process that is encountered during the cooking step of hard candy production. Generally, low pH increases the rate of sucrose inversion in combination with high temperature and high RH. Inversion of sucrose to glucose and fructose adjusts the physicochemical properties of the products in terms of storage stability, texture, taste and appearance. Products of sucrose inversion which are glucose and fructose are hygroscopic and absorb moisture, inducing crystallization and cold melt (Nadaletti et al., 2011).

1.4 Temperature

One of the most important quality factors of hard candy is temperature. Its control is important during both the production and storage stages. As examined in the previous parts, very high boiling temperatures are needed for hard candy production (Hartel et al., 2011). Temperature is also essential in the cooling period of boiled hard candy mixtures. Cooling can be done in two ways which are at room temperature or at temperature-controlled environments.

Shaping of the mixture is related to the temperature since different temperatures would bring different difficulties during shaping (Reinheimer et al., 2012) Cooling tunnels may be used for cooling hard candies. In this way, the range of temperature distribution can be reduced within each product. Otherwise, a non-uniform temperature distribution can be noticed and this may cause quality problems (Reinheimer et al., 2012). Yet, optimizing the cooling process of hard candy is not easy since it requires some high costs.

There is much research in the literature that presented different process parameters for hard candy production. If the formulation includes only sucrose and water, the mixture is generally heated to the hard-crack temperature of hard candies which changes between 145°C and 160°C (Jiang et al., 2019; Swer et al., 2019). Even though most of the cooking processes of hard candies take place at atmospheric pressure, there are some cooking processes that vacuum that was applied especially in commercial hard candy production. Under vacuum, the final temperature is reduced providing less T_g decrease and less inversion of sucrose. In addition, the removal of moisture is improved and the degradation of pigments is lowered (Reinheimer et al., 2010).

1.5 Glass Transition Temperature

Glass transition temperature (T_g) has a critical importance on the quality and stability of the product. Storage temperatures higher than T_g have a destructive effect on quality features (Tan & Kerr, 2017). On the other hand, storage temperatures below T_g keep the glassy state of the product providing restriction of molecular mobility. In a state where the temperature is higher than T_g, an increase in molecular mobility is observed which results in loss of glassy state (Balasubramanian et al., 2016). Therefore, physicochemical changes can take place within the products. As an example, if the storage temperature exceeds T_g of the product during storage, sucrose crystallization becomes possible. High molecular mobility brings sucrose crystal nucleation and then crystal growth. Temperature-caused crystallization is generally seen in the form of internal graining. In this kind of graining, crystals formed during hard candy production start to grow in the glassy structure (Bund & Hartel, 2010). Textural-sensorial disruption and loss of flavor are the undesirable results of this process (Hartel, 2002). Changes in the temperature during transportation and storage may also induce the crystallization character of hard candies.

Another factor effective on T_g is the composition of hard candies. For example, water acts as a plasticizer and it reduces T_g at a high level (Roos & Karel, 1990). Moreover, hard candies have a glass transition range due to their complex mixtures (Saavedra-

Leos et al., 2012). Thus, detecting an exact single T_g would be a problem. Differential scanning calorimetry (DSC) and thermal rheological analysis (TRA) are commonly used methods to obtain T_g (Kawai et al., 2019). DSC is based on a change of heat flow or temperature between the sample and reference pan. DSC has a small sample size and contributes to high sensitivity. Nonetheless, controlling heating and cooling rate are important and there would be inconsistent results due to this (Bund & Hartel, 2010). In recent years, TRA was introduced to determine the T_g of hard candies as a thermomechanical method (Kawai et al., 2019). Yet, mechanical T_g is not always correlated with calorimetric T_g. Thus, a calibration should be made between mechanical and calorimetric T_g (Kawai et al., 2019).

1.6 Crystallization

Crystallization is an important factor for hard candies since it plays a crucial role in quality parameters. There are two main quality problems of hard candies encountered during storage which are sugar recrystallization and increased stickiness. These unwanted changes can be prevented by temperature, RH, or both (Cardoso & De Abreu, 2004). Based on the product formulation, generally, high RH and high-temperature cause graining or stickiness (Nowakowski & Hartel, 2002). During the production of hard candies, it is aimed to bring them to a glassy state to prevent molecular mobility that may induce textural decomposition during the storage period. However, external conditions change still can start changes that result in quality disruption (Netramai et al., 2018).

To obstruct sucrose crystallization, doctoring agents such as corn syrups are added to formulations of hard candies (Hartel & Shastry, 1991). Glucose and fructose molecules in the corn syrup prevent sucrose crystallization by increasing the viscosity of the mixture. Corn syrup sugars also can hinder the incorporation of crystallizing sucrose molecules into the crystal lattice (Gabarra & Hartel, 1998; McFetridge et al., 2004). These sugars can also lower the solubility concentration of sucrose (Tjuradi & Hartel, 1995). In this way, doctoring agents increase the shelf-life of hard candies. Nevertheless, glucose and fructose in doctoring agents are better humectants than sucrose. Therefore, there would be excess moisture absorption at high glucose and fructose concentrations which results in a sticky product (Iglesias et al., 1997).

There are some differences between the temperature-caused and moisture-caused graining mechanisms. Moisture-caused graining starts from the surface of hard candy. Absorbed water forms a thin layer on the surface of hard candy where crystal nucleation starts. Then, water diffuses into the inside of the product and graining is growing with this diffused water (Levenson & Hartel, 2005). On the other hand, temperature-caused graining starts from the inside of hard candy. In a case where the storage temperature surpasses T_g of the hard candy, an increase in molecular mobility is seen and crystals first formed during the production start to grow (Liang et al., 2007). Both moisture-caused and temperature-caused graining are undesirable and necessary controls should be done to avoid this situation.

Sugar recrystallization could be seen in hard candies. It can be controlled and evaluated by many analytical methods. One of the methods used for the detection and characterization of crystalline parts in foods is microscopy (Aguilera & Lillford, 2008). For crystal sizes bigger than 5 µm, transmission and reflection simple light microscopy would be used. Yet, the separation of crystals from the product is required for this method. For a crystal size between 1 and 5 µm, to improve crystal detection, polarized light microscopy should be used (Lans et al., 2018). In addition, confocal scanning laser microscopy can be used too for observing crystallization. It is a more advanced technique and is capable to generate a three-dimensional presentation of the sample. In this method, an illumination of the sample layer by layer is obtained by laser light.

Electron microscopy such as Scanning Electron Microscopy (SEM) can be used for a crystal size of less than 1 micrometer (Bund & Hartel, 2010). Thermal analyzes like Differential Scanning Calorimetry could also be used for the determination of crystallization in hard candies. The temperature of heat flow difference associated with the crystal formation or melting can be discovered by DSC (Roos & Karel, 1990). However, for the determination of exact crystal types, DSC is not a suitable method.

Another approach for the detection and characterization of crystalline is spectroscopy. Spectroscopic approaches are nondestructive. They also require small sample size. Some of the spectroscopic methods are X-ray diffraction (XRD), infrared spectroscopy, Raman micro-spectroscopy, and nuclear magnetic resonance (NMR) (Bund & Hartel, 2010). Detection and differentiation of crystal structures can be achieved by these methods. For example, spectra that are specific for each crystal type are produced by XRD. Consequently, a detailed analysis of the crystalline phase can be done by XRD (Labuza & Labuza, 2004). XRD is the most common method used for the differentiation of crystal polymorphic types. Moreover, XRD can be used to evaluate the overall crystallinity of hard candies. Amorphous structures in hard candies just give wide non-sharpened peaks in XRD spectra. On the other hand, the crystalline structure gives sharp peaks (Roe & Labuza, 2005).

TD-NMR relaxometry is another technique to distinguish crystalline structures in an easy and fast way (DeJong & Hartel, 2016). Free induction decay (FID) with a single pulse and the consecutive proton relaxation data are used to differentiate solid and liquid fractions of a material (Wong, 2014). Nevertheless, just applying FID leads to loss of signal obtained by the solid part due to the ‘dead time’ phenomenon which is created by the delay in the record of the signal by the receiver (DeJong & Hartel, 2016). Solids relax faster than liquids because of the closer replacement of the atoms in solid materials and some part of this initial signal cannot be noticed by the hardware which causes incorrect solid to liquid fraction calculations (Enden et al., 1978). To overcome this problem, some correction factors have been formerly achieved but the necessity of calibration due to the moisture sensitivity of such factors confines the use of this approach (Kovrlija & Rondeau-Mouro, 2017). Solid Echo (SE) sequence enables the detection of the larger part of the signal coming from the solid fraction. This signal coming from solid fraction gives information about degree of crystallinity. In addition to SE measurements for the evaluation of degree of crystallinity of hard candies, T_1 measurement can also be used for the same purpose. T_1 is calculated by performing saturation recovery (SR) or inversion recovery (IR) sequences and a consequent relaxation spectrum analysis (Hashemi Ray H. et al., 2010).

Finally, Raman and IR spectroscopy are also suitable methods for getting information about crystalline parts in food products (Bund & Hartel, 2010). In IR spectroscopy, different spectra can be obtained for crystalline and amorphous parts of a sample. In Raman spectroscopy, for example, molecules are excited to a higher vibrational energy state with the help of light with a specified wavelength. In this way, Raman spectroscopy is also suitable for the detection and differentiation of crystal structures (Banwell C.N., 1983).

1.7 Time Domain NMR Relaxometry

1.7.1 Longitudinal Relaxation Time (T_1)

In NMR applications, for examining the behavior of a material, it is important to find the relaxation times. Spin-lattice relaxation time (T_1) is the time necessary for the spins to realign in the direction of the longitudinal z-axis. In other words, T_1 is the time of energy release of spins to the surrounding lattice. Eventually, spins will be at the equilibrium state since they give back their energy. This state is called relaxation because the spins are at their lowest energy state (Kirtil & Oztop, 2016).

In an NMR measurement, a radio frequency pulse is sent to a sample. After this application, the longitudinal magnetization is flipped into the x-y plane while the M_{xy} precess within the x-y plane. It oscillates around the z-axis with all protons that are rotating in phase. After the RF pulse is removed, the spins turn back to their equilibrium state and get out of phase. Therefore, the x-y component of the magnetization vector (M_{xy}) decreases directly. In addition, the z component of the magnetization vector recovers slowly in the direction of the z-axis (Kirtil & Oztop, 2016). Consequently, the rate of recovery to initial M_0 of the z component of the magnetization vector is characterized by T_1 (Figure 1.7.1.1).

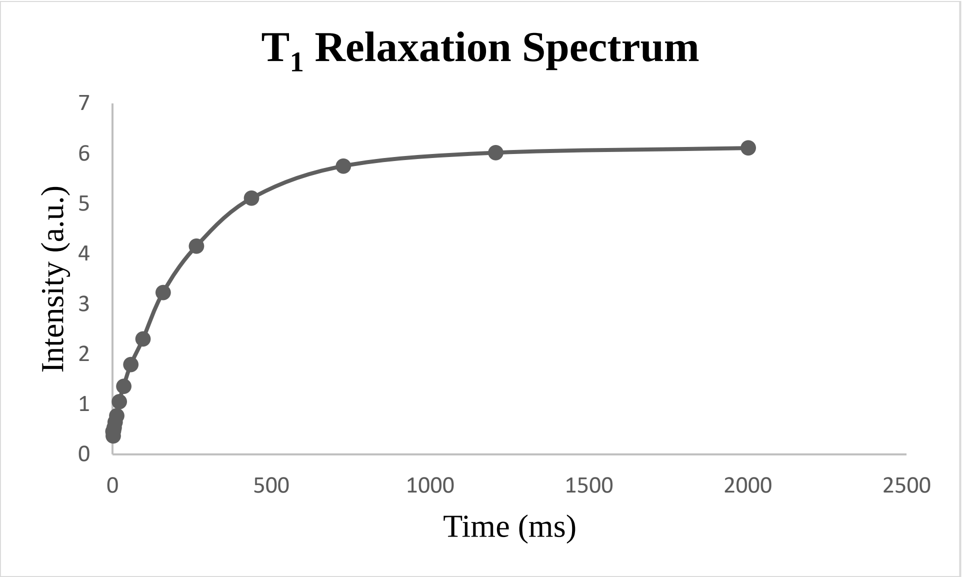

Figure 1.7.1.1 A typical T_1 Saturation Recovery Curve

Therefore, this recovery can be formulated as

$$M_z\,(t) = M_0\left(1 - e^{\left(-\frac{t}{T_1}\right)}\right)$$

T_1 time is dependent on the magnetic field strength. So, when the magnetic field strength is increased, T_1 time also increases. Moreover, T_1 is related to the proton intensity in the sample. Generally, if high number of protons exist in the sample, the T_1 value becomes high as well. For example, while pure water has a T_1 value of 2.7 seconds, solid samples (if they are not crystals) can have shorter T_1 values due to their low proton intensity which is coming from low water content inside the solids (Hu & Nayak, 2010). However, a sample with low proton intensity can still have long T_1 value. The reason for this can be crystallinity. A crystalline sample has wellordered atoms. This well orientation makes the release of energy back harder and slower which results in longer T_1 times.

1.7.2 Free Induction Decay (FID)

Free induction decay (FID) is a type of NMR signal. It is generated by a rotating magnetic field which causes an electric current in a stationary coil. FID is caused by dephasing. This results in weaker signals than expected. Subsequently, the signal will come close to the center of the x-y plane with a spiral shape with time (Hashemi et al., 2010). This decaying signal can be seen in Figure 1.7.2.1.

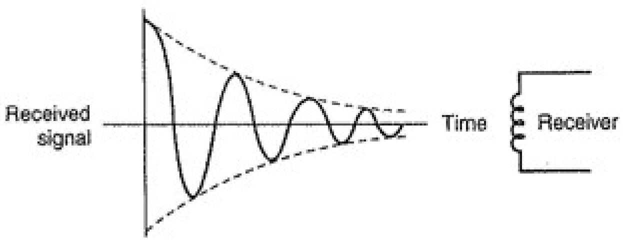

Figure 1.7.2.1 Presentation of the sinusoidal waveform of FID signal (Hashemi Ray H. et al., 2010)

A substantial application of the FID in the food industry is the Solid Fat Content determination. Solid Fat Content (SFC) is a crucial property because it is directly related to the appearance, spreadability, and organoleptic properties of foods (Teles Dos Santos et al., 2014). To evaluate the SFC content of food samples, the FID sequence has been used. Indeed, there is an official method of analysis used for that purpose (AOCS Official Method, 2009).

However, 5-10 μs of dead time (which could extend up to 20 μs) which passes just before the first recording may cause the loss of signal coming from the solid fraction. In order to overcome this problem, a correction factor (F) is usually used (DeJong & Hartel, 2016). A combination of the FID sequence with the Carr-Purcell-Meiboom-Gill (CPMG) sequence has also improved the measurement of SFC and crystal polymorphism with one experiment to evade the issue of dead time (van Duynhoven et al., 2002).

1.7.3 Solid Echo (SE) and Magic Sandwich Echo (MSE)

Other sequences have been developed to solve dead time issues. They are used to determine crystalline structures in a solid sample and to get information about amorphous parts as well (Grunin et al., 2019). Solid Echo sequence is one of those sequences. It allows partial refocusing of the solid fraction and this way to obtain crystallinity of the sample by back extrapolation over a series of measurements with carrying echo delays. As presented in Figure 1.7.3.1, it consists of two 90° pulses with a delay. When the second pulse is applied out of phase, the signal from the initial part of the FID is obtained by resolving the dead time issue (Maus et al., 2006).

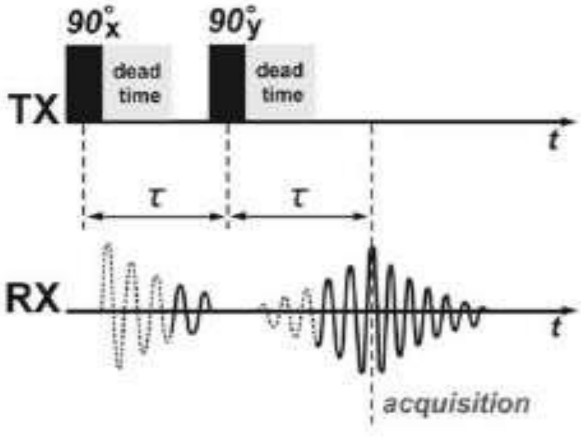

Figure 1.7.3.1 Pulse diagram for SE pulse sequence (L. Grunin et al., 2019)

While SE primarily refocuses dipole interactions within pair of spins, the first part of FID can be refocused by using Magic Sandwich Echo (MSE) sequence with a phase cycling routine (Grunin et al., 2019). It is a modified form of SE that avoids the dead time issue by refocusing the initial part of the FID. MSE is a more robust method when it is compared with SE since it provides a better refocusing of multi-spin dipolar interactions (Papon et al., 2011). Nevertheless, the SE sequence is a much shorter and faster sequence compared to MSE because MSE requires at least four phase cycling steps. In this study, only the SE sequence is used since MSE takes a longer time. An example for SE signal presentation can be seen in Figure 1.7.3.2.

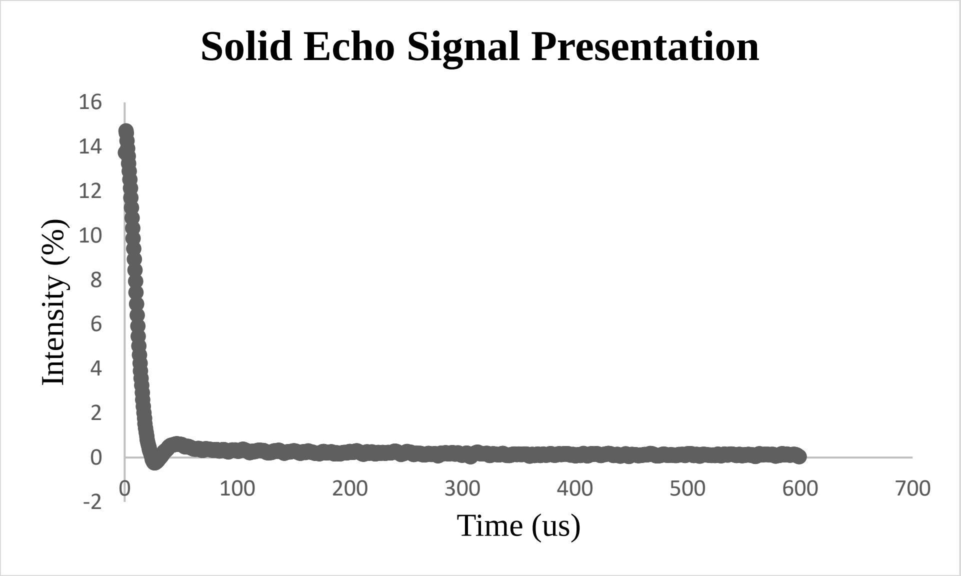

Figure 1.7.3.2 A typical Solid Echo (SE) signal

The evident approach of fitting of SE decays with classical Abrahamian or Pake functions brings usage of multiple approximation parameters and their possible ambiguous interpretation (Grunin et al., 2019). In this way, the Second Moment (M_2) values are obtained. M_2 is proportional to the crystalline content and it can be simply calculated in different ways (Grunin et al., 2019). To calculate M_2 values, two methods can be used. The first one is based on time-domain area, and it focused on approximation of the FID with an analytical function. The other method is based on fast Fourier transform (FFT) integration of the SE signal (Grunin et al., 2019).

1.8 Objectives

TD-NMR is a non-destructive, efficient, and cost-effective method for quality control analyses. Thus, it can be applied in the food industry since it provides easier solutions to measurements which generally take long experiment times. The main goal of the whole study is to evaluate whether TD-NMR can measure the moisture content and crystallinity of hard candies.

This study includes two parts. In the first part, hard candies cooked at different temperatures and stored at different temperatures were analyzed. The objective of this part is to see the effect of cooking temperature and storage temperature on hard candies in terms of moisture content and crystallinity. Cooking temperatures were changed between 135°C and 145°C with an interval of 2.5°C. Storage temperatures of 25°C (room temperature), 4°C (refrigerator temperature), -18°C (freezing condition) and -80°C (extreme condition) were used. Solid Echo (SE) sequence was used to measure the relative crystallinity. Karl-Fischer method was used to measure moisture content values. To support the information obtained from SE and KF-titration, TD-NMR, total soluble solids, and X-ray diffraction experiments were also conducted.

The aim of the second part of the study is to investigate the effect of citric acid concentration and cooking temperature on akide candies in terms of moisture content and crystallinity. The same procedure was followed in this part of the study as well.

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

Commercial sucrose (Bal Kupu, Turkey) was purchased from a local seller. Glucose syrup was purchased from METRO (Metro Grossmarket Ltd., Türkiye). Citric acid (ISOLab) was used. Distilled water which is obtained from city water was used.

2.2 Methods

2.2.1 Sample Preparation

In the first part of the sample preparation, hard candy samples were prepared. In order to prepare hard candy samples; sucrose, glucose syrup, and water were used. Glucose syrup with brix 85° accounted for 43% of total formulation. The percentage of sucrose was 47% and the remaining 10% was water. Ingredients were mixed. Then, mixture was boiled up to high temperatures in a vacuum cooker. Cooking temperature ranged between 135°C and 145°C with an interval of 2.5°C. Boiled mixture of hard candy was poured into molds. After pouring, all samples were cooled down until they reach to the room temperature. For each cooking temperature, same procedure was applied. Samples which were stored at room temperature were divided into two sets. First set was kept at room temperature for two days. Second set was kept at room temperature for two months. Other samples were first kept at room temperature for two months. Following these two months, they were kept at different storage temperatures for 3 days which are 4°C, -18°C and -80°C. The aim of using different storage temperatures was to produce a crystalline phase in hard candies and, if any, detect this phase with TD-NMR relaxometry.

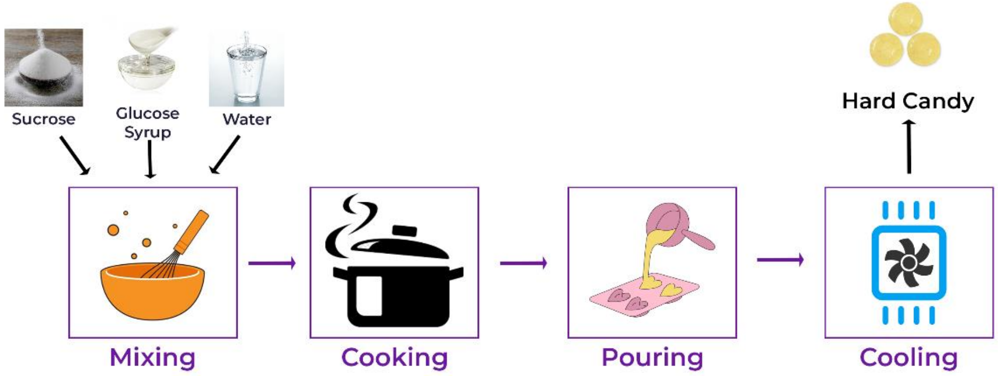

Figure 2.2.1.1 Flow Chart for Hard Candy Sample Preparation

In the second part of the sample preparation, akide candy samples were prepared. Sucrose, citric acid, and water were used as the ingredients. Ingredients were mixed in a pot. The mixture was boiled to high temperatures which changed between 150°C and 170°C with an interval of 5°C. The boiled mixture was poured into molds. After pouring, all samples were cooled down to room temperature. For each cooking temperature, the same steps were applied.

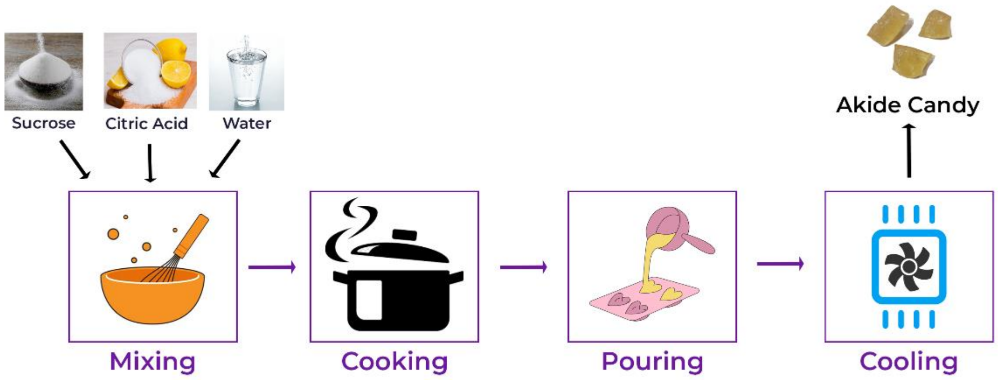

Figure 2.2.1.2 Flow Chart for Akide Candy Sample Preparation

Table 2.2.1.1 Ingredients Table for Sample Preparation

Sample	**Ingredients**
Hard Candy	Sucrose Glucose Syrup Water
Akide Candy	Sucrose Citric Acid Water

2.2.2 Moisture Content Analysis

Karl-Fischer (KF) titration method was used for the determination of moisture content of hard candies and akide candies since they have low moisture content (Lans et al., 2018). The experiment was made by Karl Fischer Titrator (TitraLab KF1000 Series, HACH, UK) at 25 °C with three replicates.

2.2.3 Total Soluble Solids (TSS)

TSS values of the fresh hard candies were determined by using solid refractive index method (ATC 0-90 Refractometer, AKYOL Instruments, Turkey). Freshly produced samples were put on top the refractometer and the value was read by looking from the binocular.

TSS values of the stored hard candies and all akide candies were determined by using the refractive index method (HI 96801 Refractometer, HANNA Instruments, USA) (Sherwin & Labuza, 2006b). Both hard candy and akide candies were broken into smaller pieces until they become powder form. Powder candies were dissolved in water with a specified dilution ratio of 1:5. Experiments are conducted at room temperature and the mixtures of candy and water were stirred for 3 hours. After stirring, the solution was dripped on the refractometer and the measurements were done. Three replicates were used.

2.2.4 X-ray Diffraction (XRD) Analysis

X-ray diffraction analysis was applied to hard candies and akide candies (METU Central Laboratory). Samples were broken into smaller pieces to obtain the powder form of the candies. Then, these powder form of samples were sent for the XRD analysis. The sampling width, scan axis, scan range, and scan speed were decided as 0.02°, 2θ, 3°–80°, and 2°/min, respectively.

2.2.5 Time Domain Nuclear Magnetic Resonance (TD-NMR) Relaxometry

TD-NMR experiments were conducted with 0.5 Tesla (20.34 MHz) low-resolution NMR System (Spin Track, Resonance Systems GmbH, Kirchheim/Teck, Germany) having a 10 mm radiofrequency (RF) coil.

2.2.5.1 Longitudinal Relaxation Time (T_1) Measurements

The saturation recovery (SR) sequence with a relaxation period of 2 s, a delay time between 1000 – 1500 ms, and point number as 16 was used with 4 scans to measure T_1 (spin-lattice relaxation). Mono- and multi-exponential fittings of the relaxation spectra were evaluated by the Relax8 software package (Resonance Systems GmBH, Kirchheim, Germany).

2.2.5.2 Solid Echo Measurements for Relative Crystallinity

Both hard candy and akide candy samples were placed into the low-resolution NMR System (Spin Track, Resonance Systems GmbH, Kirchheim/Teck, Germany) with a magnet strength of 0.5 Tesla (20.34 MHz). M_2 values were obtained by using a sequence called Solid Echo (SE) sequence having a repetition delay of 10 s and 32 scans.

Relax8 (Resonance Systems GmBH, Kirchheim, Germany) “Solid Lab” module was used to calculate the second moment ‘$\mathbf{M_2}$’ values. Crystallinity values are known to be related with 2nd moment values (Uguz et al., 2022). The principle of the second moment calculation via “averaging of FID regions” assumes that the apparent spin-spin relaxation time T_2 of the crystalline structures is shorter than the one in amorphous areas of the same sample, due to smaller averaged *inter-hydrogen* distance and less mobility in denser packed crystallites. The method implemented in the module uses the averaged transverse relaxation decay value on top A_0 (at the 0-time point – this value contains both crystalline and amorphous signals amplitudes) and at the selected time as A_1, in case of this research it’s chosen around 17 μs, where the amorphous FID contributes more into the signal than the crystalline protons due to the mentioned relaxation time difference. Then the parameter ξ of crystallinity (*and the second moment*) is calculated proportionally to $\xi \sim (A_0 - A_1)/A_0$ and, finally, the module is calibrated by the simulated model signals with known M_2.

2.2.6 Statistical Analysis

For all the experimental results obtained in the study, the general linear model of the Minitab (Minitab Inc., Coventry, UK) software was used to carry out statistical analysis by analysis of variance (ANOVA). The comparison between the results was done by using Tukey’s comparison test with a confidence interval of 95%. Three replicates were used for analysis. Moreover, to find the correlation coefficients between the different parameters, the Pearson Correlation ($\alpha \leq 0.05$) was used.

2.2.7 Experimental Design

Table 2.2.7.1 Experimental Design for Hard Candies in the 1st Part

Factors	Levels
Cooking Temperature	135°C
	137.5°C
	140°C
	142.5°C
	145°C
Storage Temperature	25°C
	4°C
	-18°C
	-80°C

Table 2.2.7.2 Experimental Design for Akide Candies in the 2nd Part

Factors	Levels
Cooking Temperature	150°C
	155°C
	160°C
	165°C
	170°C
Citric Acid Concentration	0.03%
	0.05%
	0.07%
	0.21%
	0.35%
	0.49%
	0.63%

CHAPTER 3

RESULTS AND DISCUSSION

In the first part of the study, the effect of cooking temperature and storage temperature on hard candies will be assessed using TD-NMR. T_1 relaxation times and M_2 values are going to be discussed. As complementary methods, moisture content, total soluble solids, water activity, and X-ray diffraction analyses were done and the results obtained are also going to be evaluated.

In the second part of the study, the effect of citric acid concentration and cooking temperature on akide candies will be analyzed by using again TD-NMR. Likely, T_1 relaxation times and M_2 values are going to be discussed. Moisture content, total soluble solids, water activity, and X-ray diffraction methods were applied as complementary, and the results obtained also are going to be inspected.

3.1 Effect of Cooking Temperature and Storage Temperature on Hard Candies

3.1.1 Moisture Content

For the physical characterization of hard candies, moisture content determination plays an important role. Moisture content results of hard candies are shown in Table 3.1.1.1. A significant change was observed when the cooking temperature and storage temperature were changed ($p \leq 0.05$). When there is an increase in cooking temperature, the rate of evaporation also increases. This causes lower moisture content in hard candies (Helt, 1976). Thus, when the cooking temperature was increased from 135°C to 145°C, the moisture content of hard candies decreased. For the storage temperatures of 25°C and 4°C, moisture content change did not have a trend but mostly it decreased. For the storage temperatures of -18°C and -80°C, it can be said that moisture contents decreased significantly. The lowest moisture content values were obtained for the samples stored at -80°C. When the storage temperature was 25°C, the moisture content of hard candies increased. However, at the storage temperatures of -18°C, and -80°C, hard candies probably lost moisture to the surrounding air since the storage environment nearly had zero RH (W. C. Schotsmans et al., 2011).

Table 3.1.1.1 Moisture Content Results for All Hard Candy Measurements

Cooking Temperature (°C)	**Fresh Samples (%)**	**Samples Stored at 25°C (%)**	**Samples Stored at 4°C (%)**	**Samples Stored at -18°C (%)**	**Samples Stored at -80°C (%)**
135	$4.82 \pm 0.157^{a,B}$	$5.14 \pm 0.250^{a,A}$	$4.03 \pm 0.340^{a,D}$	$4.42 \pm 0.162^{a,C}$	$3.86 \pm 0.068^{a,E}$
137.5	$4.06 \pm 0.209^{b,C}$	$4.27 \pm 0.062^{b,B}$	$3.90 \pm 0.143^{ab,D}$	$4.39 \pm 0.005^{a,A}$	$3.66 \pm 0.044^{a,E}$
140	$3.39 \pm 0.228^{c,D}$	$3.57 \pm 0.202^{bc,B}$	$3.52 \pm 0.296^{abc,C}$	$3.84 \pm 0.119^{b,A}$	$3.03 \pm 0.186^{b,E}$
142.5	$3.31 \pm 0.223^{c,D}$	$3.49 \pm 0.337^{c,B}$	$3.40 \pm 0.112^{bc,C}$	$3.64 \pm 0.121^{bc,A}$	$2.94 \pm 0.272^{b,E}$
145	$3.29 \pm 0.051^{c,C}$	$3.47 \pm 0.387^{c,A}$	$2.96 \pm 0.139^{c,D}$	$3.43 \pm 0.021^{c,B}$	$2.85 \pm 0.045^{b,E}$

¶Errors are represented as standard deviations. Lowercase letters represent the comparison test between the column elements. Uppercase letters represent the comparison between the row elements.

3.1.2 Total Soluble Solids (TSS)

Total soluble solids (TSS) is also an important factor for hard candies. TSS results were shown in Table 3.1.2.1. TSS values of fresh samples were measured while they were in solid form with a refractometer, but other samples were diluted and then measurements were done. When the cooking temperature was increased, TSS values significantly increased ($p \leq 0.05$) except for the samples stored at 25°C. Increase in cooking temperature caused an increase in moisture loss as well. Thus, more concentrated samples were attained and probably this was the main reason for the increase in TSS of the most of hard candies cooked at higher temperatures (Helt, 1976). Nonetheless, samples stored at 25°C showed a stable TSS profile with changing cooking temperatures. Moreover, the TSS results of the samples stored at 25°C were higher than other hard candy samples which were stored at lower temperatures ($p \leq 0.05$). At lower storage temperatures, sucrose in the hard candies may have been utilized for crystallization. Depending on the results obtained for M_2 values (Table 3.1.4.2.), which will be discussed in part 3.1.4.2., decrease in storage temperature caused an increase in the crystallinity of hard candies. Solubility properties of the sugars in a mixture generally affect the TSS results (Zumbé et al., 2001). All sugars existing in the hard candies probably experienced a decrease in solubility at low-temperature conditions. This was also correlated with the M_2 results of the samples because a higher degree of crystallinity is attainable when the solubility of sugar in the mixture importantly decreases (Hartel et al., 2011). Therefore, decrease in TSS values can be related to the crystallinity properties of the hard candies.

Table 3.1.2.1 TSS Results for All Hard Candy Measurements

Cooking Temperature (°C)	Fresh Samples (°)	Samples Stored at 25°C (°)	Samples Stored at 4°C (°)	Samples Stored at -18°C (°)	Samples Stored at -80°C (°)
135	82-83	$18.77\pm0.00^{a,A}$	$16.23\pm0.00^{c,C}$	$15.93\pm0.00^{c,D}$	$17.00\pm0.00^{b,B}$
137.5		$17.87\pm0.00^{c,A}$	$15.37\pm0.01^{d,D}$	$16.60\pm0.00^{b,C}$	$16.70\pm0.00^{cd,B}$
140		$18.80\pm0.00^{a,A}$	$16.50\pm0.00^{bc,C}$	$16.73\pm0.01^{ab,B}$	$16.73\pm0.00^{c,B}$
142.5		$18.23\pm0.01^{b,A}$	$16.57\pm0.00^{b,C}$	$16.70\pm0.00^{ab,B}$	$16.57\pm0.00^{d,C}$
145		$18.67\pm0.00^{a,A}$	$17.00\pm0.00^{a,C}$	$16.93\pm0.00^{a,D}$	$17.40\pm0.00^{a,B}$

¶Errors are represented as standard deviations. Lowercase letters represent the comparison test between the column elements. Uppercase letters represent the comparison between the row elements.

3.1.3 Time Domain NMR (TD-NMR)

3.1.3.1 Longitudinal Relaxation Time (T_1)

Longitudinal relaxation time (T_1) measurements play a crucial role in analyzing the moisture content and crystallinity of hard candies. T_1 data was analyzed by fitting them to a monoexponential model. As demonstrated in Table 3.1.3.1, T_1 values for hard candies cooked at various temperatures and stored under different conditions exhibited significant variations. Generally, an increase in cooking temperature resulted in longer T_1 values, as evident from the measurements of fresh samples (Le Botlan et al., 1998). However, samples stored at 25°C showed an exception, where the highest T_1 value was observed at a cooking temperature of 140°C, likely indicating the attainment of the hard crack temperature, the point at which most of the water in hard candy is lost. The difference in T_1 values between cooking temperatures of 135°C and 140°C was found to be twice as large as the difference between temperatures of 140°C and 145°C in the samples stored at 25°C. This suggests that the hard candy became more stable after reaching the cooking temperature of 140°C, presumably due to the passage of the hard crack temperature. A similar trend was observed in samples stored at other temperatures as well. Furthermore, storage temperature also had an impact on T_1 values, with decreasing storage temperature leading to increased T_1 values. Specifically, storage temperatures of 4°C, -18°C, and -80°C resulted in higher T_1 values, while a storage temperature of 25°C decreased the T_1 values compared to results of fresh samples. The decrease in T_1 values at 25°C storage could be attributed to the hard candies being in a glassy state, causing a reduction in moisture content, which in turn prolonged the T_1. These findings indicate that T_1 serves as a suitable parameter for investigating the solid-state relaxation properties of low-moisture products like hard candies.

Table 3.1.3.1 T_1 Results for All Hard Candy Measurements

Cooking Temperature (°C)	**Fresh Samples (ms)**	**Samples Stored at 25°C (ms)**	**Samples Stored at 4°C (ms)**	**Samples Stored at -18°C (ms)**	**Samples Stored at -80°C (ms)**
135	$165.83 \pm 2.05^{d,C}$	$153.03 \pm 12.55^{b,D}$	$176.08 \pm 7.56^{d,A}$	$172.84 \pm 3.45^{d,B}$	$171.76 \pm 2.69^{d,B}$
137.5	$179.93 \pm 8.99^{c,C}$	$169.32 \pm 5.57^{ab,D}$	$193.09 \pm 0.66^{c,A}$	$185.50 \pm 6.17^{c,B}$	$194.04 \pm 2.77^{c,A}$
140	$199.32 \pm 13.52^{b,D}$	$211.38 \pm 11.12^{a,C}$	$217.15 \pm 0.46^{b,B}$	$215.16 \pm 1.29^{b,BC}$	$225.51 \pm 6.69^{b,A}$
142.5	$207.81 \pm 15.92^{ab,C}$	$174.30 \pm 6.54^{ab,D}$	$220.28 \pm 3.79^{b,B}$	$222.58 \pm 6.72^{b,AB}$	$228.63 \pm 2.47^{b,A}$
145	$209.50 \pm 15.38^{a,C}$	$185.37 \pm 5.69^{ab,D}$	$245.93 \pm 5.37^{a,A}$	$243.46 \pm 3.07^{a,B}$	$243.62 \pm 6.76^{a,B}$

¶Errors are represented as standard deviations. Lowercase letters represent the comparison test between the column elements. Uppercase letters represent the comparison between the row elements.

3.1.3.2 Second Moment (M_2)

In this study, to calculate the second moment values, Solid Echo (SE) sequence was used. The second moment (M_2) serves as a parameter used to evaluate crystallinity. According to the findings presented in Table 3.1.3.2, both variations in cooking and storage temperatures had a significant effect ($p \leq 0.05$) on the M_2 values. Increasing the cooking temperature caused to higher M_2 values, which can be attributed to the increased moisture loss in the hard candy samples due to higher cooking temperatures. As a result, the candy mixtures became more concentrated. Among the cooking temperatures, samples cooked at 145°C generally exhibited the highest M_2 values, indicating higher crystallinity ($p \leq 0.05$). Storage temperatures of 4°C, -18°C, and -80°C showed a similar trend to the fresh samples concerning cooking temperature, except for the storage temperature of 25°C, which showed a different pattern. The highest M_2 value for samples stored at 25°C was obtained at a cooking temperature of 140°C. This observation may be attributed to the occurrence of the hard crack temperature, as discussed earlier in Section 3.1.3.1 regarding T_1 results. Comparing the M_2 differences between cooking temperatures of 135°C and 140°C with those of 140°C and 145°C, the former difference was more than double the latter. This trend was correlated with the findings for T_1 results, reinforcing the significance of the hard crack temperature phenomenon (Hartel et al., 2018). Additionally, decreasing storage temperature caused higher M_2 values, consistent with the trends observed in the T_1 results. These consistent results between M_2 and T_1 were expected because they generally show strong positive correlations (Le Botlan et al., 1998).

Table 3.1.3.2 Second Moment ($M_2*10^8*Hz^2$) Results for All Hard Candy Measurements

Cooking Temperature (°C)	**Fresh Samples**	**Samples Stored at 25°C**	**Samples Stored at 4°C**	**Samples Stored at -18°C**	**Samples Stored at -80°C**
135	$11.93\pm0.07^{d,C}$	$11.57\pm0.33^{c,D}$	$12.13\pm0.05^{d,B}$	$12.19\pm0.03^{d,A}$	$12.15\pm0.04^{d,B}$
137.5	$12.20\pm0.04^{c,C}$	$11.92\pm0.26^{bc,D}$	$12.39\pm0.00^{c,AB}$	$12.36\pm0.04^{c,B}$	$12.41\pm0.03^{c,A}$
140	$12.55\pm0.02^{b,B}$	$12.74\pm0.37^{a,A}$	$12.73\pm0.06^{b,A}$	$12.75\pm0.08^{b,A}$	$12.73\pm0.07^{b,A}$
142.5	$12.62\pm0.03^{ab,C}$	$12.13\pm0.39^{b,D}$	$12.71\pm0.04^{b,B}$	$12.73\pm0.02^{b,AB}$	$12.77\pm0.01^{b,A}$
145	$12.70\pm0.03^{a,D}$	$12.23\pm0.45^{b,E}$	$13.05\pm0.03^{a,A}$	$13.00\pm0.01^{a,B}$	$12.92\pm0.04^{a,C}$

¶Errors are represented as standard deviations. Lowercase letters represent the comparison test between the column elements. Uppercase letters represent the comparison between the row elements.

3.1.4 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a technique utilized to assess crystallinity. Although hard candies are typically amorphous, the objective of this study was to examine any potential crystalline characteristics they might possess. Therefore, XRD analysis was conducted. Figure 3.1.4.1 illustrates the results solely for hard candy samples stored at 25°C. A comparison between these samples and sucrose revealed distinct differences: while sucrose exhibited sharp peaks indicative of crystalline behavior, the hard candy samples lacked such well-defined peaks, confirming their amorphous nature. To investigate the impact of storage temperature on XRD results, XRD analysis was also performed on both fresh samples (Figure 3.1.4.2) and samples stored at -80°C (Figure 3.1.4.3). The findings for both fresh and -80°C stored samples also displayed amorphous behavior. However, M_2 values indicated the presence of minor crystalline components in these hard candies. These subtle crystalline regions or crystal particles were not detectable by XRD due to its macro size-based nature (Lopez-Rubio et al., 2008). Contrarily, M_2 measurements conducted by using TD-NMR relaxometry focused on molecular size rather than macro size (Becher et al., 2022). Thus, TD-NMR relaxometry provides valuable insights into the crystallinity characteristics of the hard candies.

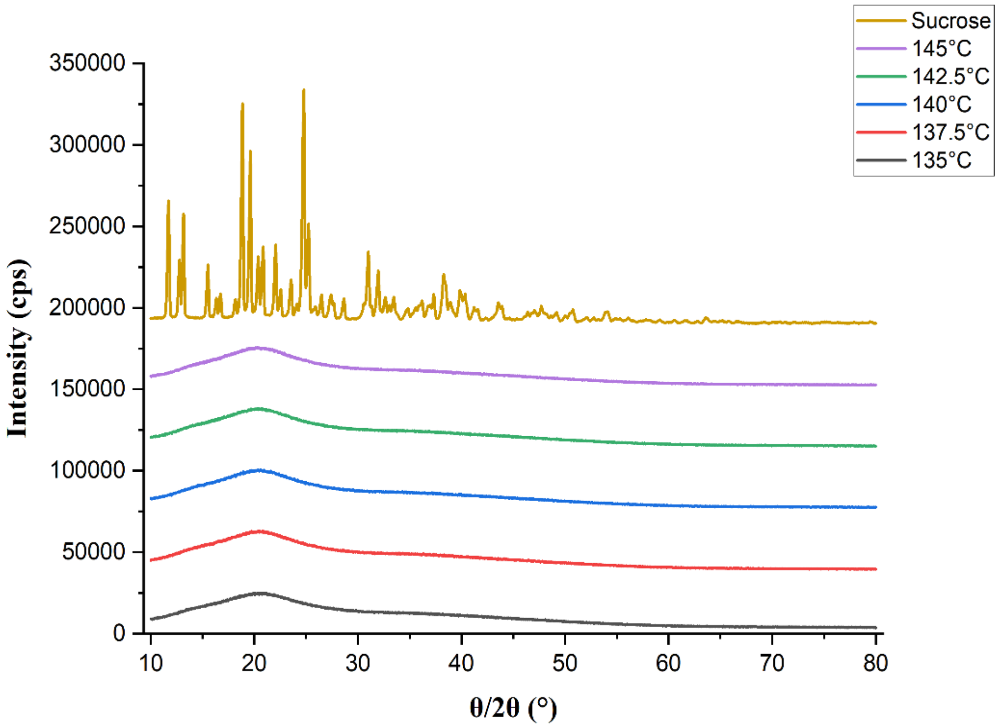

Figure 3.1.4.1 XRD curves for the hard candies cooked at different temperatures (135°C, 137.5°C, 140°C, 142.5°C, 145°C) and stored at the temperature of 25°C.

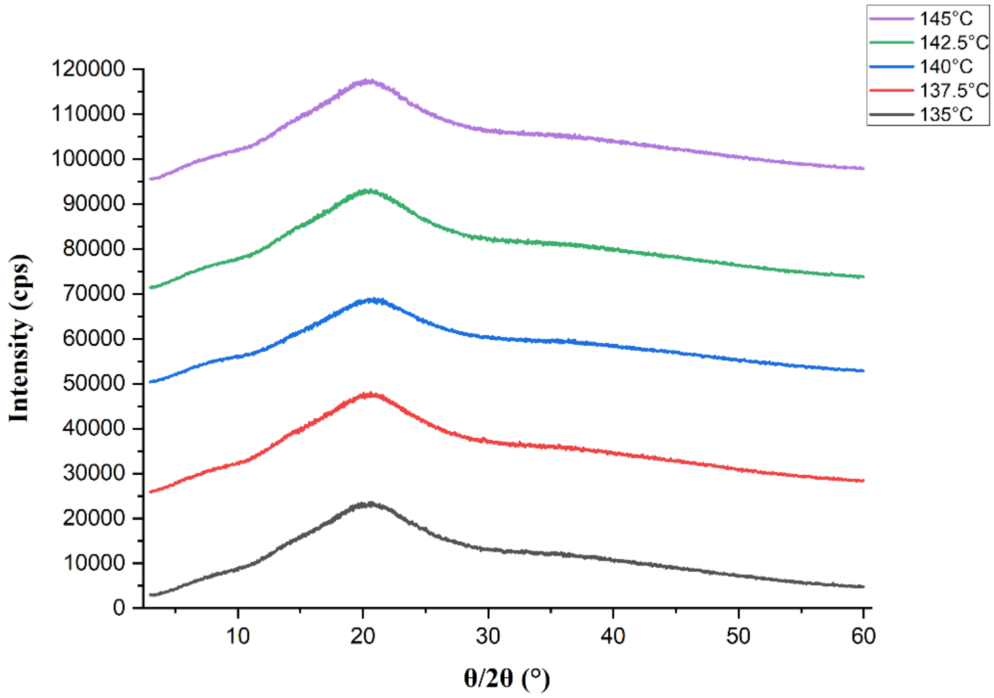

Figure 3.1.4.2 XRD curves for the fresh hard candies cooked at different temperatures (135°C, 137.5°C, 140°C, 142.5°C, 145°C).

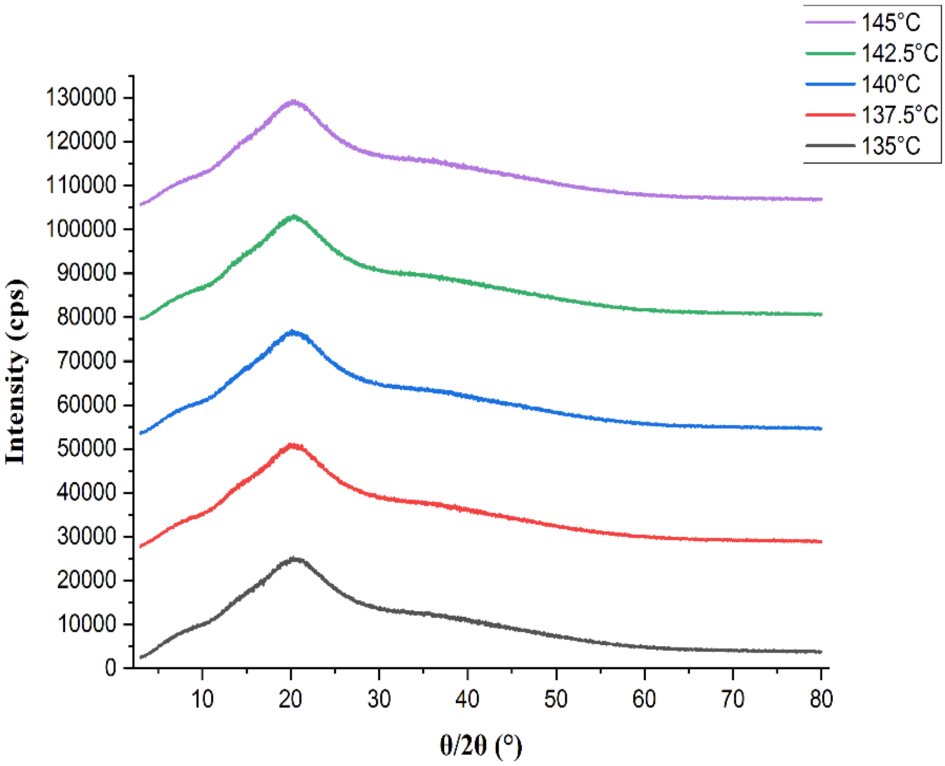

Figure 3.1.4.3 XRD curves for the hard candies cooked at different temperatures (135°C, 137.5°C, 140°C, 142.5°C, 145°C) and stored at the temperature of -80°C.

3.1.5 Correlations

The Pearson Correlation test was applied to analyze all relevant results. As demonstrated in Table 3.1.5.1, nearly all correlation values exceeded 0.85, indicating strong associations (Mukaka MM, 2012). Both moisture content and M_2 values exhibited correlations with T_1 values. Normally, increasing the cooking temperature causes a decrease in moisture content, which would have resulted in lower T_1 values. However, T_1 values increased due to the formation of crystalline structures. This phenomenon was further supported by the correlation between T_1 values and M_2 values. Upon evaluating the correlation values between moisture content and T_1

values, it was clear that storage temperature had a positive impact on the correlations, except at 25°C. The lower correlation value at 25°C could be attributed to the hard crack temperature once again (Hartel et al., 2018). At this temperature, although moisture content decreased, T_1 values increased due to the crystallization process. The most notable correlation value was observed between M_2 and T_1 values for samples stored at -80°C, likely because these samples had the lowest moisture content. Consequently, the results of T_1 and M_2 provided a more realistic framework for low moisture systems like glassy state-hard candies, as explored in this study.

Table 3.1.5.1 Correlation Values for Moisture Content, T_1 and M_2 Results of Hard Candies

Factors	**T_1 of Fresh Samples (ms)**	**T_1 of Samples Stored at 25°C (ms)**	**T_1 of Samples Stored at 4°C (ms)**	**T_1 of Samples Stored at -18°C (ms)**	**T_1 of Samples Stored at -80°C (ms)**
Moisture Content (%)	-0.986	-0.752	-0.908	-0.913	-0.968
M_2	0.993	0.877	0.997	0.993	1

3.2 Effect of Citric Acid Concentration and Cooking Temperature on Akide Candies

3.2.1 Moisture Content

Moisture content results of akide candies are shown in Table 3.2.1.1. The moisture content of akide candies substantially changed when citric acid concentration and cooking temperatures were changed ($p \leq 0.05$). In 3.1.1. section, the effect of cooking temperature was discussed. Similarly, it was observed that increasing cooking temperature decreased moisture content due to the increased rate of evaporation (Helt, 1976). When the effect of cooking temperature was evaluated at the same citric acid concentration, it was seen that increasing cooking temperature caused higher decrease in moisture content in akide candies compared to hard candies. Specifically at the citric acid concentration of 0.63%, three times higher moisture loss was observed when the cooking temperature was increased. Different from hard candy, akide candy contains citric acid. Citric acid causes sucrose inversion. As a result, glucose and fructose are produced. These glucose and fructose in the formulation increases the interaction of water with the mixture(Wang & Hartel, 2022). Because of this, at high cooking temperatures, more moisture loss was observed. In addition to the cooking temperature, citric acid concentration had also an important effect on moisture content results. Decrease in citric acid concentration caused a decrease in moisture content as well. Decrease in moisture content caused by decrease in citric acid concentration is more observable compared to decrease in moisture content caused by increase in cooking temperature. The reason for this can be that citric acid in the formulation plays a role like moisture absorber. It increases the interaction of akide candy with the environment. Because of this, when the amount of citric acid was increased, the moisture contents of akide candies also increased.

Table 3.2.1.1 Moisture Content Results for All Akide Candy Measurements

Citric Acid Concentration (%)	Samples Cooked at 150°C (%)	Samples Cooked at 155°C (%)	Samples Cooked at 160°C (%)	Samples Cooked at 165°C (%)	Samples Cooked at 170°C (%)
0.03	$2.64\pm0.05^{g,A}$	$2.27\pm0.08^{g,B}$	$2.27\pm0.11^{f,B}$	$1.94\pm0.09^{g,C}$	$1.60\pm0.06^{g,D}$
0.05	$3.04\pm0.02^{f,A}$	$2.44\pm0.03^{f,C}$	$2.33\pm0.05^{e,D}$	$2.59\pm0.07^{f,B}$	$1.85\pm0.06^{f,E}$
0.07	$6.33\pm0.32^{e,A}$	$3.67\pm0.35^{d,D}$	$4.14\pm0.26^{d,B}$	$3.95\pm0.01^{e,C}$	$2.09\pm0.25^{e,E}$
0.21	$6.88\pm0.34^{d,A}$	$3.88\pm0.21^{c,D}$	$4.17\pm0.18^{c,B}$	$3.98\pm0.26^{d,C}$	$2.14\pm0.24^{d,E}$
0.35	$7.24\pm0.29^{c,A}$	$3.49\pm0.21^{e,D}$	$4.72\pm0.01^{b,B}$	$4.12\pm0.06^{c,C}$	$2.17\pm0.02^{c,E}$
0.49	$7.63\pm0.07^{b,A}$	$3.95\pm0.22^{b,D}$	$4.73\pm0.08^{b,B}$	$4.21\pm0.08^{b,C}$	$2.22\pm0.09^{b,E}$
0.63	$7.73\pm0.04^{a,A}$	$4.06\pm0.39^{a,D}$	$5.25\pm0.53^{a,B}$	$4.38\pm0.01^{a,C}$	$2.30\pm0.03^{a,E}$

¶Errors are represented as standard deviations. Lowercase letters represent the comparison test between the column elements. Uppercase letters represent the comparison between the row elements.

3.2.2 Total Soluble Solids (TSS)

Total soluble solid results for akide candies can be seen in Table 3.2.2.1. Both cooking temperature and citric acid concentration significantly affected TSS results ($p\leq0.05$). When the cooking temperature was increased, TSS values also increased due to the increased concentration in akide candies (Helt, 1976). Likely, when the citric acid concentration was increased, TSS values increased. At higher concentrations of citric acid, moisture loss is lowered due to higher amounts of citric acid. In this situation, it was expected to have less concentrated akide candies. However, when the citric acid concentration was increased, more concentrated akide candies were obtained. The reason for this can be that after the final product was obtained, it directly absorbed moisture from the environment, even at very short storage times. Thus, akide candies had both higher moisture content and higher TSS values.

Table 3.2.2.1 TSS Results for All Akide Candy Measurements

Citric Acid Concentration (%)	**Samples Cooked at 150°C (°)**	**Samples Cooked at 155°C (°)**	**Samples Cooked at 160°C (°)**	**Samples Cooked at 165°C (°)**	**Samples Cooked at 170°C (°)**
0.03	$17.6\pm0.01^{e,C}$	$17.7\pm0.01^{e,B}$	$16.4\pm0.06^{g,E}$	$17.2\pm0.06^{f,D}$	$17.9\pm0.01^{g,A}$
0.05	$19.1\pm0.06^{a,D}$	$20.7\pm0.58^{a,B}$	$19.4\pm0.06^{b,C}$	$18.9\pm0.01^{e,E}$	$21.6\pm0.06^{b,A}$
0.07	$18.6\pm0.06^{b,D}$	$18.9\pm0.46^{c,C}$	$18.5\pm0.06^{e,E}$	$19.3\pm0.06^{d,B}$	$19.9\pm0.32^{e,A}$
0.21	$17.5\pm0.06^{f,E}$	$18.9\pm0.69^{c,C}$	$18.2\pm0.52^{f,D}$	$19.8\pm0.23^{b,B}$	$20.3\pm0.01^{d,A}$
0.35	$18.4\pm0.06^{c,E}$	$19.5\pm0.21^{b,C}$	$18.7\pm1.82^{c,D}$	$19.6\pm0.01^{c,B}$	$22.3\pm0.12^{a,A}$
0.49	$17.7\pm0.06^{d,D}$	$18.9\pm0.64^{c,B}$	$20.1\pm1.36^{a,A}$	$18.9\pm0.10^{e,B}$	$18.3\pm0.06^{f,C}$
0.63	$18.4\pm0.06^{c,D}$	$18.2\pm0.14^{d,E}$	$18.6\pm0.07^{d,C}$	$19.9\pm0.06^{a,B}$	$21.3\pm0.06^{c,A}$

¶Errors are represented as standard deviations. Lowercase letters represent the comparison test between the column elements. Uppercase letters represent the comparison between the row elements.

3.2.3 Time Domain NMR (TD-NMR)

3.2.3.1 Longitudinal Relaxation Time (T_1)

As demonstrated in Table 3.2.3.1, akide candies with different citric acid concentrations and cooking temperatures showed significant differences in terms of T_1 values ($p\leq0.05$). When the effect of cooking temperature was assessed, it can be concluded that increasing cooking temperature increases T_1 values. But, in section 3.2.1., it was observed that increasing the cooking temperature decreased the moisture content due to higher moisture loss. Thus, this increase in T_1 values can be related to increase in crystallinity. On the other hand, when the effect of citric acid concentration was examined, increase in citric acid concentration caused decrease in T_1 values. Again, in section 3.2.1., results showed that increasing citric acid concentration increased moisture content values as well. Similarly, this increase in T_1 values can be associated with increase in crystallinity. As a result, citric acid in low concentration has a positive effect on akide candies in terms of crystallinity. These outcomes displayed that T_1 was a suitable parameter to inspect the solid-state relaxation properties of low moisture products such as akide candy (Li et al., 2000).

Table 3.2.3.1 T_1 Values for All Akide Candy Measurements

Citric Acid Concentration (%)	**Samples Cooked at 150°C (ms)**	**Samples Cooked at 155°C (ms)**	**Samples Cooked at 160°C (ms)**	**Samples Cooked at 165°C (ms)**	**Samples Cooked at 170°C (ms)**
0.03	237.9±5.21^{a,E}	281.2±2.93^{a,D}	293.2±0.33^{a,C}	309.9±2.14^{a,B}	318.0±10.65^{a,A}
0.05	229.3±1.25^{b,E}	277.4±0.23^{b,D}	283.4±3.83^{b,C}	299.8±1.22^{b,B}	315.7±8.97^{b,A}
0.07	225.3±1.27^{c,E}	255.9±5.15^{c,D}	263.6±1.53^{c,C}	297.1±4.85^{c,B}	313.3±0.07^{c,A}
0.21	221.6±5.81^{d,E}	241.4±3.01^{d,D}	256.4±3.85^{d,C}	275.5±0.66^{d,B}	297.1±0.91^{d,A}
0.35	205.4±2.23^{e,E}	235.0±2.80^{e,D}	240.4±1.80^{e,C}	272.2±4.24^{e,B}	284.0±0.85^{e,A}
0.49	198.2±0.86^{f,E}	228.5±1.94^{f,D}	236.1±4.97^{f,C}	267.6±0.13^{f,B}	274.6±0.67^{f,A}
0.63	194.4±0.91^{g,E}	216.9±1.69^{g,D}	233.2±0.64^{g,C}	265.2±0.59^{g,B}	272.4±1.44^{g,A}

¶Errors are represented as standard deviations. Lowercase letters represent the comparison test between the column elements. Uppercase letters represent the comparison between the row elements.

3.2.3.2 Second Moment (M_2)

Second Moment (M_2) is a parameter that is used for crystallinity evaluation. Based on the results presented in Table 3.2.3.2, both changing cooking temperature and citric acid concentration significantly ($p \leq 0.05$) affected the M_2 values. When the cooking temperature was increased, M_2 values also increased. Increasing the cooking temperature resulted in more moisture loss from the akide candy as explained previously. In addition to this, their cooling time was increased, so they cooled down more slowly. Based on the previous findings, decrease in the cooling rate caused an increase in the crystallization rate (Helt, 1976). Accordingly, akide candies cooked at 170°C showed the highest M_2 values which was related to crystallinity ($p \leq 0.05$). Besides, when citric acid concentration was decreased, M_2 values increased. The reason why high citric acid concentration resulted in lower crystallinity is that higher acidity increases the amount of sucrose inversion. Thus, higher amount of glucose and fructose were produced. Samples with high citric acid concentration absorbed more moisture because they consist of more glucose and fructose(Wang & Hartel, 2022). This high moisture absorption resulted in lower crystallinity. These results showed that decreasing citric acid concentration caused increase in crystallinity which was correlated with T_1 values that discussed in 3.2.3.1. section.

Table 3.2.3.2 Second Moment (M_2*10^8*Hz^2) Results for All Akide Candy Measurements

Citric Acid Concentration (%)	Samples Cooked at 150°C	Samples Cooked at 155°C	Samples Cooked at 160°C	Samples Cooked at 165°C	Samples Cooked at 170°C
0.03	12.66±0.010^{a,E}	13.13±0.007^{a,C}	13.15±0.014^{a,D}	13.32±0.014^{a,A}	13.36±0.025^{a,B}
0.05	12.56±0.065^{b,E}	13.11±0.042^{b,D}	13.12±0.001^{b,C}	13.19±0.001^{b,B}	13.23±0.205^{b,A}
0.07	12.52±0.076^{c,E}	13.02±0.049^{c,C}	12.73±0.021^{c,D}	13.17±0.028^{c,A}	13.14±0.021^{c,B}
0.21	11.84±0.211^{d,E}	12.47±0.021^{d,C}	12.32±0.099^{d,D}	12.91±0.001^{d,A}	12.75±0.014^{d,B}
0.35	11.64±0.046^{e,E}	12.43±0.001^{e,C}	12.32±0.071^{e,D}	12.78±0.021^{e,A}	12.72±0.007^{e,B}
0.49	11.53±0.045^{f,E}	12.41±0.014^{f,C}	11.78±0.064^{f,D}	12.75±0.007^{f,A}	12.70±0.001^{f,B}
0.63	11.41±0.141^{g,D}	12.18±0.014^{g,C}	11.15±0.042^{g,E}	12.72±0.007^{g,A}	12.64±0.021^{g,B}

¶Errors are represented as standard deviations. Lowercase letters represent the comparison test between the column elements. Uppercase letters represent the comparison between the row elements.

3.2.4 X-ray Diffraction (XRD)

The results for akide candies that were cooked at 170°C were shown at Figure 3.2.4.1. In this XRD graph, additionally, one more citric acid concentration was added which was 0.01%. But its texture was not like akide candy. The only crystalline XRD belongs to the 0.01% akide candy which cannot be named as akide candy. The other graphs demonstrated amorph behavior. However, M_2 values showed that there were some small crystalline parts in these all akide candies. XRD may not detect them since it is based on macro size (Lopez-Rubio et al., 2008). However, M_2 measurements obtained by TD-NMR relaxometry focused on molecular size other than macro size level (Becher et al., 2022). Hence, TD-NMR relaxometry presented some information related to the crystallinity characteristics of the akide candies.

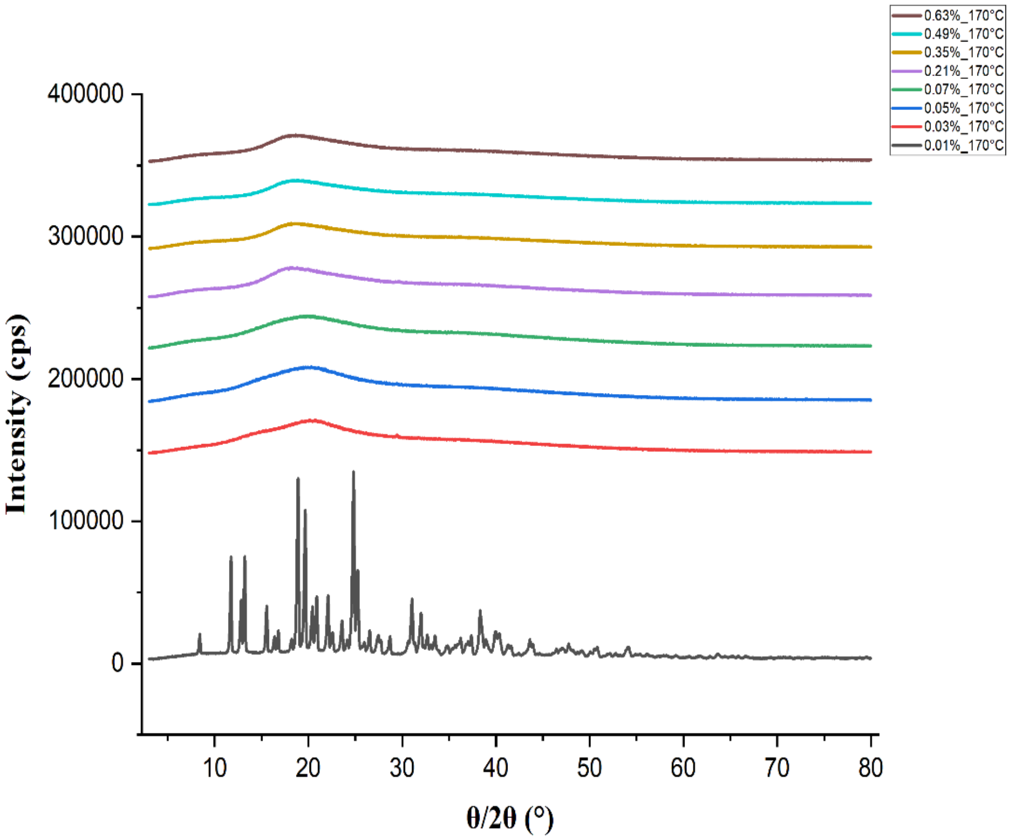

Figure 3.2.4.1 XRD curves for the akide candies with different citric acid concentrations(0.01%, 0.03%, 0.05%, 0.07%, 0.21%, 0.35%, 0.49%, 0.63%) that cooked at 170°C.

3.2.5 Correlations

Pearson Correlation test was performed for all related results of akide candies. As shown in Table 3.2.5.1, almost all correlation values were higher than 0.85 showing strong correlations (Mukaka MM, 2012). Both moisture content and M_2 values showed a correlation with T_1 values. Normally, increasing the cooking temperature led to a reduction in moisture content, which would logically result in lower T_1 values. However, contrary to this expectation, T_1 values increased due to the formation of crystalline structures. This observation was further supported by the correlation between T_1 values and M_2 values.

When evaluating the correlation between moisture content and T_1 values, it became apparent that citric acid concentration had a decreasing impact on the correlations. The highest correlation value was observed between M_2 and T_1 values for the samples with the lowest citric acid concentration of 0.03%. Higher acidity results in more inversion. More inversion generates fructose and glucose. Glucose has significantly longer T_1 times (Le Botlan et al., 1998). Thus, the presence of even small amount of glucose could cause deviation in the overall T_1 values and decrease moisture content. Consequently, the results of T_1 and M_2 offered a more accurate framework for low moisture systems, such as glassy state-hard candies, as explored in this study.

Table 3.2.5.1 Correlation Values for All Moisture Content, T1 and M2 Results of Akide Candies

Factors	**Samples with 0.03% C.A.**	**Samples with 0.05% C.A.**	**Samples with 0.07% C.A.**	**Samples with 0.21% C.A.**	**Samples with 0.35% C.A.**	**Samples with 0.49% C.A.**	**Samples with 0.63% C.A.**
T_1 - M_2	0.936	0.955	0.868	0.861	0.932	0.868	0.726
T_1 - M.C.	-0.927	-0.868	-0.876	-0.885	-0.847	-0.873	-0.817
M_2 - M.C.	-0.825	-0.812	-0.830	-0.833	-0.890	-0.834	-0.732

CHAPTER 4

CONCLUSION

Time domain NMR relaxometry is an easy and non-destructive analytical technique. It can be carried out on benchtop, low to medium field systems. Lots of quality control measurements and characterization experiments on food systems can be performed by using a single NMR device. Solid Echo (**SE**) sequence is a fast and easy sequence that is used for measuring the crystal content of the samples. It is based on Free Induction Decay (FID).

In the first part of the study, hard candies were monitored. Hard candies were cooked at different temperatures changing between 135°C and 145°C with an interval of 2.5°C. They were stored at four different temperatures which are 25°C, 4°C, -18°C and -80°C. The moisture content of hard candies was measured by Karl-Fischer titration. It was seen that when the cooking temperature was increased and the storage temperature was decreased, the moisture content of the samples decreased. TD-NMR measurements were carried out. T_1 measurements showed that increasing cooking temperature and decreasing storage temperature had a positive effect on T_1 values. This increase in T_1 was related to crystallinity since moisture content decreased when the cooking temperature was increased and the storage temperature was decreased. In order to verify this relation, second moment (M_2) measurements were performed. According to the results obtained, when the cooking temperature was increased and the storage temperature was decreased, the crystallinity of hard candies increased. For industrial applications, low crystallinity value is desirable. The lowest crystallinity value was obtained at cooking temperature of 135°C and storage temperature of 25°C. Thus, cooking temperature of 135°C and storage temperature of 25˚C are the best conditions for industrial applications of hard candy.

In the second part of the study, akide candies were evaluated. Akide candies were cooked at different temperatures changing between 150°C and 170°C with an interval of 5°C. Different citric acid concentrations were used which are 0.03%, 0.05%, 0.07%, 0.21%, 0.35%, 0.49%, and 0.63%. Again, for moisture content determination, Karl-Fischer titration was used. When the cooking temperature was increased and citric acid concentration was decreased, the moisture contents of akide candies were decreased. Likely, TD-NMR experiments were performed. It can be realized that when the cooking temperature was increased and citric acid concentration was decreased, T_1 values increased. Similar to hard candy results, this increase in T_1 can be related to crystallinity. In order to prove this, second moment measurements are done. The results showed that when the cooking temperature was increased and citric acid concentration was decreased, the crystallinity of akide candies increased. For industrial applications, low crystallinity value is desirable. The lowest crystallinity value was obtained at cooking temperature of 150°C and citric acid ocentration of 0.63%. Thus, cooking temperature of 150°C and citric acid concentration of 0.63% are the best conditions for industrial applications of akide candy.

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APPENDICES

A. Statistical Analysis for Hard Candies

COOKING TEMPERATURE

Comparisons for T_1 of Fresh Hard Candy

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

```
C1     N  Mean     Grouping
145.0  3  202.790  A
140.0  3  199.287    B
142.5  3  187.103      C
137.5  3  169.317        D
135.0  3  153.027          E
```

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for T_1 of Hard Candy Samples Stored at 25°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

```
C1     N  Mean     Grouping
145.0  3  202.790  A
140.0  3  199.287    B
142.5  3  187.103      C
137.5  3  169.317        D
135.0  3  153.027          E
```

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for T_1 of Hard Candy Samples Stored at 4°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
145.0	3	245.933	A
142.5	3	220.277	B
140.0	3	217.150	B
137.5	3	193.087	C
135.0	3	176.083	D

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for T_1 of Hard Candy Samples Stored at -18°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
145.0	3	243.46	A
142.5	3	222.58	B
140.0	3	215.16	B
137.5	3	185.50	C
135.0	3	172.84	D

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for T_1 of Hard Candy Samples Stored at -80°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
145.0	3	243.617	A
142.5	3	228.633	B
140.0	3	225.510	B
137.5	3	194.037	C
135.0	3	171.760	D

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for M_2 of Fresh Hard Candy Samples

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
140.0	3	12.5333	A
145.0	3	12.4867	B
142.5	3	12.3533	C
137.5	3	12.0500	D
135.0	3	11.7500	E

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for M_2 of Hard Candy Samples Stored at 25°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
140.0	3	12.5333	A
145.0	3	12.4867	B
142.5	3	12.3533	C
137.5	3	12.0500	D
135.0	3	11.7500	E

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for M_2 of Hard Candy Samples Stored at 4°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
145.0	3	13.0500	A
140.0	3	12.7300	B
142.5	3	12.7133	B
137.5	3	12.3900	C
135.0	3	12.1333	D

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for M_2 of Hard Candy Samples Stored at -18°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
145.0	3	13.0033	A
140.0	3	12.7467	B
142.5	3	12.7267	B
137.5	3	12.3633	C
135.0	3	12.1900	D

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for M_2 of Hard Candy Samples Stored at -80°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
145.0	3	12.9233	A
142.5	3	12.7667	B
140.0	3	12.7300	B
137.5	3	12.4067	C
135.0	3	12.1533	D

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for Brix of Hard Candy Samples Stored at 4°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
145.0	3	17.0000	A
142.5	3	16.5667	B
140.0	3	16.5000	B C
135.0	3	16.2333	C
137.5	3	15.3667	D

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for Moisture Content of Hard Candy Samples Stored at 4°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping		
135.0	3	4.02727	A		
137.5	3	3.89617	A	B	
140.0	3	3.52250	A	B	C
142.5	3	3.39500		B	C
145.0	3	2.95480			C

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for Brix of Hard Candy Samples Stored at -18°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping		
145.0	3	16.9333	A		
140.0	3	16.7333	A	B	
142.5	3	16.7000	A	B	
137.5	3	16.6000		B	
135.0	3	15.9333			C

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for Moisture Content of Hard Candy Samples Stored at -18°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping		
135.0	3	4.42073	A		
137.5	3	4.38870	A		
140.0	3	3.83830		B	
142.5	3	3.63440		B	C
145.0	3	3.42550			C

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for Brix of Hard Candy Samples Stored at -80°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
145.0	3	17.4000	A
135.0	3	17.0000	B
140.0	3	16.7333	C
137.5	3	16.7000	C D
142.5	3	16.5667	D

Means that do not share a letter are significantly different.

COOKING TEMPERATURE

Comparisons for Moisture Content of Hard Candy Samples Stored at -80°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
135.0	3	3.85853	A
137.5	3	3.66150	A
140.0	3	3.03227	B
145.0	3	2.84700	B
142.5	3	2.70957	B

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for T_1 of Hard Candy Samples Cooked at 135°C

Tukey Pairwise Comparisons: T Bir_1

Grouping Information Using the Tukey Method and 95% Confidence

T Bir_1	N	Mean	Grouping
4C	3	176.083	A
-18C	3	172.840	B
-80C	3	171.760	B
2 Month	3	153.027	C
Fresh	3	153.027	D

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for T_1 of Hard Candy Samples Cooked at 137.5°C

Tukey Pairwise Comparisons: T Bir_1

Grouping Information Using the Tukey Method and 95% Confidence

T Bir_1	N	Mean	Grouping		
-80C	3	194.037	A		
4C	3	193.087	A		
-18C	3	185.500		B	
2 Month	3	169.317			C
Fresh	3	169.317			C

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for T_1 of Hard Candy Samples Cooked at 140°C

Tukey Pairwise Comparisons: T Bir_1

Grouping Information Using the Tukey Method and 95% Confidence

T Bir_1	N	Mean	Grouping		
-80C	3	225.510	A		
4C	3	217.150		B	
-18C	3	215.160		B	
2 Month	3	199.287			C
Fresh	3	199.287			C

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for T_1 of Hard Candy Samples Cooked at 142.5°C

Tukey Pairwise Comparisons: T Bir_1

Grouping Information Using the Tukey Method and 95% Confidence

T Bir_1	N	Mean	Grouping	
-80C	3	228.633	A	
-18C	3	222.580	A	B
4C	3	220.277	A	B
2 Month	3	187.103		B
Fresh	3	187.103		B

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for T_1 of Hard Candy Samples Cooked at 145°C

Tukey Pairwise Comparisons: T Bir_1

Grouping Information Using the Tukey Method and 95% Confidence

T Bir_1	N	Mean	Grouping
4C	3	245.933	A
-80C	3	243.617	A
-18C	3	243.460	A
2 Month	3	202.790	B
Fresh	3	202.790	B

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for M_2 of Hard Candy Samples Cooked at 135°C

Tukey Pairwise Comparisons: Second moment_1

Grouping Information Using the Tukey Method and 95% Confidence

Second moment_1	N	Mean	Grouping
-18C	3	12.1900	A
-80C	3	12.1533	B
4C	3	12.1333	C
2 Month	3	11.7500	D
Fresh	3	11.7500	D

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for M_2 of Hard Candy Samples Cooked at 137.5°C

Tukey Pairwise Comparisons: Second moment_1

Grouping Information Using the Tukey Method and 95% Confidence

Second moment_1	N	Mean	Grouping
-80C	3	12.4067	A
4C	3	12.3900	B
-18C	3	12.3633	C
2 Month	3	12.0500	D
Fresh	3	12.0500	D

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for M_2 of Hard Candy Samples Cooked at 140°C

Tukey Pairwise Comparisons: Second moment_1

Grouping Information Using the Tukey Method and 95% Confidence

Second moment_1	N	Mean	Grouping
-18C	3	12.7467	A
-80C	3	12.7300	A
4C	3	12.7300	A
Fresh	3	12.5333	B
2 Month	3	12.5333	B

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for M_2 of Hard Candy Samples Cooked at 142.5°C

Tukey Pairwise Comparisons: Second moment_1

Grouping Information Using the Tukey Method and 95% Confidence

Second moment_1	N	Mean	Grouping
-80C	3	12.7667	A
4C	3	12.7300	B
-18C	3	12.7267	B
2 Month	3	12.3533	C
Fresh	3	12.3533	C

Means that do not share a letter are significantly different.

STORAGE TEMPERATURE

Comparisons for M_2 of Hard Candy Samples Cooked at 145°C

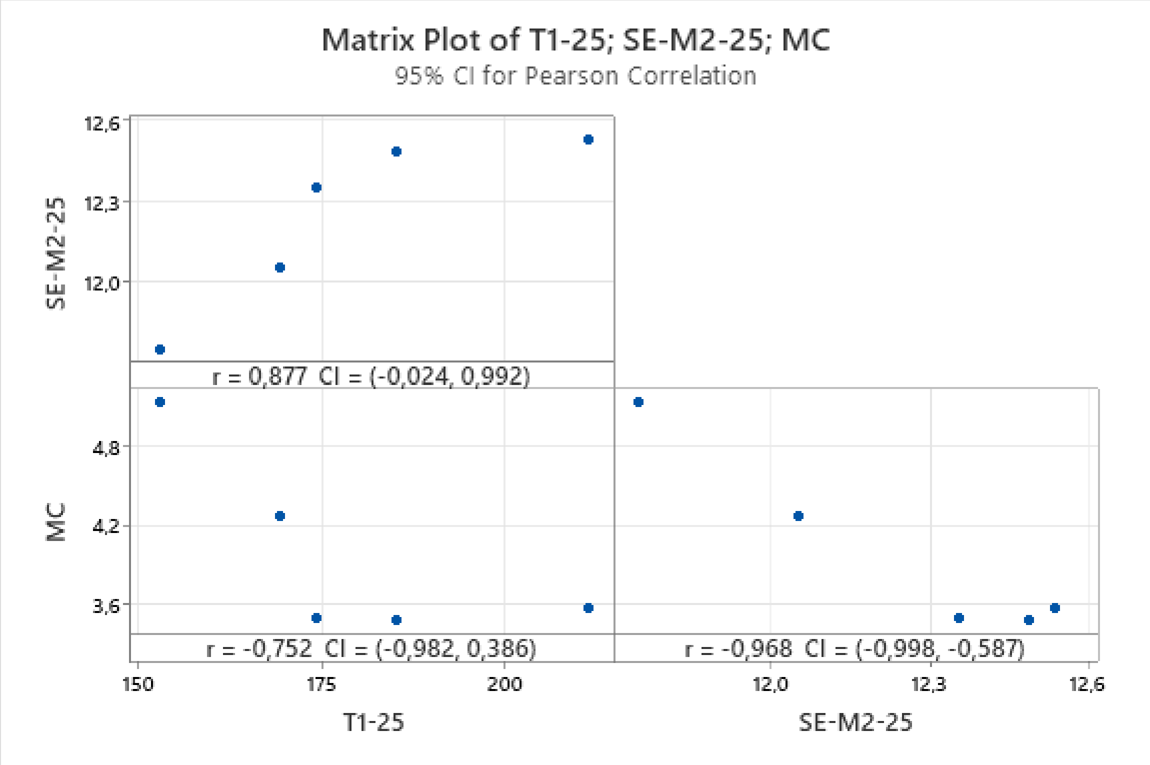
Tukey Pairwise Comparisons: Second moment_1

Grouping Information Using the Tukey Method and 95% Confidence

Second moment_1	N	Mean	Grouping
4C	3	13.0500	A
-18C	3	13.0033	A
-80C	3	12.9233	A
2 Month	3	12.4867	A
Fresh	3	12.4867	A

CORRELATION

Correlation of T_1, M_2 and Moisture Content of Samples Stored at 25°C



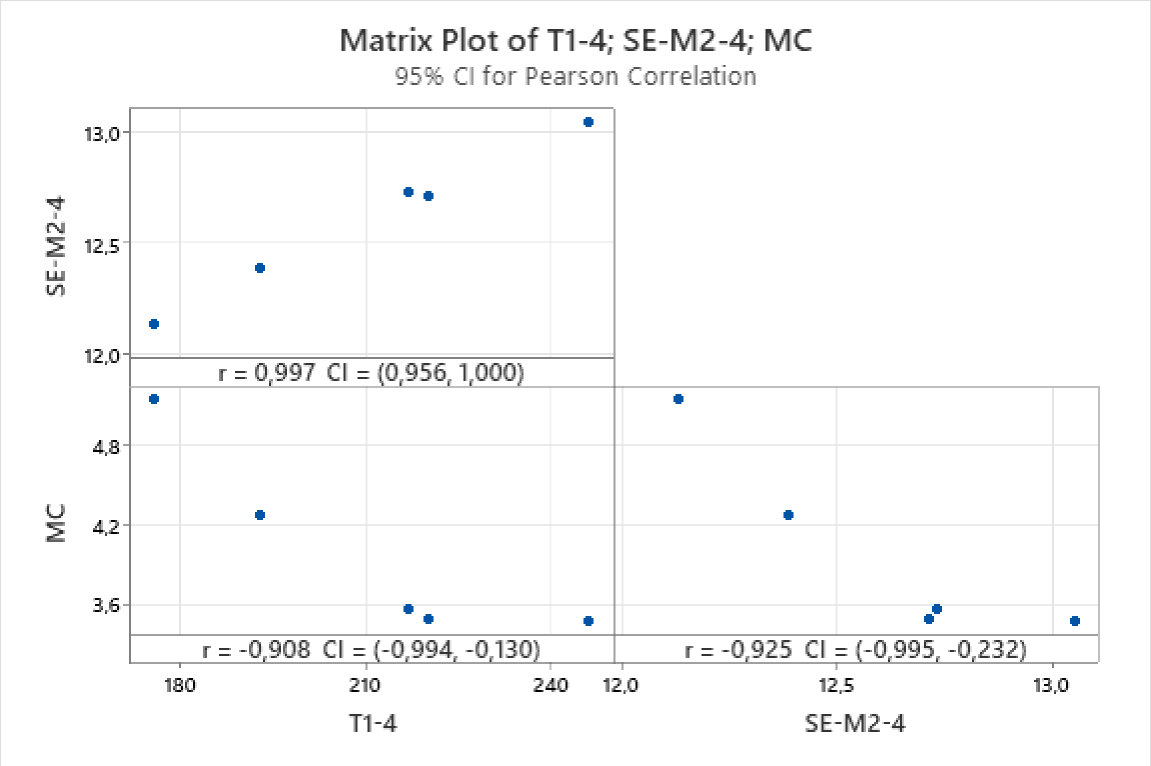
Method

Correlation type	Pearson
Number of rows used	5

Correlations

	T1-25	**SE-M2-25**
SE-M2-25	0,877	
MC	-0,752	-0,968

Correlation of T_1, M_2 and Moisture Content of Samples Stored at 4°C



Method

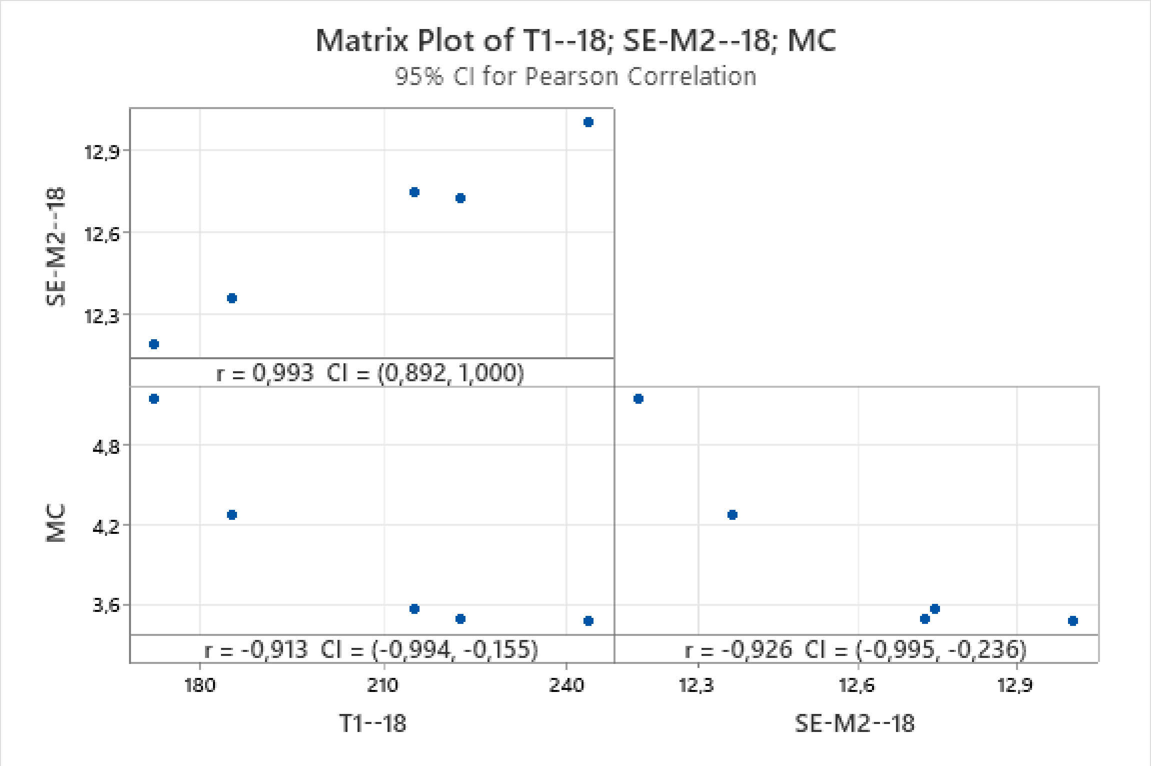
Correlation type	Pearson
Number of rows used	5

Correlations

	T1-4	SE-M2-4
SE-M2-4	0,997	
MC	-0,908	-0,925

CORRELATION

Correlation of T_1, M_2 and Moisture Content of Samples Stored at -18°C



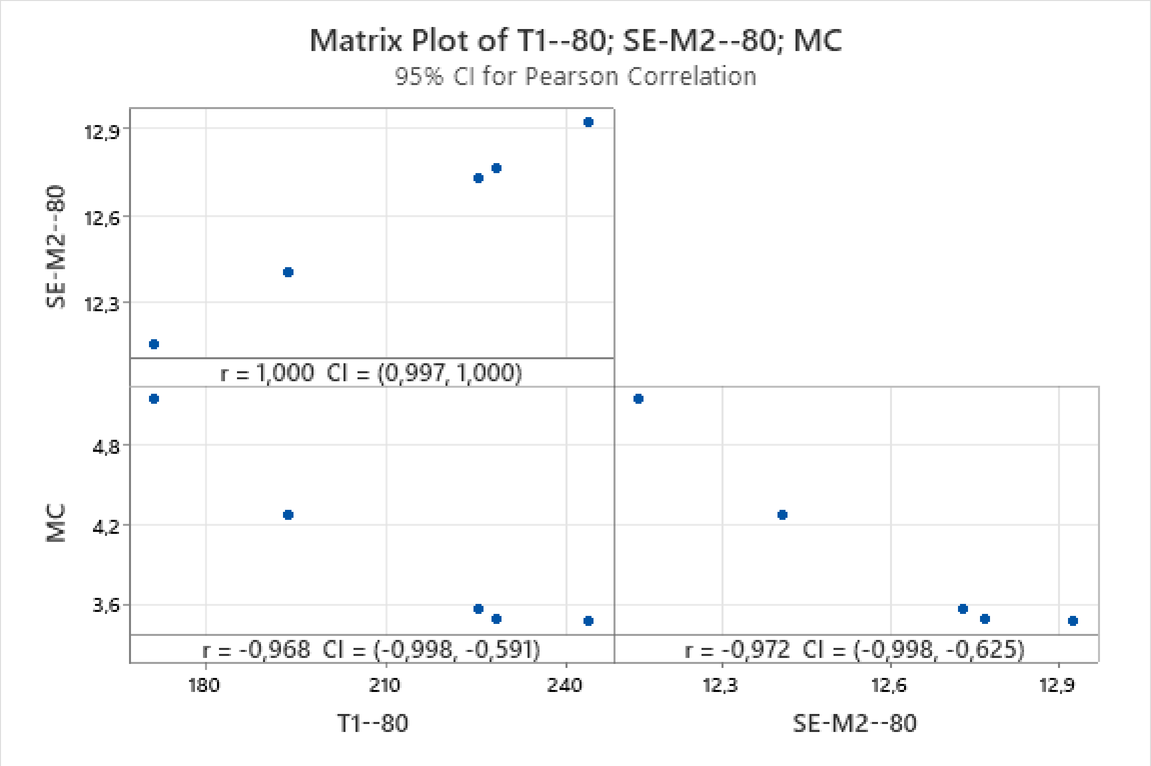
Method

Correlation type	Pearson
Number of rows used	5

Correlations

	T1--18	SE-M2--18
SE-M2--18	0,993	
MC	-0,913	-0,926

Correlation of T_1, M_2 and Moisture Content of Samples Stored at -80°C



Method

Correlation type	Pearson
Number of rows used	5

Correlations

	T1--80	SE-M2--80
SE-M2--80	1,000	
MC	-0,968	-0,972

B. Statistical Analysis for Akide Candies

T1

Comparisons for T_1 of Akide Candy Samples Cooked at 150°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,03	2	237.850	A
0,05	2	229.315	B
0,07	2	225.275	C
0,21	2	221.590	D
0,35	2	205.420	E
0,49	2	198.245	F
0,63	2	194.400	G

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples Cooked at 155°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,03	2	281.205	A
0,05	2	277.380	B
0,07	2	255.900	C
0,21	2	241.380	D
0,35	2	235.010	E
0,49	2	228.535	F
0,63	2	216.935	G

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples Cooked at 160°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,03	2	293.155	A
0,05	2	283.370	B
0,07	2	263.560	C
0,21	2	256.380	D
0,35	2	240.420	E
0,49	2	236.120	F
0,63	2	233.220	G

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples Cooked at 165°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,03	2	309.875	A
0,05	2	299.810	B
0,07	2	297.050	C
0,21	2	275.510	D
0,35	2	272.240	E
0,49	2	267.555	F
0,63	2	265.225	G

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples Cooked at 170°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,03	2	318.033	A
0,05	2	315.695	B
0,07	2	313.270	C
0,21	2	297.135	D
0,35	2	284.010	E
0,49	2	274.645	F
0,63	2	272.385	G

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples with 0.03% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	318.033	A
165	2	309.875	B
160	2	293.155	C
155	2	281.205	D
150	2	237.850	E

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples with 0.05% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	315.695	A
165	2	299.810	B
160	2	283.370	C
155	2	277.380	D
150	2	229.315	E

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples with 0.07% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	313.270	A
165	2	297.050	B
160	2	263.560	C
155	2	255.900	D
150	2	225.275	E

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples with 0.21% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	297.135	A
165	2	275.510	B
160	2	256.380	C
155	2	241.380	D
150	2	221.590	E

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples with 0.35% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	284.01	A
165	2	272.24	B
160	2	240.42	C
155	2	235.01	D
150	2	205.42	E

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples with 0.49% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	274.645	A
165	2	267.555	B
160	2	236.120	C
155	2	228.535	D
150	2	198.245	E

Means that do not share a letter are significantly different.

T1

Comparisons for T_1 of Akide Candy Samples with 0.63% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping				
170	2	272.385	A				
165	2	265.225		B			
160	2	233.220			C		
155	2	216.935				D	
150	2	194.400					E

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples Cooked at 150°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping						
0,03	2	12.6600	A						
0,05	2	12.5633		B					
0,07	2	12.5167			C				
0,21	2	11.8400				D			
0,35	2	11.6367					E		
0,49	2	11.5333						F	
0,63	2	11.4100							G

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples Cooked at 155°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping						
0,03	2	13.245	A						
0,05	2	13.110		B					
0,07	2	13.015			C				
0,21	2	12.465				D			
0,35	2	12.430					E		
0,49	2	12.410						F	
0,63	2	12.180							G

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples Cooked at 160°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,03	2	13.130	A
0,05	2	13.120	B
0,07	2	12.725	C
0,21	2	12.320	E
0,35	2	12.320	D
0,49	2	11.775	F
0,63	2	11.150	G

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples Cooked at 165°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,03	2	13.360	A
0,05	2	13.190	B
0,07	2	13.170	C
0,21	2	12.910	D
0,35	2	12.775	E
0,49	2	12.745	F
0,63	2	12.715	G

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples Cooked at 170°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,03	2	13.315	A
0,05	2	13.225	B
0,07	2	13.135	C
0,21	2	12.750	D
0,35	2	12.715	E
0,49	2	12.700	F
0,63	2	12.635	G

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples with 0.03% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
165	2	13.360	A
170	2	13.315	B
155	2	13.245	C
160	2	13.130	D
150	2	12.660	E

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples with 0.05% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	13.2250	A
165	2	13.1900	B
160	2	13.1200	C
155	2	13.1100	D
150	2	12.5633	E

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples with 0.07% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
165	2	13.1700	A
170	2	13.1350	B
155	2	13.0150	C
160	2	12.7250	D
150	2	12.5167	E

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples with 0.21% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
165	2	12.910	A
170	2	12.750	B
155	2	12.465	C
160	2	12.320	D
150	2	11.840	E

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples with 0.35% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
165	2	12.7750	A
170	2	12.7150	B
155	2	12.4300	C
160	2	12.3200	D
150	2	11.6367	E

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples with 0.49% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
165	2	12.7450	A
170	2	12.7000	B
155	2	12.4100	C
160	2	11.7750	D
150	2	11.5333	E

Means that do not share a letter are significantly different.

M2

Comparisons for M_2 of Akide Candy Samples with 0.63% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
165	2	12.715	A
170	2	12.635	B
155	2	12.180	C
150	2	11.410	D
160	2	11.150	E

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples Cooked at 150°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,63	2	7.72760	A
0,49	2	7.63295	B
0,35	2	7.23695	C
0,21	2	6.87595	D
0,07	2	6.32720	E
0,05	2	3.03790	F
0,03	2	2.64025	G

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples Cooked at 155°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,63	2	4.05810	A
0,49	2	3.95317	B
0,21	2	3.87720	C
0,07	2	3.67060	D
0,35	2	3.49113	E
0,05	2	2.43535	F
0,03	2	2.26845	G

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples Cooked at 160°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,63	2	5.25190	A
0,49	2	4.72665	B
0,35	2	4.72145	C
0,21	2	4.16890	D
0,07	2	4.13960	E
0,05	2	2.33135	F
0,03	2	2.27415	G

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples Cooked at 165°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,63	2	4.38400	A
0,49	2	4.21265	B
0,35	2	4.12420	C
0,21	2	3.98065	D
0,07	2	3.94570	E
0,05	2	2.59460	F
0,03	2	1.93565	G

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples Cooked at 170°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,63	2	2.30393	A
0,49	2	2.21697	B
0,35	2	2.17193	C
0,21	2	2.14367	D
0,07	2	2.08815	E
0,05	2	1.84817	F
0,03	2	1.59673	G

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples with 0.03% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
150	2	2.64025	A
160	2	2.27415	B
155	2	2.26845	C
165	2	1.93565	D
170	2	1.59673	E

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples with 0.05% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
150	2	3.03790	A
165	2	2.59460	B
155	2	2.43535	C
160	2	2.33135	D
170	2	1.84817	E

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples with 0.03% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
150	2	6.32720	A
160	2	4.13960	B
165	2	3.94570	C
155	2	3.67060	D
170	2	2.08815	E

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples with 0.21% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
150	2	6.87595	A
160	2	4.16890	B
165	2	3.98065	C
155	2	3.87720	D
170	2	2.14367	E

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples with 0.35% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
150	2	7.23695	A
160	2	4.72145	B
165	2	4.12420	C
155	2	3.49113	D
170	2	2.17193	E

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples with 0.49% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping				
150	2	7.63295	A				
160	2	4.72665		B			
165	2	4.21265			C		
155	2	3.95317				D	
170	2	2.21697					E

Means that do not share a letter are significantly different.

MC

Comparisons for Moisture Content of Akide Candy Samples with 0.03% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping				
150	2	7.72760	A				
160	2	5.25190		B			
165	2	4.38400			C		
155	2	4.05810				D	
170	2	2.30393					E

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples Cooked at 150°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping						
0,05	2	19.0667	A						
0,07	2	18.6333		B					
0,63	2	18.4333			C				
0,35	2	18.4333				D			
0,49	2	17.7333					E		
0,03	2	17.6000						F	
0,21	2	17.5333							G

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples Cooked at 155°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,05	2	20.7333	A
0,35	2	19.5333	B
0,07	2	18.9333	D
0,49	2	18.9333	C
0,21	2	18.9000	E
0,63	2	18.2000	F
0,03	2	17.7000	G

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples Cooked at 160°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,49	2	20.0667	A
0,05	2	19.4333	B
0,35	2	18.7000	C
0,63	2	18.5500	D
0,07	2	18.4667	E
0,21	2	18.2000	F
0,03	2	16.3667	G

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples Cooked at 165°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,63	2	19.8667	A
0,21	2	19.7667	B
0,35	2	19.6000	C
0,07	2	19.3333	D
0,49	2	18.9000	E
0,05	2	18.9000	F
0,03	2	17.1667	G

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples Cooked at 170°C

Tukey Pairwise Comparisons: C1

Grouping Information Using the Tukey Method and 95% Confidence

C1	N	Mean	Grouping
0,35	2	22.3333	A
0,05	2	21.6333	B
0,63	2	21.3333	C
0,21	2	20.2667	D
0,07	2	19.9000	E
0,49	2	18.2667	F
0,03	2	17.8667	G

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples with 0.03% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	17.8667	A
155	2	17.7000	B
150	2	17.6000	C
165	2	17.1667	D
160	2	16.3667	E

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples with 0.05% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	21.6333	A
155	2	20.7333	B
160	2	19.4333	C
150	2	19.0667	D
165	2	18.9000	E

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples with 0.07% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	19.9000	A
165	2	19.3333	B
155	2	18.9333	C
150	2	18.6333	D
160	2	18.4667	E

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples with 0.21% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	20.2667	A
165	2	19.7667	B
155	2	18.9000	C
160	2	18.2000	D
150	2	17.5333	E

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples with 0.35% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping
170	2	22.3333	A
165	2	19.6000	B
155	2	19.5333	C
160	2	18.7000	D
150	2	18.4333	E

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples with 0.49% Citric Acid

Tukey Pairwise Comparisons: C8

Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping				
160	2	20.0667	A				
155	2	18.9333		B			
165	2	18.9000			C		
170	2	18.2667				D	
150	2	17.7333					E

Means that do not share a letter are significantly different.

BRIX

Comparisons for Brix of Akide Candy Samples with 0.63% Citric Acid

Tukey Pairwise Comparisons: C8

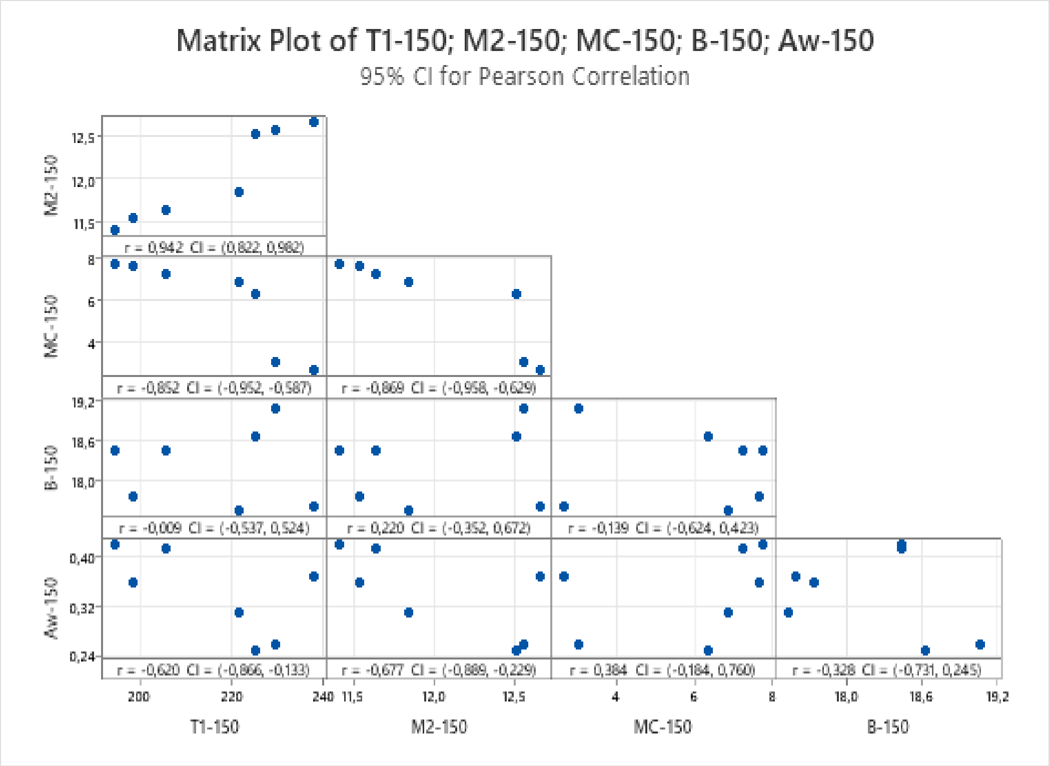
Grouping Information Using the Tukey Method and 95% Confidence

C8	N	Mean	Grouping				
170	2	21.3333	A				
165	2	19.8667		B			
160	2	18.5500			C		
150	2	18.4333				D	
155	2	18.2000					E

Means that do not share a letter are significantly different.

CORRELATIONS - TEMP

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples Cooked at 150°C



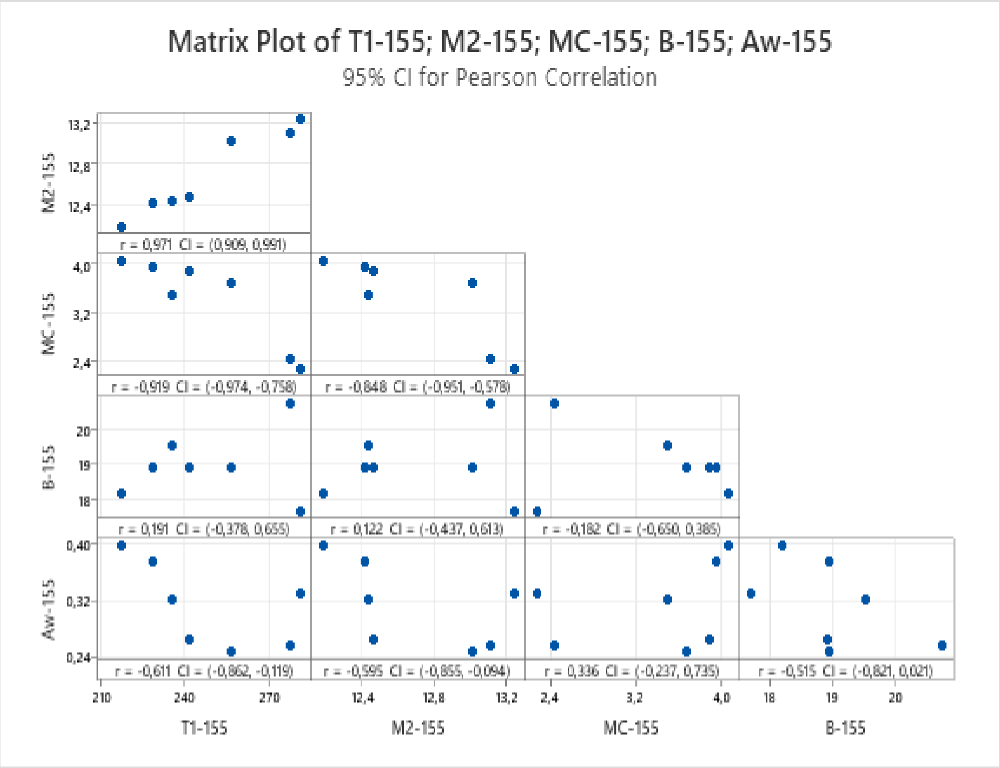
Method

Correlation type	Pearson
Number of rows used	14

Correlations

	T1-150	M2-150	MC-150	B-150
M2-150	0,942			
MC-150	-0,852	-0,869		
B-150	-0,009	0,220	-0,139	
Aw-150	-0,620	-0,677	0,384	-0,328

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples Cooked at 155°C



Method

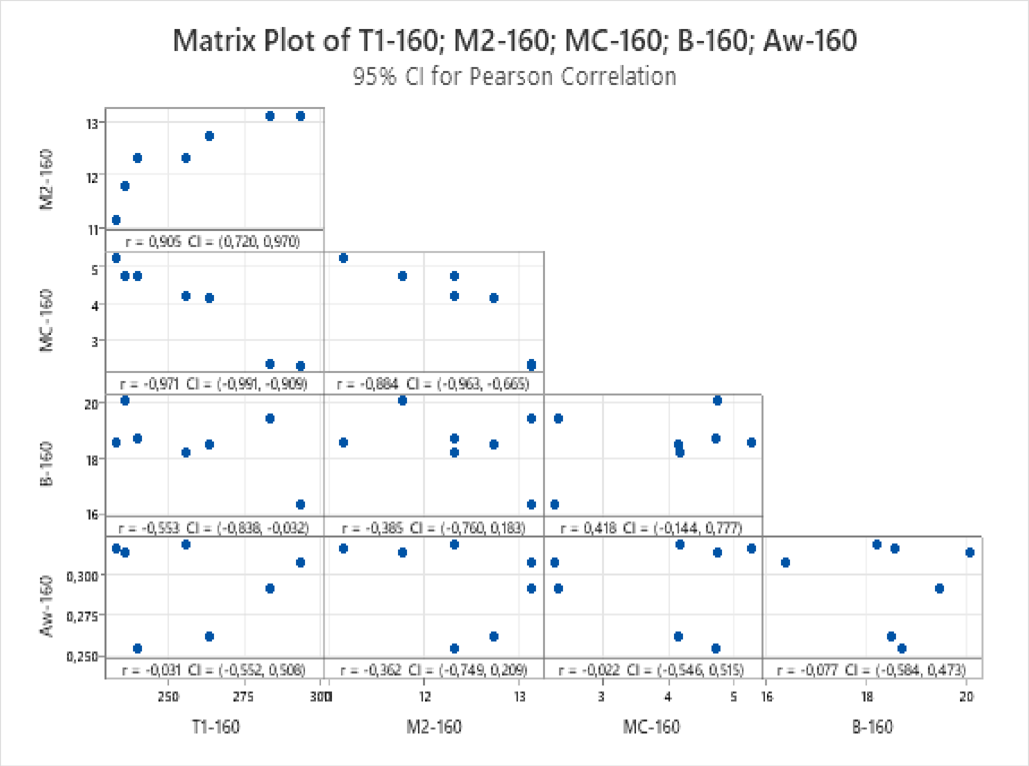
Correlation type	Pearson
Number of rows used	14

Correlations

	T1-155	M2-155	MC-155	B-155
M2-155	0,971			
MC-155	-0,919	-0,848		
B-155	0,191	0,122	-0,182	
Aw-155	-0,611	-0,595	0,336	-0,515

CORRELATIONS - TEMP

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples Cooked at 160°C



Method

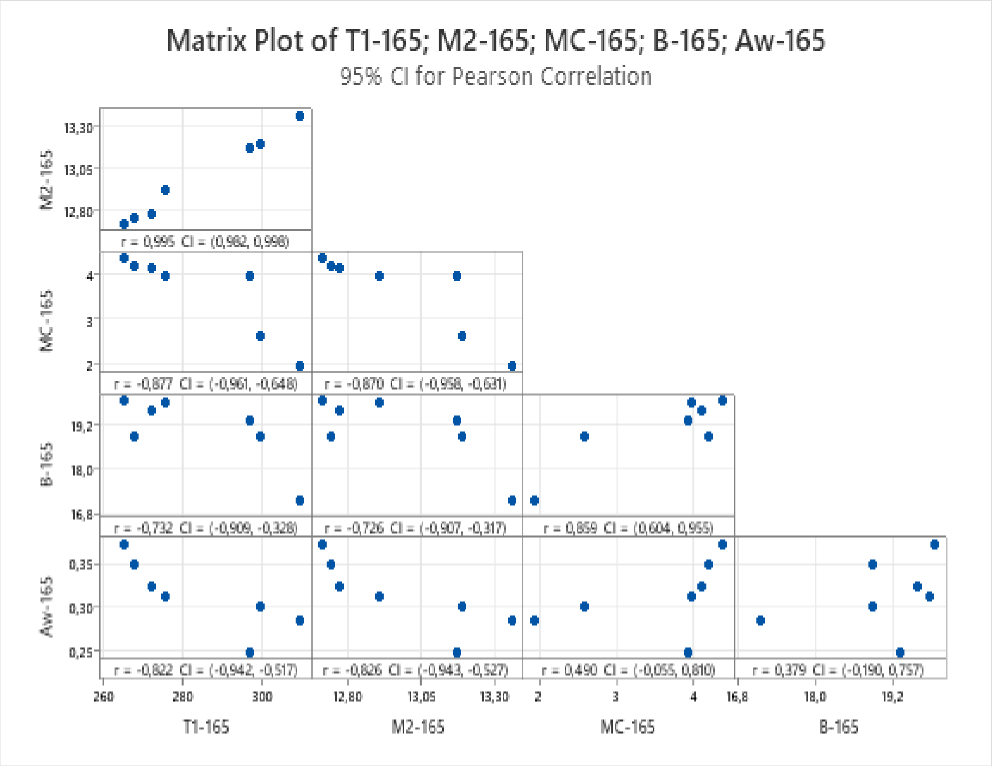
Correlation type	Pearson
Number of rows used	14

Correlations

	T1-160	M2-160	MC-160	B-160
M2-160	0,905			
MC-160	-0,971	-0,884		
B-160	-0,553	-0,385	0,418	
Aw-160	-0,031	-0,362	-0,022	-0,077

CORRELATIONS - TEMP

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples Cooked at 165°C



Method

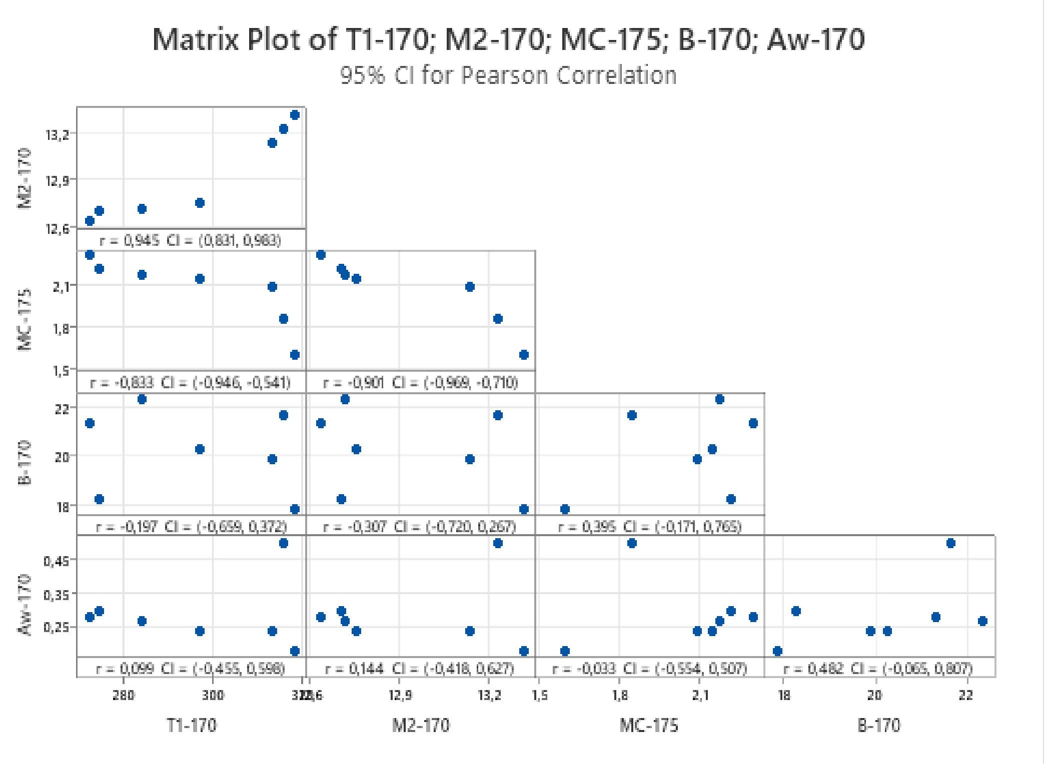
Correlation type	Pearson
Number of rows used	14

Correlations

	T1-165	M2-165	MC-165	B-165
M2-165	0,995			
MC-165	-0,877	-0,870		
B-165	-0,732	-0,726	0,859	
Aw-165	-0,822	-0,826	0,490	0,379

CORRELATIONS - TEMP

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples Cooked at 170°C



Method

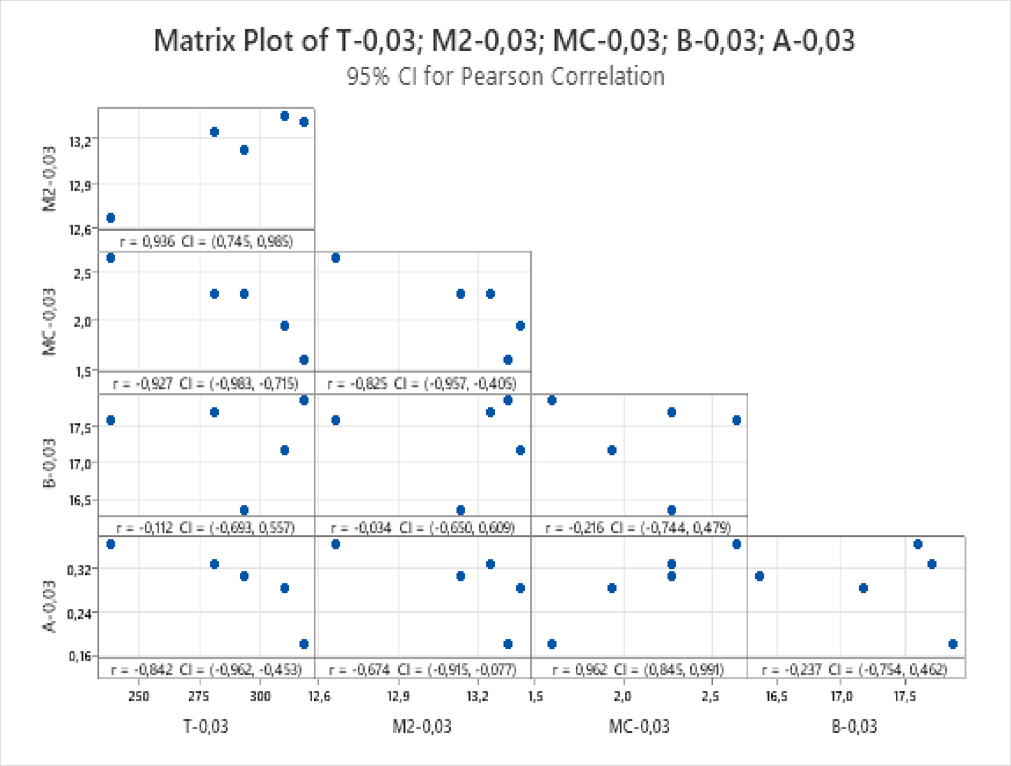
Correlation type	Pearson
Number of rows used	14

Correlations

	T1-170	M2-170	MC-175	B-170
M2-170	0,945			
MC-175	-0,833	-0,901		
B-170	-0,197	-0,307	0,395	
Aw-170	0,099	0,144	-0,033	0,482

CORRELATION-CA

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples with 0.03% Citric Acid



Method

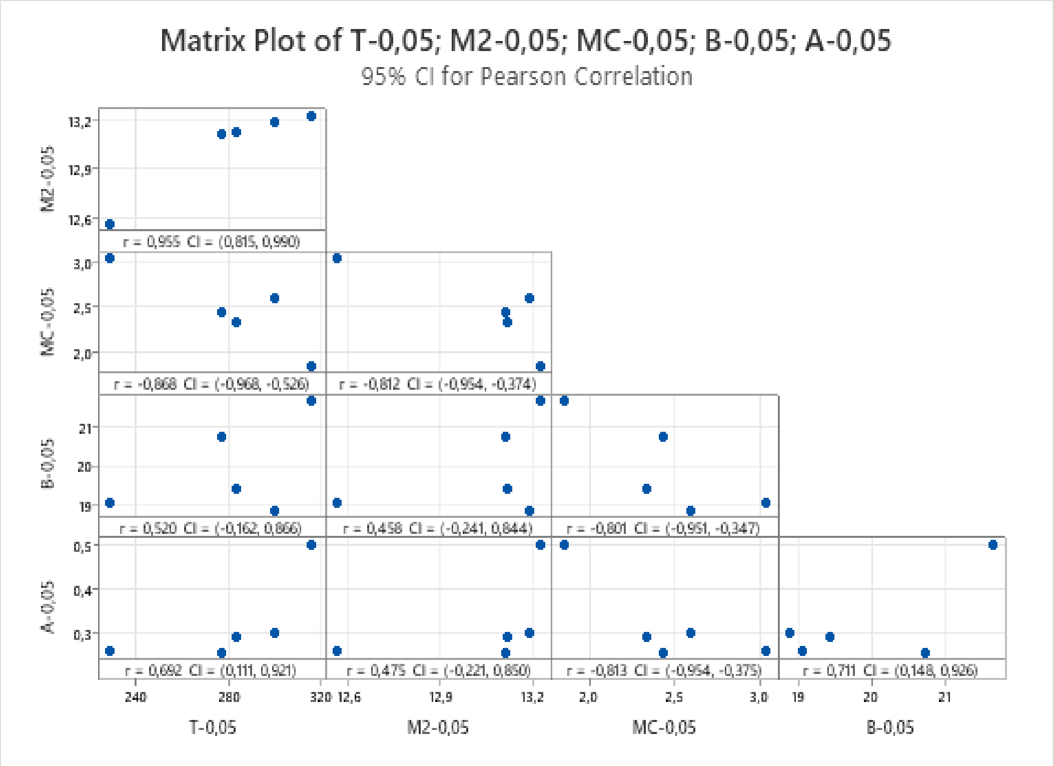
Correlation type	Pearson
Number of rows used	10

Correlations

	T-0,03	M2-0,03	MC-0,03	B-0,03
M2-0,03	0,936			
MC-0,03	-0,927	-0,825		
B-0,03	-0,112	-0,034	-0,216	
A-0,03	-0,842	-0,674	0,962	-0,237

CORRELATION-CA

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples with 0.05% Citric Acid



Method

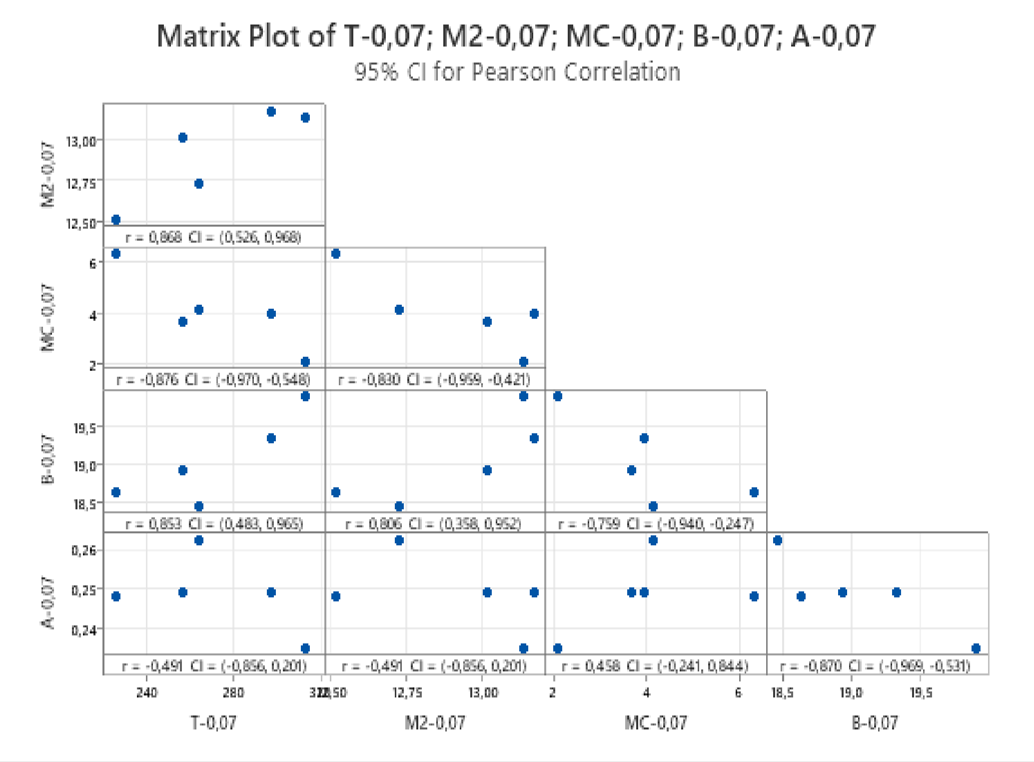
Correlation type	Pearson
Number of rows used	10

Correlations

	T-0,05	M2-0,05	MC-0,05	B-0,05
M2-0,05	0,955			
MC-0,05	-0,868	-0,812		
B-0,05	0,520	0,458	-0,801	
A-0,05	0,692	0,475	-0,813	0,711

CORRELATION-CA

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples with 0.07% Citric Acid



Method

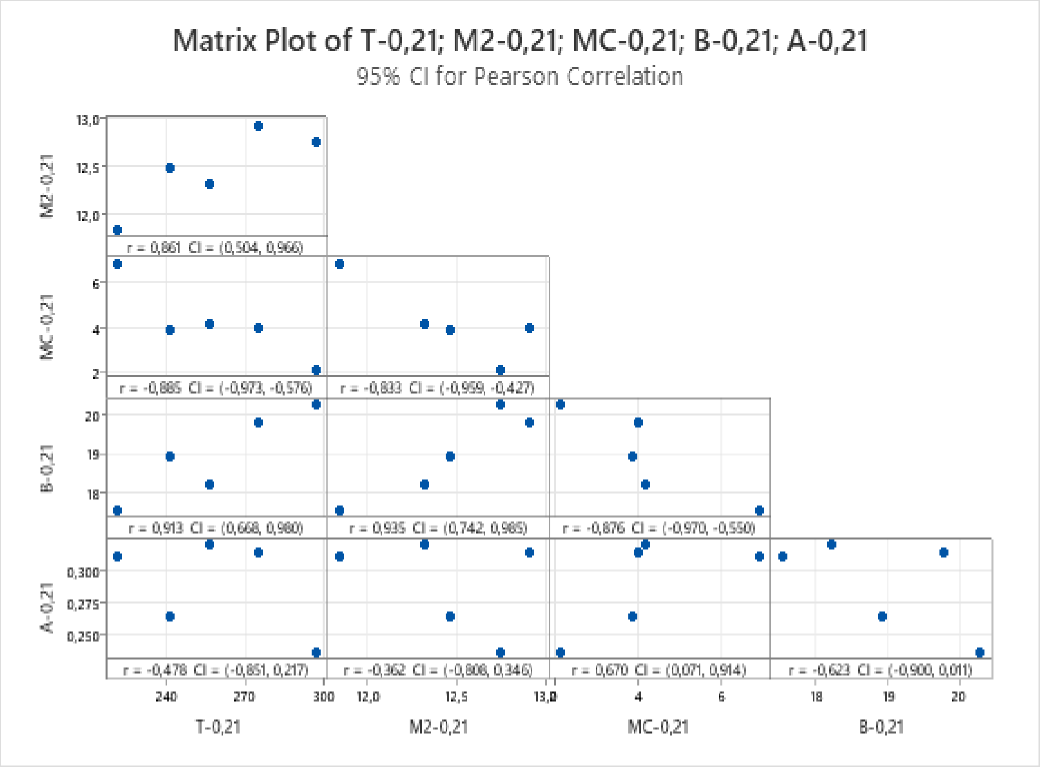
Correlation type	Pearson
Number of rows used	10

Correlations

	T-0,07	M2-0,07	MC-0,07	B-0,07
M2-0,07	0,868			
MC-0,07	-0,876	-0,830		
B-0,07	0,853	0,806	-0,759	
A-0,07	-0,491	-0,491	0,458	-0,870

CORRELATION-CA

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples with 0.21% Citric Acid



Method

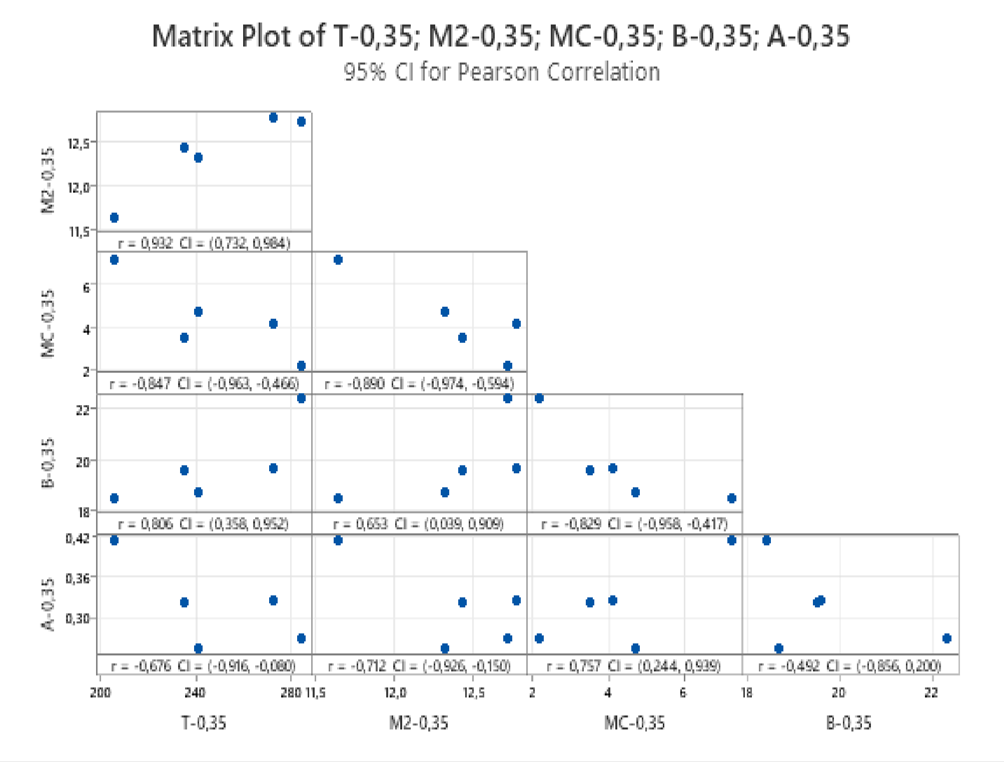
Correlation type	Pearson
Number of rows used	10

Correlations

	T-0,21	M2-0,21	MC-0,21	B-0,21
M2-0,21	0,861			
MC-0,21	-0,885	-0,833		
B-0,21	0,913	0,935	-0,876	
A-0,21	-0,478	-0,362	0,670	-0,623

CORRELATION-CA

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples with 0.35% Citric Acid



Method

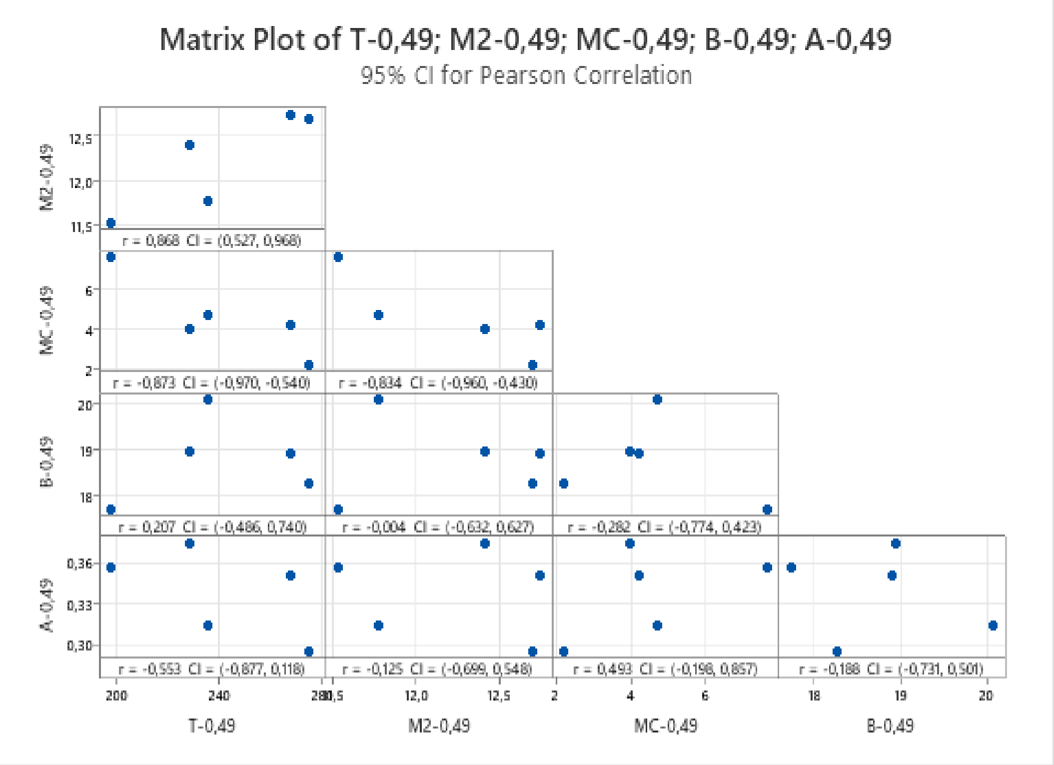
Correlation type	Pearson
Number of rows used	10

Correlations

	T-0,35	M2-0,35	MC-0,35	B-0,35
M2-0,35	0,932			
MC-0,35	-0,847	-0,890		
B-0,35	0,806	0,653	-0,829	
A-0,35	-0,676	-0,712	0,757	-0,492

CORRELATION-CA

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples with 0.49% Citric Acid



Method

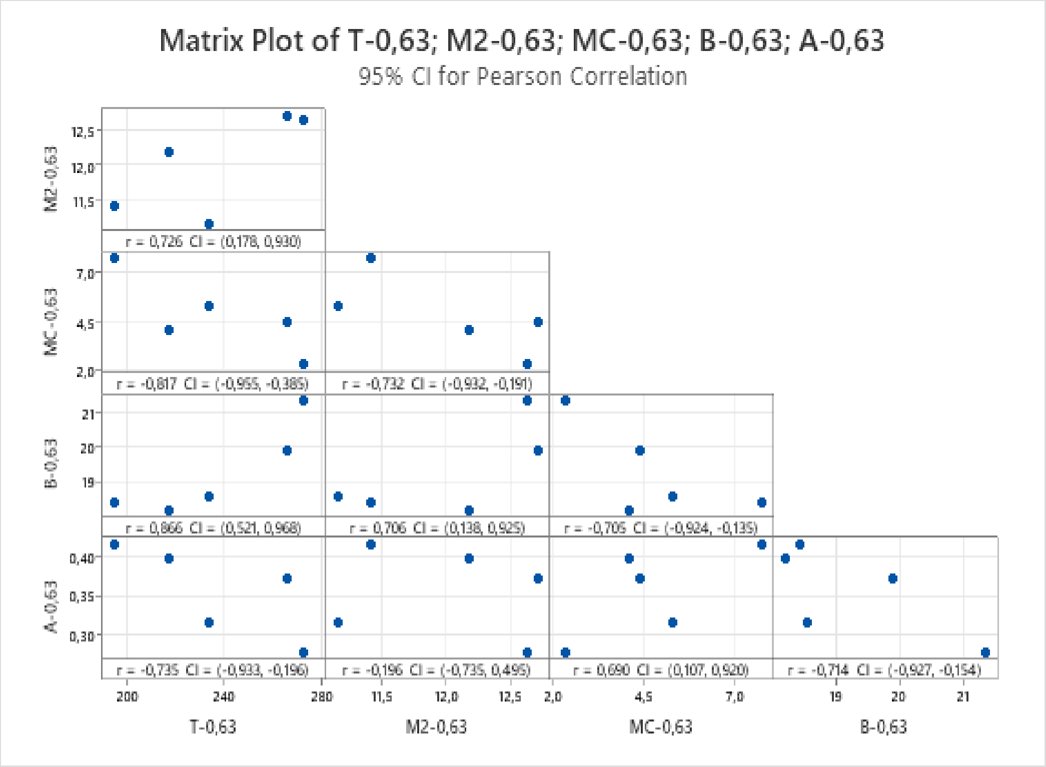
Correlation type	Pearson
Number of rows used	10

Correlations

	T-0,49	M2-0,49	MC-0,49	B-0,49
M2-0,49	0,868			
MC-0,49	-0,873	-0,834		
B-0,49	0,207	-0,004	-0,282	
A-0,49	-0,553	-0,125	0,493	-0,188

CORRELATION-CA

Correlation of T_1, M_2, M.C., Brix and A_w of Akide Candy Samples with 0.63% Citric Acid



Method

Correlation type	Pearson
Number of rows used	10

Correlations

	T-0,63	M2-0,63	MC-0,63	B-0,63
M2-0,63	0,726			
MC-0,63	-0,817	-0,732		
B-0,63	0,866	0,706	-0,705	
A-0,63	-0,735	-0,196	0,690	-0,714