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# Purification of Crude Glycerol Derived from Hydrogenated Cottonseed and Its Use in Confectionary Products

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**Abstract.** Glycerol is a versatile substance used in food, beverages, cosmetics, and technical applications. It can be derived from fats and oils through 4 different reactions, including: transesterification, directed hydrogenation, hydrolysis, and saponification. Glycerol derived from fat hydrolysis yields superior quality and quantity when compared to saponification. The resulting glycerol water is purified and concentrated through evaporation to yield crude glycerol with a concentration of 86-88%. Two distinct methods are recognized for further improving quality of glycerol: distillation, and the purification of glycerol water through the ion exchange process followed by evaporation. The goal of this research was to improve the purification process of glycerol, for obtaining premium-quality glycerol without the need for distillation, through the utilization of cations. Several combinations of activated carbon and clay were tested, and it was determined that a combination of 70:30 yielded the optimal results, considering the amount of glycerol and ash content. Technological parameters such as reaction durations, pH, and process temperatures were investigated, and it was discovered that the appropriate combination was a process duration of more than 40 minutes, a pH value of 2, and a temperature of 70°C. Besides, it was also determined that the concentration and quality of glycerol derived from cottonseed oil can be enhanced through distillation or purification with cationite. Moreover, different concentrations of glycerol on the elaboration of gingerbread were tested, and the conclusion is that adding 5% of the resulting glycerol to the gingerbread recipe could ensure better preservation of its quality during its shelf life.

**Key words:** glycerol, purification, activated carbon, adsorption.

## Introduction

Glycerol is a versatile substance used in various fields such as food production, beverages, cosmetics, and technical applications. It serves multiple purposes including being a moisturizer, solvent, preservative, and flavouring source. Glycerol is valued for its ability to preserve food for extended periods and is even utilized as a sugar substitute in certain food products due to its sweetness, which is 60% as sweet as sucrose, the reason why it is known as Scheele's 'sweet oil' source (Awuchi, 2017). The calories of the same amount of sugar and glycerol are different, since 5 grams (a teaspoon) of sugar contains 20 kilocalories, while the same amount of glycerol contains 27 kilocalories. In the food industry, glycerol is designated as E422 and is used as a fat substitute, humectant and thickener in items like biscuits. Glycerol added to food products differs from glycerol used for medical, cosmetic, and technical purposes by its sensory properties and absence of potentially toxic impurities (EFSA Panel on Food Additives and Nutrient Sources added to Food (ANS) *et al*., 2017).

Glycerol can be derived from fats and oils through 4 different reactions, including: transesterification as it occurs in the production of diesel; direct hydrogenation reaction where alcohol is produced from fatty acids; hydrolysis, during the production of fatty acids; and saponification, during the production of soap (Attarbachi, Kingsley, & Spallina, 2023). The transesterification reaction yields the smallest quantity of glycerol (30-60%), while the hydrolysis reaction produces the highest amount (88-90%).

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Glycerol obtained through hydrolysis is of the highest purity, whereas the quality of glycerol obtained from saponification and transesterification is inferior (Chol *et al*., 2018).

In Uzbekistan, glycerol and fatty acids are obtained through the hydrolysis of fats without the use of any reagent. This approach results in a higher quality and greater quantities of glycerol, and fatty acids compared to the extraction of glycerol through fat saponification. In addition to glycerol and water, the 'sweet water' (glycerol water) obtained from the non-reactive breakdown of fats contains a variety of organic and mineral compounds. The majority of these compounds are lipids, particularly fatty acids, constituting 0.3-1.5% of the glycerol water. Additionally, the sweet water contains 0.05-0.1% amino compounds, including 0.02-0.04% amino acids, 0.04-0.08% carbonyl compounds, 0.004-0.008% carbohydrates, and mineral salts, and other constituents (Abdul Raman, Tan, & Buthiyappan, 2019; Ruzibayev, Salijonova, & Polatovich, 2021; Tan, Abdul Aziz, & Aroua, 2013). These components have surface activity and enhance the stability of water-oil emulsions, what increases the difficulty of processing of glycerol water. The purified glycerol water is concentrated through evaporation to yield crude glycerol with a concentration of 86-88%. Due to the high viscosity of a concentrated glycerol solution, an intensive circulation method is employed during the evaporation process. To prevent the evaporation of glycerol and its thermal decomposition, the evaporation of water with glycerol is conducted under vacuum condition using vacuum-evaporation devices with liquid circulation (Hájek & Skopal, 2009; Pal *et al*., 2018; Pott, Howe, & Dennis, 2014; Ruzibayev, Salijonova, & Polatovich, 2021).

Distilled glycerol, with a concentration of 98%, exhibits superior quality when compared to technical glycerol, obtained through evaporation of glycerol water. In Uzbekistan, glycerol distillation is carried out at temperatures ranging from 170-180 °C under vacuum at a pressure of 2000-2666 Pa. The glycerol rich steam generated during the glycerol distillation process is gradually or fractionally condensed, resulting in the condensation of glycerol at a high concentration of glycerol (98%) (Tan, Abdul Aziz, & Aroua, 2013). To enhance the colour and aroma of the product and achieve the highest quality and premium-grade glycerol in the industry, distilled glycerol further undergoes a bleaching process using activated carbon. Ion exchange can be utilized to purify glycerol without the need for distillation. Tan, Abdul Aziz, & Aroua, in 2013, examined the use of cations for glycerol purification and evaluated their efficacy. The results demonstrated that impurities like free ions and inorganic salts were eliminated through the use of an ion exchange method (Tan, Abdul Aziz, & Aroua, 2013). Therefore, two distinct methods are recognized for obtaining high-quality glycerol: distillation, and the purification of glycerol water through the ion exchange process followed by evaporation.

Currently, the glycerol sourced from hydrogenated cottonseed oil in Uzbekistan falls short of the desired quality standards concerning colour and transparency. Despite undergoing distillation and subsequent refinement with activated carbon, the clarity remains subpar. Hence, there is a need to enhance the purification process of glycerol. Moreover, with the escalating costs of fuel and energy, the distillation approach is proving to be inefficient. Consequently, a decision has been made to explore the purification of glycerol derived from hydrogenated cottonseed oil through the ion exchange method as an alternative to distillation.

In this study, efforts were made to enhance the quality of glycerol derived from hydrolysing hydrogenated cottonseed oil. The aim of this research was to improve the purification process of glycerol, for obtaining premium-quality glycerol without the need for distillation, through the utilization of cations.

## Materials and Methods

*Materials*

Distilled and non-distilled glycerol, produced at 'Urgench fat & oil' JSC enterprise (Urgench, Uzbekistan), were used as raw material. The adsorbents used in the study were: Top Carbon brand activated carbon (Perdomini, Italy) with a moisture content of 10%, and Zarafshan bentonite (bleaching earth) (Zarafshan, Uzbekistan) with a moisture content of 9.0%, a oil content of 45%, and a bulk density of 0.8 g $cm^{-3}$.

KU-2-8 cationite, manufactured by Smolly LLC (Moscow, Russia) (styrene - divinylbenzene - copolymer, gel-type, total static capacity - 1.9 mg-mol $ml^{-1}$, moisture content - 43%, grain size - 0.315-1.250 mm, volume fraction of working fraction - 96%, homogeneity coefficient - 1.7, specific volume in H-form - 2.8 ml $g^{-1}$, osmotic stability - 95%, bulk mass - 0.83 g $l^{-1}$), was used for ion exchange purification purposes.

Mixtures (MA) of activated carbon and bleaching earth in different ratios, from 100:0 to 0:100 (w/w), were prepared to study how they affect the glycerol bleaching process. The mixtures of adsorbents (MA), consisting of bleaching earth and activated carbon, were prepared in different proportions as depicted in Table 1.

*Methods*

Physico-chemical properties (Amount of glycerol, Ash content, Amount of non-volatile organic residues,

Table 1

**Mixtures (MA) of activated carbon and bleaching earth in different proportions**

| Sample | Activated Carbon (%) | Bleaching earth (%) |
|---|---|---|
| MA-1 | 100 | 0 |
| MA-2 | 90 | 10 |
| MA-3 | 80 | 20 |
| MA-4 | 70 | 30 |
| MA-5 | 60 | 40 |
| MA-6 | 50 | 50 |
| MA-7 | 40 | 60 |
| MA-8 | 30 | 70 |
| MA-9 | 20 | 80 |
| MA-10 | 10 | 90 |
| MA-11 | 0 | 100 |

Colour, and Density) of glycerol were analysed according to GOST 6824.

FTIR analyses were conducted to study the purification process of crude glycerol to refined glycerol. A JASCO FT/IR-4600 FT/IR Spectrometer (Jasco, Japan) equipped with a diamond crystal ATR model ATR PRO ONE (Jasco, Japan) was used for the analysis of the glycerol. Samples were scanned in the range of 4000-650 $cm^{-1}$ with a resolution of 0.74 $cm^{-1}$ and 32 scans per sample.

The amount of glycerol was determined on a Shimadzu GC 2030 gas chromatograph (Shimadzu, Japan) equipped with a capillary column SH-Rtx-5; 0.25 mm ID; 0.25 mm df; 30 m. Chromatographic conditions: Detector temperature – 250 °C, injector temperature – 250 °C, Oven temperature program: initial temperature of 150 °C, which was increased to 220°C at a rate of 16°C $min^{-1}$, final temperature (220 °C) was held for 3.62 min. Hydrogen flow rate – 30 ml $min^{-1}$, air flow rate – 30 ml $min^{-1}$, mobile phase – helium, injection volume - 1 µl. Standard of glycerol was sourced from Shimadzu Corporation (Shimadzu, Japan) "Glycerol in water 872 µg $ml^{1}$", which was used to identify the retention time of glycerol in the chromatogram.

The colour of glycerol was determined by using the method described in GOST 7482. According to this method, the main solution (GOST 18481, Table 4) and distilled water are placed in test tubes (T2-19-150XC) in the ratios specified in the standard. A test tube filled with glycerol in the same volume as the reference solution is examined against a background of white paper and the colour of the test glycerol is visually determined to match the colour of the standards. The colour number of glycerol is considered as equal to the colour number of the iodine scale reference solution with the same colour.

The density of glycerol was determined by using the method described in GOST 7482. According to this method, the glycerol sample is placed in a clean, dry cylinder so that the liquid level does not reach the top edge by 3-4 cm, and kept for 20 minutes in an oven at a temperature of 20±1 °C. Then, temperature of glycerol is measured by gently stirring it with a thermometer. Once the glycerol temperature reaches the desired level of 20±1 °C, a dry and clean hydrometer is gently placed into the cylinder. The distance between the lower end of the hydrometer, immersed in the sample, to the bottom of the cylinder, must be of at least 3 cm. The hydrometer should be held until it starts to float freely without making contact with the cylinder's walls or bottom. After immersion according to the division indicated on the hydrometer scale aligned with the bottom of the liquid meniscus, a 3–4-minute countdown is initiated. The arithmetic mean of two parallel measurements are taken as the measurement result, with a permissible absolute discrepancy which should not exceed 0.005 g $cm^{-1}$ with a confidence interval of 0.95.

The ash content of glycerol is determined by using the method described in GOST 7482. According to this method, a sample of glycerol is weighed on a scale into a crucible (only a high crucible may be used), previously calcined to a constant weight. Sample is then carefully heated on an electric stove until the release of vapours stops and the glycerol chars. The

residue undergoes calcination in a muffle furnace at 700±50 °C for 2 hours. Following calcination, the crucible is cooled in a desiccator, weighed, and then returned to the muffle furnace for an additional 30-minute calcination. After the crucible cools, it is weighed again. If a constant mass is attained, the ash mass fraction, in percentage, is determined using the formula outlined in GOST 7482.

The amount of non-volatile organic residues in the glycerol is determined by using the method described in GOST 7482. According to this method, an aliquot of 5±0.5 g of the glycerol sample (either distilled or non-distilled) is placed in a 100 mL volumetric flask and diluted using twice the volume of distilled water. Afterwards, the resulting solution is neutralized with a specified volume of either sodium carbonate (0.1 N) or a hydrochloric acid solution (0.1 N), as outlined in GOST 7482. The volume of the solution is adjusted to 100 ml with distilled water, and an aliquot of 10 ml, measured with a pipette, is transferred to a cup that had been previously dried at 170±2 °C to a constant weight. The cup containing the glycerol solution is placed inside a drying cabinet pre-heated to a temperature of 105-110 °C, on top of an asbestos plate. The cabinet's temperature is then increased to 170±2 °C, and the cup remains there for one hour to evaporate the glycerol to dryness, while ensuring it does not burn by periodically opening the cabinet door for checking status. After evaporation is complete, the cup containing the dry residue is placed in a desiccator and allowed to cool completely. Without weighing, the residue is dissolved in 3-8 cm of water. The cup with the solution is then transferred to the drying cabinet, cooled to 105-110 °C, for evaporation. The temperature is then raised back to 170±2 °C to evaporate the water again. The process of dissolving the residue and evaporating the water is repeated twice. After the second evaporation, the cup with the residue is cooled in a desiccator and weighed. This cycle of dissolution, evaporation, cooling, and weighing is repeated until the weight difference after one hour of drying is no more than 0.001 g. The percentage mass fraction of non-volatile organic residue is calculated using the formula described in GOST 7482.

*Purification of technical (crude) glycerol*

*First step of purification process: acid cleaning*

A 500 ml Erlenmeyer flask was used for the experiment, and 300 g of crude glycerol plus 150 g of phosphoric acid (85%) were added to it. The Erlenmeyer containing the solution was then agitated at a constant speed of 200 rpm and heated at temperature of 75 °C using a magnetic stirrer for 60 minutes. The acid cleaning process of crude glycerol was investigated with variations in pH values (2, 4, 6), process temperatures (20, 40, 60 °C), and reaction durations (20, 40, 60 minutes). The mixture was separated into three layers. The upper layer, which contains fatty acids, was separated by decantation; and the bottom layer, the salt precipitate, was removed by filtration using a 0.45 μm nylon filter. The middle layer containing glycerol was neutralized using 5M NaOH. Salts of mineral and fatty acids formed during the neutralization stage were separated with a 0.45 μm nylon filter.

*Second step of purification process: processing with cationite (ion exchange)*

The glycerol previously cleaned was further purified by ion exchange using cationite. It was placed in a 300 ml glass tube, and purification was achieved by gradually passing glycerol through the cationite. The purity of glycerol is defined by its grade.

Before determining the flow rate of glycerol, its volume is accurately measured. The flow rate is measured according to the decrease in the amount of glycerol in the container per unit of time. A stopwatch is used for this. The flow rate of glycerol is determined by the formula $Q = V \times t^{-1}$ where V is the volume of acid-treated glycerol in a container with a measuring rod, ml; t is the time of releasing glycerol in a container with a measuring rod, minutes.

*Preparation of gingerbread*

Gingerbreads were prepared in laboratory conditions, where part of the sugar was replaced with glycerol in quantities ranging from 1% to 10%. (Standard recipe of gingerbread: wheat flour, sugar, syrup, fat, ammonium carbonate, baking soda, vanillin and water; as shown in Table 2). For preparing gingerbread, the following procedure was used: Hot water at a temperature of 70-80 ºC was poured into a container filled with sugar, corn syrup, glycerol; then heated with constant stirring (30-35 rpm) until the sugar was completely dissolved (60-75 ºC). The prepared syrup and glycerol were poured into a Singer Arcobaleno MP20 dough mixer (Singer, Boston, USA) where the other raw materials according to the recipe were added and mixed at a speed of 150 rpm for 2-4 minutes. Then, chemical baking powder ("Fargonaazot" JSC, Fergana City, Uzbekistan) and flour (first grade wheat flour with a weight content of crude gluten, - 30%, whiteness, c.u. - 36, FN, s- - 186, ash content - 0,73%, moisture, - 14,0%, non-bleached, preservative-free) ("MillMaxGroup" LLC, Tashkent, Uzbekistan) dissolved in water were added. Kneading the dough was continued for 1.5-2 minutes until a homogeneous consistency was obtained (the temperature of the dough was 20 ºC, and the humidity was 24%). The dough was sent to the funnel of the moulding machine and shaped. Moulded pieces of dough were placed on sheets previously greased with vegetable oil. Gingerbread cookies were baked in the

Table 2

**Gingerbread recipes**

| Name | Contents, g kg$^{-1}$ | | Contents, % | |
|---|---|---|---|---|
| | Control | Sample | Control | Sample |
| Wheat flour | 510 | 510 | 51 | 51 |
| Sugar | 216 | 166-211 | 21.6 | 16.6-21.1 |
| Syrup | 110 | 110 | 11 | 11 |
| Oil | 60 | 50 | 6 | 5 |
| Ammonium carbonate | 4 | 4 | 0.4 | 0.4 |
| Baking soda | 1 | 1 | 0.1 | 0.1 |
| Vanillin | 2 | 2 | 0.2 | 0.2 |
| Glycerol | 0 | 10-100 | 0 | 1-10 |
| Water | 97 | 47-92 | 9.7 | 4.7-9.2 |
| Total | 1000 | 1000 | 100 | 100 |

oven for 12–14 minutes at temperatures: zone 1 – at 210 ºC for 4-6 minutes; zone 2 – at 190 ºC for 4-5 minutes; zone 3 – 180 ºC for 3-4 minutes. After baking, the product was cooled to 45-50 ºC for 5-10 minutes and dried for 40-50 minutes on the sheets. Gingerbreads prepared according to each recipe were stored in separate plastic food containers for up to 30 days. Storage conditions included a relative humidity of 75%, a room temperature of 22-23°C, and no direct sunlight.

*Sensory analyses*

The Hedonic test was conducted using 10 points. Thirteen panellists (7 males and 6 females between the ages of 20 and 45, comprising staff and students from the Faculty of Food Products Technology of the TICT) performed the evaluation of the gingerbread samples based on attributes such as hardness, sweetness, consistency, and taste. The evaluations were performed 24 hours after baking. The study adhered to the institute's ethics guidelines, and each panellist provided consent to participate in the research and have their feedback utilized. Criteria for evaluation is as follows: 10-Excellent, 9-Very good, 8-Good, 7-Above Average, 6-Average,5-Below Average, 4-neither good nor poor, 3-Poor, 2-Very poor, 1-Pass, 0-Fail

*Data processing*

Excel from Microsoft 365 (Microsoft, USA) was used for data processing and tabulation. For statistics, several tests were performed, including One-Way Analysis of Variance (ANOVA), Scheffé multiple comparison, Bonferroni and Holm multiple comparison (both "all pairs simultaneously compared" and "only pairs relative to control -0% glycerol-simultaneously compared"), and Tukey's Honestly Significant Difference (HSD) test. Differences between groups (glycerol levels in this case) were considered significant at a 95% confidence level ($p < 0.05$). Statistical analyses were conducted in astatsa.com by Navendu Vasavada (most recent access, May 15, 2024), and in Minitab 21.64 (Minitab LLC, USA).

## Results and Discussion

The physico-chemical properties of glycerol used in the experiments are presented in Table 3. As expected, the amount of glycerol (in %) increases as purification steps are being taken, while the amount of non-volatile, organic residues, and ash content (in %) decrease accordingly. This results are in agreement with reports by Chol and co-workers, where percentage of glycerol incremented from crude (40%) to treated (86.4%) to enriched glycerol (93.7%) (in their case, after membrane filtration, activated charcoal adsorption, and solvent and water evaporation), and ash content reduced from 4.9 to 2.8 to 1.2 % respectively (Chol *et al*., 2018).

Activated carbon effectively removes carotenoids but has limited effectiveness in removing chlorophylls (Tzima, Brunton, & Rai, 2020). This is why activated carbon is commonly used in the bleaching of glycerol. However, the small size of activated carbon particles leads to their loss during filtration, making it necessary to mix them with a filtering additive such as bleaching clay. Despite the high absorption capacity of bleaching clay, it is recommended to minimize its usage during bleaching. To determine the optimal amount of bleaching clay, various mixtures

Table 3

**Physico-chemical properties of glycerol samples used in the experiments**

| Glycerol | Amount of glycerol, % | Ash content, % | Amount of non-volatile organic residues, % | Colour, $J_2$ mg 100 $cm^{-3}$ | Density, g $cm^{-3}$, 20 °C |
|---|---|---|---|---|---|
| Non-distilled | 78.5 | 2.9 | 8.5 | 14 | 1.2032 |
| Non-distilled | 86.4 | 3.1 | 4.5 | 16 | 1.2249 |
| Distilled | 96.3 | 0.8 | 0.2 | 9 | 1.2514 |

of bleaching clay and activated carbon (MA) were prepared in different proportions (refer to Table 1). The bleaching of distilled glycerol was conducted at 80°C using a mixture of the prepared adsorbents, with the adsorbents introduced at a concentration of 0.8% by weight of glycerol. The results of this study can be found in Table 4. According to Table 3, MA-3, MA-4, MA-5, and MA-6 show the greatest effect. This effect is attributed to the ability of adsorbent material (MA) to adsorb the impurities present in the raw materials. The accompanying substances of the oil are adsorbed on the active surface of MA, leading to this observed effect. By using a composition with a ratio of 70:30 (MA-4), the quality standards outlined in GOST 6824 were met. This success can be attributed to the presence of bleaching earth in the mixture, which aids in reducing the colour of glycerol by eliminating residual activated carbon particles. The best outcomes were obtained when using mixtures of activated carbon and clay in a 70:30 ratio. Additionally, the results of the analysis by an FT-IR spectrometer of glycerol purification are presented in Figures 1 and 2.

The IR spectrum of unbleached glycerol is complex due to the multitude of molecular vibrations and rotations that may occur in a substance, which leads to a wide range of absorption frequencies. Therefore, the resulting spectrum is a composite of multiple overlapping peaks, each corresponding to specific vibrational transitions and indicating the presence of various functional groups (Figure 1). The O-H stretching band was observed at 3325.64 $cm^{-1}$, which characterizes the presence of glycerol and water. Band at 1736.58 $cm^{-1}$ is attributed to the presence of C=O of esters in crude glycerol, while the $COO^-$ group showed a peak at 1560.13 $cm^{-1}$, which represents dissolved salts in crude glycerol. Based on the insights from Table 2, it was established that refined glycerol exhibited superior performance in mixtures of activated carbon and clay at a 70:30 ratio (MA-4). The IR spectrum of purified MA-4 glycerol is shown in Figure 2.

Upon examining the IR spectra depicted in Figure 2, as well as Figure 1, a striking similarity is evident. This similarity likely arises from the close

Table 4

**Impact of bleaching clay content on the adsorption purification process of glycerol**

| Code name | Colour mg $J_2$ 100 $cm^{-3}$ | Density, g $cm^{-3}$, 20 °C | Amount of glycerol, % | Ash content, % |
|---|---|---|---|---|
| MA-1 | 6 | 1.2514 | 96.3 | 0.21 |
| MA-2 | 6 | 1.2516 | 96.4 | 0.20 |
| MA-3 | 5 | 1.2548 | 97.6 | 0.18 |
| MA-4 | 5 | 1.2563 | 98.2 | 0.16 |
| MA-5 | 5 | 1.2540 | 97.3 | 0.15 |
| MA-6 | 6 | 1.2519 | 96.5 | 0.18 |
| MA-7 | 7 | 1.2493 | 95.5 | 0.20 |
| MA-8 | 7 | 1.2490 | 95.4 | 0.22 |
| MA-9 | 8 | 1.2485 | 95.2 | 0.24 |
| MA-10 | 8 | 1.2483 | 95.1 | 0.26 |
| MA-11 | 8 | 1.2480 | 95.0 | 0.26 |

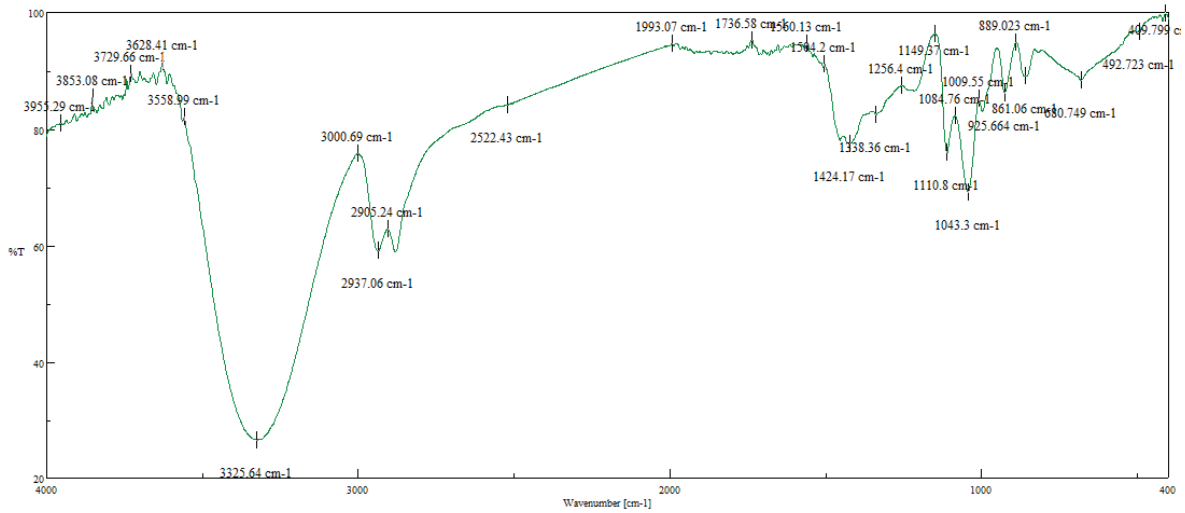


Figure 1. IR spectrum of unbleached distilled glycerol.

resemblance in quality parameters between impurified and purified glycerol. By analysing the IR spectrum MA-4 glycerol, there is an O-H stretching band at 3338.15 $cm^{-1}$, while C-H stretching was identified in the 2800-2950 $cm^{-1}$ region. The C=O stretching band, present in unbleached glycerol at 1736.58 $cm^{-1}$, was absent in the spectra of eluted glycerol. Additionally, bands above 3600 $cm^{-1}$ were no longer observable, indicating the purification of the phenolic group of substances in refined glycerol.

In today's context, there is a shift towards more cost-effective methods as energy-intensive technologies are being phased out. Given the high energy demand of glycerol distillation, research has focused on purifying technical glycerol through ion exchange methods to obtain high-quality glycerol. The process involves purifying glycerol derived from cotton wool to eliminate fatty acids, reduce water content, and yield technical glycerol. This technical glycerol contains metal salts that diminish its quality and elevate ash content. Treatment with phosphoric acid is employed to disintegrate salts and bind fabrics.

The impact of the different technological parameters on the treatment of technical glycerol with $H_3PO_4$ was investigated, with variations in pH values (2, 4, 6), process temperatures (20, 40, 60 °C), and reaction durations (20, 40, 60 minutes). The outcomes of this study are detailed in Table 5.

The data presented in Table 3 highlights that the primary factor influencing the acid treatment process and product quality is pH, followed by temperature and process duration. The findings indicate that pH plays a crucial role not only in the acid treatment process but also in the quality of the resulting product. Optimal outcomes were observed at a pH of 2, a temperature of 70°C, and a process duration exceeding 40 minutes.

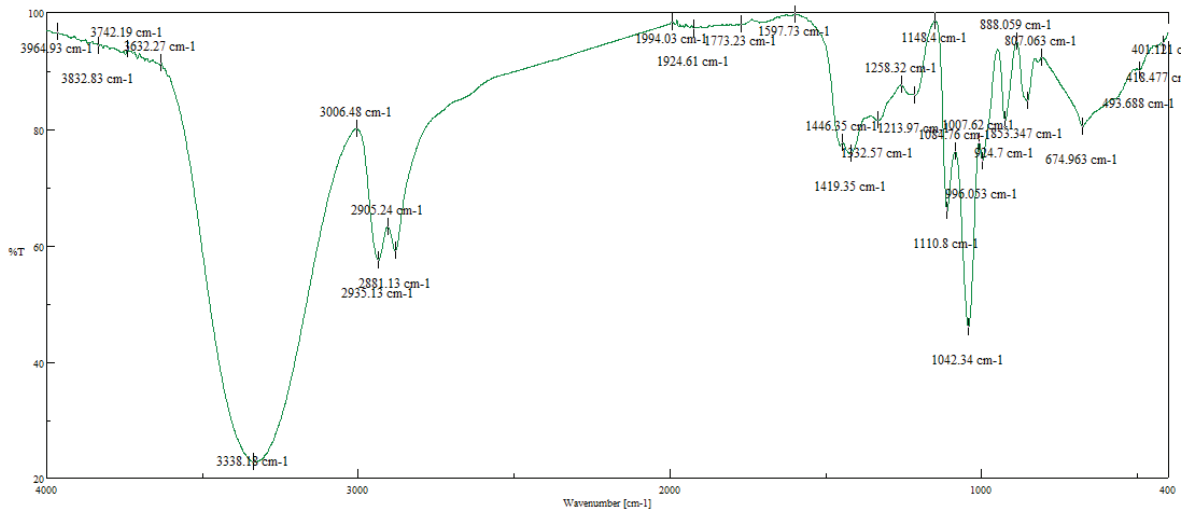


Figure 2. IR spectrum of distilled glycerol purified with MA-4.

Table 5

**Impact of process parameters in the treatment of technical glycerol with $H_3PO_4$ on the variation of glycerol concentration**

| Procedure duration, minutes | Process temperature, pH and glycerol concentration (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | pH=2 | | | pH=4 | | | pH=6 | | |
| | 30°C | 50°C | 70°C | 30°C | 50°C | 70°C | 30°C | 50°C | 70°C |
| 20 | 83.1 | 85.0 | 86.2 | 82.5 | 83.6 | 84.5 | 79.2 | 79.5 | 81.4 |
| 40 | 84.5 | 86.1 | 88.37 | 83.6 | 85 | 85.8 | 81.0 | 82.0 | 83.5 |
| 60 | 85.2 | 86.5 | 88.3 | 84.5 | 85.5 | 86 | 82.5 | 83 | 84.2 |

Table 6

**Impact of process parameters in the treatment of acid-treated glycerol with cationite on the variation of glycerol concentration**

| Amount of cationite, g | Flow rate of glycerol entering the process (ml $min^{-1}$) and concentration of glycerol at the exit (%) | | |
|---|---|---|---|
| | 20 | 40 | 60 |
| 20 | 89.25 | 88.13 | 87.04 |
| 40 | 97.02 | 93.65 | 91.84 |
| 60 | 97.36 | 94.89 | 92.47 |

In order to enhance the colour of glycerol and reduce its ash content, the metal salts within it are removed with cationite. In this process, cations within the cationite absorb the metal ions, extracting them from the glycerol composition. The acid-treated glycerol underwent filtration through a cationite bed, with a pump used to circulate the glycerol. This procedure was conducted at a temperature of 25°C, with glycerol flow rates set at 20, 40, and 60 ml $min^{-1}$, and cationite amounts ranging from 20 to 60 g. The results obtained from this process are detailed in Table 6.

Analysing the data presented in Table 6 reveals that the primary factors influencing the purification process quality and the product quality of glycerol pre-treated with phosphoric acid are the amount of cationite and the flow rate of glycerol. The experimental results indicate that the purity of the extracted glycerol is inversely proportional to the flow rate of glycerol and directly proportional to the amount of cationite. An increase in the cationite amount from 20 g to 60 g led to a rise in glycerol purity from 89% to 97%. Nevertheless, this increase varied based on the glycerol flow rate. When the glycerol flow rate increased from 20 ml $min^{-1}$ to 60 ml $min^{-1}$ (using 20 g of cationite), the purity of the extracted glycerol decreased from 89% to 87%. In conclusion, the optimal amount of cationite for purifying phosphoric acid-treated glycerol through the ion exchange method was determined to be 40 g, with a glycerol flow rate of 20 ml $min^{-1}$.

Following treatment with phosphoric acid and cationite, the obtained glycerol appeared clear and highly concentrated, yet exhibited a light-yellow colour with a greenish hue, impacting its sensory attributes. To address this, the glycerol was whitened using a blend of activated carbon and clay. The quality of the resulting glycerol was further assessed through chromatographic analysis.

In preparation for the chromatographic analysis of the purified glycerol, a glycerol standard was initially examined, with the resulting chromatogram depicted in Figure 3.

The chromatogram depicted in Figure 3 shows the glycerol peak at 1.728 min. The peak's width spans from 1.631 minutes to 4.270 minutes. By calculating the surface area of the triangle formed by the peak, the glycerol amount was determined to be 99.43.

Subsequently, the purified glycerol treated with activated carbon underwent further analysis. The resulting chromatogram is illustrated in Figure 4.

The chromatogram depicted in Figure 4 illustrates the presence of the glycerol peak at 1.694 min. The width of the peak ranges from 1.631 minutes to 3.589 minutes. By calculating the surface area of the triangle formed by the peak, the determined value for the glycerol amount was 97.04%. Subsequent to this analysis, bleached glycerol treated with bleaching clay was subjected to testing. The resulting chromatogram is displayed in Figure 5.

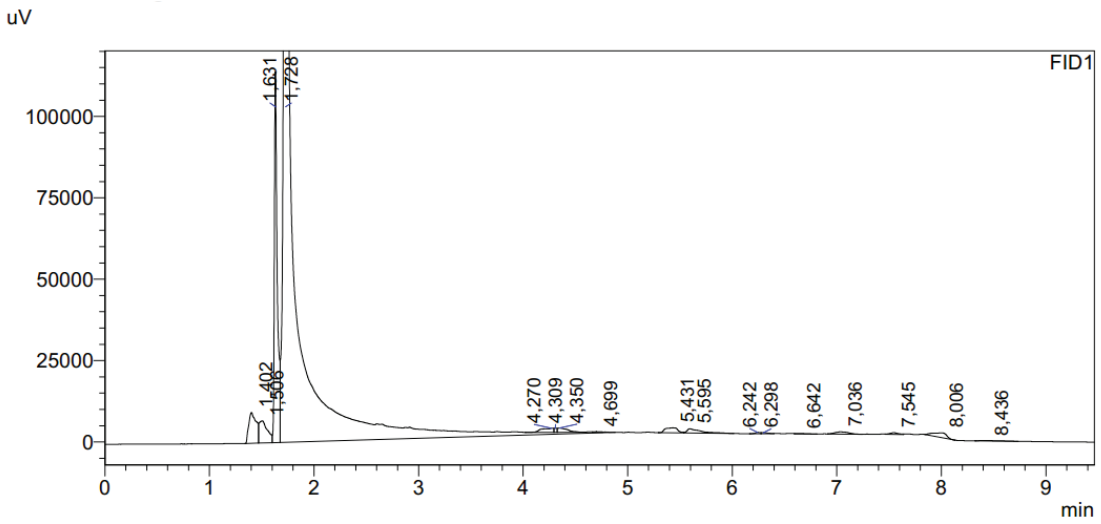


Figure 3. Chromatogram of glycerol standard.

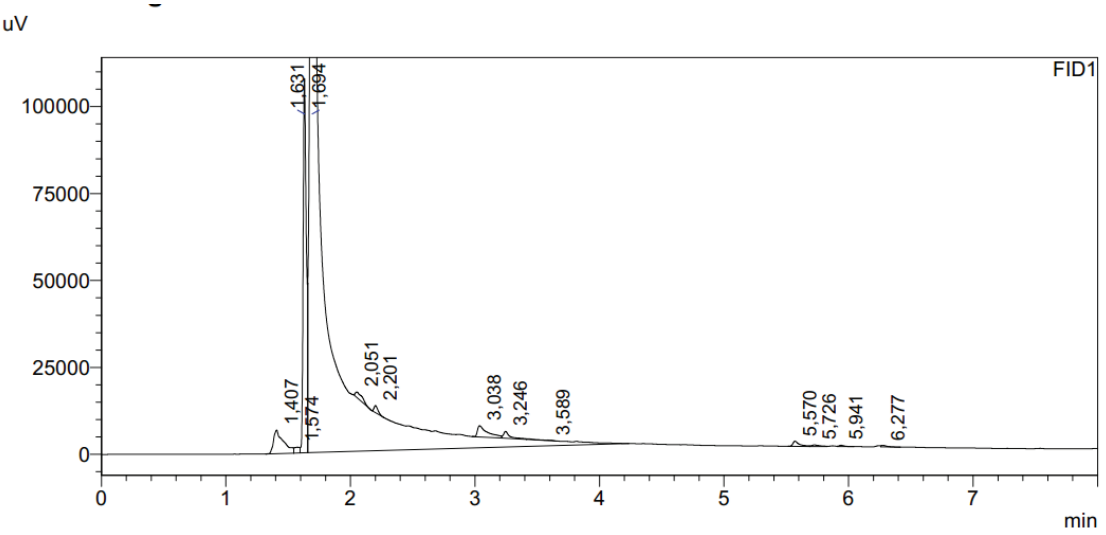


Figure 4. Chromatogram of glycerol eluted with activated carbon.

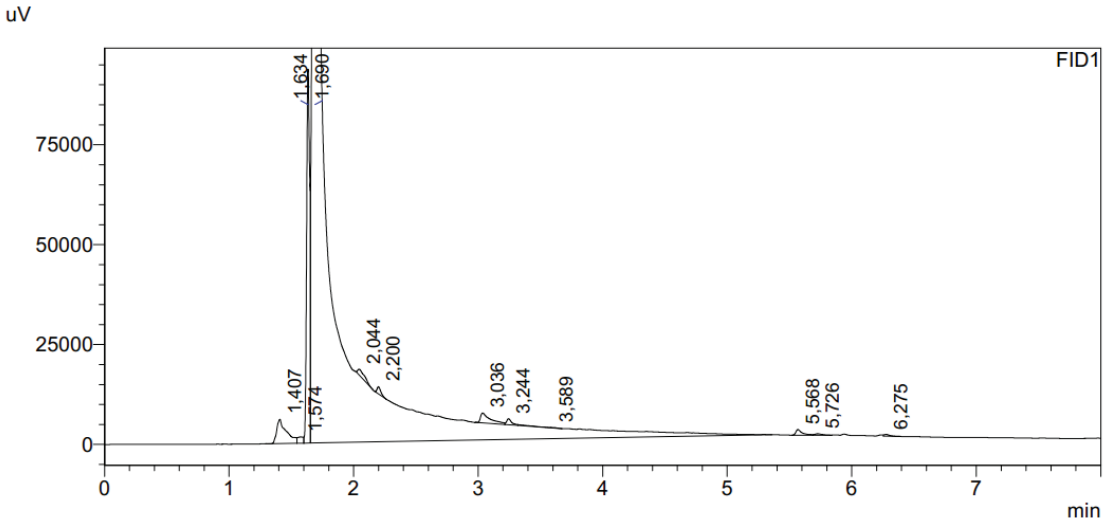


Figure 5. Chromatogram of glycerol bleached with bleaching clay.

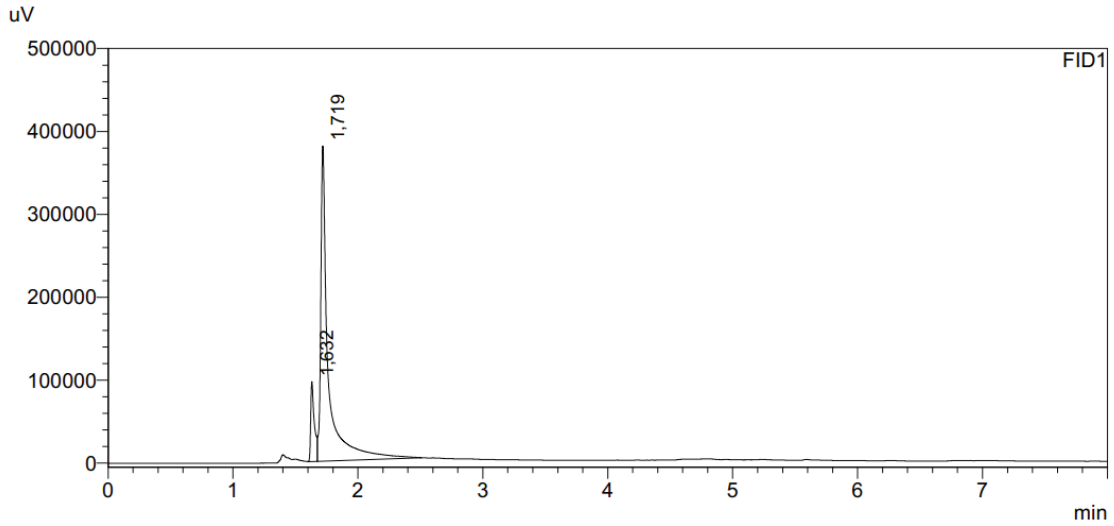


Figure 6. Chromatogram of glycerol bleached with 30:70 mixture of activated carbon and bleaching earth (MA-4).

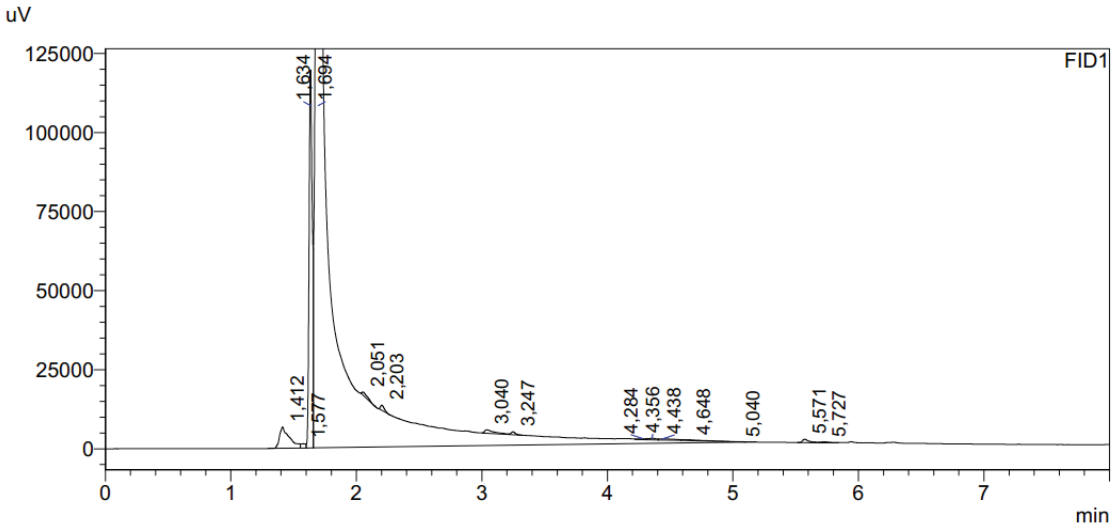


Figure 7. Chromatogram of unbleached glycerol.

In the next analysis, bleached glycerol was tested using a 30:70 mixture of activated carbon and bleaching clay (MA-4 in Table 2). The resulting chromatogram is shown in Figure 6.

The chromatogram shown in Figure 6 indicates the presence of the glycerol peak at 1.719 minutes. The peak width ranges from 1.632 minutes to 2.210 minutes. By calculating the surface area of the triangle formed by the peak, the determined value for the glycerol amount was 98.09.

To facilitate a comparison with the chromatogram results of the purified glycerol discussed earlier, a chromatogram of unrefined glycerol was obtained. The resulting chromatogram is displayed in Figure 7.

The chromatogram displayed in Figure 7 reveals the presence of the glycerol peak at 1.694 minutes. The width of the peak spans from 1.634 minutes to 4.438 minutes. By calculating the surface area of the triangle formed by the peak, the determined value for the glycerol amount was 97.26%.

To assess the efficacy of the performed experiments, raw glycerol, acid-treated glycerol, and cationite-treated glycerol's physico-chemical parameters were analysed and compared. These comparative results are detailed in Table 7.

Table 7 illustrates that technical glycerol comprises 78.5% glycerol, with elevated levels of ash content, moisture, and mass percentages of volatile substances and non-volatile organic residues. Following treatment with $H_3PO_4$ and cationite, the glycerol content increased from 78.5% to 97.3%, while the mass fraction of moisture and volatile matter

Table 7

**Physico-chemical parameters of crude glycerol, acid-treated and cationite-treated glycerol**

| Indicator name | Distilled glycerol (control) | Initial technical glycerol | Treated with cationite | Bleached with adsorbent |
|---|---|---|---|---|
| Mass fraction of glycerol, % | 96.3 | 78.5 | 97.3 | 98.1 |
| Mass percentage of moisture and volatile substances, % | 2.7 | 4.1 | 1.4 | 1.7 |
| Ash content, % | 0.8 | 6.9 | 0.1 | 0.1 |
| Colour, mg $J_2$ $cm^{-3}$ | Colourless | Brown | Yellow | Colourless |
| Clarity | Dim | Dim | Clear | Clear |
| Amount of non-volatile organic residue, % | 0.2 | 10.5 | 1.2 | 0.1 |

decreased from 2.1% to 1.4%. Additionally, the ash content decreased from 8.9% to 0.1%, and the non-volatile organic residue amount reduced from 10.5% to 1.2%. Further purification with adsorbents led to enhanced physico-chemical parameters of glycerol, with the glycerol amount rising to 98.1%, the mass percentage of moisture and volatile substances decreasing to 1.7%, and the ash and non-volatile organic residue amounts decreasing to 0.1%.

Gingerbreads are a popular confectionery item in Uzbekistan, primarily composed of flour, oil, water, and sugar. These treats tend to harden rapidly if left unpacked. In a research endeavour aimed at maintaining the quality of gingerbread during its shelf life, investigations were carried out to incorporate glycerol into the recipe. This involved altering the proportions of sugar and water in the recipe and adding glycerol in quantities ranging from 1% to 10%. The resulting recipe is outlined in Table 2 in Materials and Methods section.

Using the formulations outlined in Table 6, unglazed gingerbreads were prepared, stored for 24 hours, and subjected to sensory analyses evaluation. The evaluation was conducted using a 10-point system, and the results obtained are depicted in Figure 8.

The incorporation of glycerol in gingerbread impacts its hardness, taste, sweetness, and consistency (Figure 8), albeit no statistical significance was achieved due to differences in glycerol percentage in any of the performed tests. p-value was higher than 0.05 in all the tests performed. For One-Way Analysis of Variance (ANOVA), p= 0.9564; for Scheffé multiple comparison, the smaller p-value is p=0.9837529 (for 4% vs 10% of glycerol) (p-values

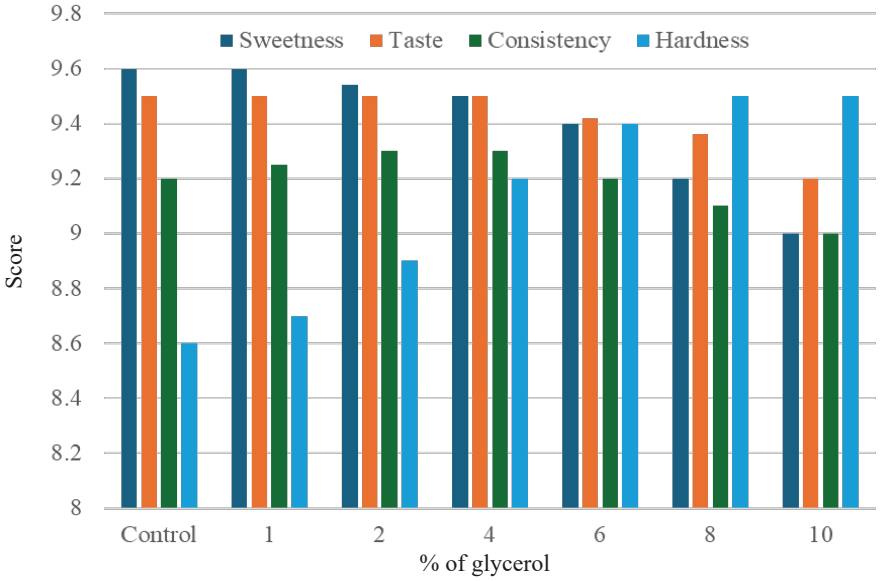


Figure 8. Effect of glycerol content on sensory properties of gingerbread.

for other pairs are higher); for Bonferroni and Holm, the smaller Holm p-value is p=0.9220311 (for 4% vs 6% glycerol levels); and in Tukey's HSD, p-value is p= 0.8999947. Nevertheless, based on the information depicted in Figure 8, it may be observed that with an increase in glycerol content from 1% to 5%, there was minimal change in the taste, sweetness, and consistency of gingerbread, while a further increase from 5% to 10% led to a higher decrease in these properties. The perceived softness of the gingerbread improved across all glycerol levels, attributed to the reduced sugar and water content in the recipe. The initial taste and sweetness in gingerbread was not affected by a slight reduction in sugar content, since it was compensated by the sweetness of glycerol. As sugar content decreased further, the added glycerol also compensated for the sweetness. In the case of control gingerbread, perceived hardness increased during prolonged storage (30 days) (data not shown). Therefore, based on the findings, it was concluded that adding up to 5% glycerol to the gingerbread recipe is recommended to improve its quality.

## Conclusions

The objective of this study was to improve the glycerol purification process to achieve higher quality glycerol, obtained from cottonseed oil, without the need for distillation. Various combinations of activated carbon and bleaching clay were examined, revealing that a 70:30 ratio produced the best results in terms of glycerol quantity, colour, and ash content. Key technological parameters such as reaction time, pH, and process temperature were also analysed. The findings indicated that optimal conditions included a processing time of over 40 minutes, a pH of 2, and a temperature of 70 °C. Additionally, it was found that the concentration and quality of glycerol obtained from cottonseed oil could be improved through purification using cationite. Furthermore, different glycerol concentrations were tested in gingerbread production, concluding that incorporating 5% of the glycerol into the gingerbread recipe could enhance its quality preservation throughout its shelf life.

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