Changes in the Quality and Oxidation Indices of Cow's and Buffaloe's Butter During Cold Storage

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Abstract: Butter fat undergoes oxidation process, causing a sequence of unfavorable steps changes causing its deterioration with inferior sensory properties and decrease in nutritious value. Several factors affect the quality and oxidation process such as storage conditions, acidity of cream and the type of milk fat. The aim of this study was to assess the changes in quality characteristics and oxidation process in both cow's and buffaloe's butter made from sweet or sour cream stored at 5 °C compared with traditionally stored at -20 °C. It was found that butter stored at 5 °C increased the oxidation process expressed as peroxide value, thiobarbaturic acid reactive substances, as well as raised the fat acidity and refractive index with higher decreasing rate for iodine values. Butter made from sour cream accelerated the oxidation process and decreased its quality properties than that made from sweet cream. Generally, cow's butter had higher oxidation rate than that of buffaloe's butter.

Keywords: Butter; Keeping quality; Oxidation, Sour butter, Sweet butter, Cow's butter; Buffaloe's butter.

INTRODUCTION

Butter is one of the dairy products has quite large area of use. The annual world production of butter at 2013 rose to be 10.375 million ton. The top producers of butter are New Zealand, European Union, United States (FAO, 2016). In Egyptian Food standards, butter is defined as a product made from milk or cream, which most of the water and fat-free dry matter are removed, with a minimum of 80% fat, solids not fat 2% as maximum and 16% water as maximum (ESO, 2005). Butter is rich in terms of aroma such that can't be compared with other fats (German and Dillard, 1998; Tekinşen, 2000).

Butter fat can undergoes oxidation process, through several steps leading to its deterioration with inferior sensory properties and decrease in its nutritious value (Gray, 1978). Autoxidation is a free radical chain reaction, leading to increase the reactive radicals and hydroperoxides, which initiate further transmutations (Frankel, 1985). Interest in the changes which occur in butter during storage periods has been arisen with attempts to preserve this product in large quantities for longer storage period. Investigators have made many observations of the types of change that appear in butter during storage and of conditions which might be correlated with them. The influence of air, light, temperature of storage, acidity of the cream at time of churning, ferments and enzymes, salt, metals as catalytic oxidizing agents, and organic compounds as inhibitors of oxidation have all been studied (Krause et al., 2008; Najgebauer-Lejko et al., 2009; Flavia et al., 2014; Zaptalov et al., 2015).

Butter keeping quality and physical stability during transport and storage is dependent on the temperature distribution through product's transport. Understanding the changes which correlated to storage temperature is vital importance for the dairy industry with regard to butter manufacture, storage and handling conditions. Frozen storage of butter helps to maximize its keeping quality due to minimization of oxidation and microbial spoilage and also increases product rigidity. In some cases, in order to meet customer requirements or decreasing cost of transportation, the product is then raised from frozen to chilled temperatures prior to marketing.

The aim of this study was to assess the changes in quality characteristics and oxidation process in both cow's and buffaloe's butter made from sweet and sour cream stored at 5 °C compared to traditionally stored at -20 °C.

MATERIALS AND METHODS

Materials:

Standardized cow's and buffaloe's cream (35% fat) was obtained from Dairy processing center, Dairy department, Faculty of Agriculture, Suez Canal University, Ismailia governorate, Egypt. Butter starter culture FD-DVS Flora Danica starter is multiple mixed strains which consist of *Lactococcus lactis* ssp. *lactis*, *Lactococcus lactis* ssp. *lactis*, *Lactococcus lactis* ssp. *cremoris*, *Leuconostoc mesentroids* ssp. *mesentroids*, *Leuconostoc mesentroids* ssp. *cremoris* and *Lactococcus lactis* ssp. *lactis biovar diacetilactis*. This culture was obtained from CHR-Hansen's laboratories, Denmark.

Methods:

The fat content and titratable acidity of cream were determined according to the methods described by AOAC (2000). Butter was analyzed for moisture, fat, solids not fat and iodine value according to the methods described by AOAC (2000). Butter serum was obtained by melting butter at 40-45 °C and removing the butter fat. The pH of butter serum was measured using pH meter, Jenway 3505, Italy. Peroxide value expressed as mleq. O_2/kg butter was determined according the method described by AOCS (1990). Thiobarbaturic acid reactive substances (TBARS) value was determined according to methods described by Kuruppu *et al.* (1983). The refractive index of clear butter fat obtained by melting butter at 40-45 °C using PAL-refractometer (Tokyo, Japan).

Butter samples were melted using a thermostatically controlled oven adjusted at 45-50 °C. The fat in upper layer was filtered. The clear fat was

used to determine fat acidity expressed as oleic acid %. Butter fat was neutralized with alcoholic potassium hydroxide 0.1 N, using phenolphthalein, as an indicator. Acid degree values were calculated as described by ESO (2005). All obtained data were done in trireplicates, and analysis of variance with two factorial (treatments and storage period) were conducted by the procedure of General Linear Model (GLM) according to Snedcor and Cochran (1967) using Costat under windows software version 6.311 and least significant difference test were employed to determine significant difference at p < 0.01.

Butter making:

Butter was made according to the following diagram:-

Cream 35 % fat Butter Pasteursation (85 °C/1 min) Work Cool to 25 °C Washig with tab water Starter addition (50 units/ton for 120 min) (in case of producing sour butter till 0.18% as lactic acid) Cold storage of cream — Churning (14-16 °C)

Experiments:

Cow's or buffaloe's butter was manufactured from sweet and sour cream. Six treatments of cow's or buffaloe's butter were carried out as follows: treatment I: sweet cow's butter stored at -20 °C served as control, treatment II: sweet cow's butter stored at 5 °C, treatment III: sour cow's butter stored at 5 °C made from cultured cream to 0.18% as lactic acid, treatment IV: sweet buffaloe's butter stored at -20 °C served as control, treatment V: sweet buffaloe's butter stored at 5 °C made from cultured cream to 0.18% as lactic acid. Butter stored at 5 °C made from cultured cream to 0.18% as lactic acid. Butter from the different treatments was stored for 150 days.

RESULTS AND DISCUSSIONS

Chemical composition of butter:

Table (1) shows the chemical composition of different butter samples. It was found that all butter samples were characterized with the fat, water and solids not fat contents which met the Egyptian standard requirements for unsalted butter: fat content > 80%. water content \leq 16% and solids not fat \leq 2% (ESO, 2005). There were no significant (p < 0.01) differences between treatments in moisture, fat and solids not fat contents. So, it can be said that, using cow's or buffaloe's cream whatever sweet or sour type at 0.18% lactic acid had no significant effect on the chemical composition of butter samples. Similar findings were reported by Mehanna (1973). The obtained results are in accordance with those reported by Baer et al. (2001) who reported that total solid content was found to be 83% for the butter containing 81% fat.

| Table (1): Chemical composition of different fresh butter samples (average of three replicates) |
|---|
|---|

| Tuestment | Chemical composition | | | | | |
|-----------|----------------------|----------|---------|--|--|--|
| Treatment | Moisture | Fat | SNF | | | |
| Ι | 15.14 bc | 83.50 ab | 1.36 d* | | | |
| II | 15.10 c | 83.60 a | 1.30 f | | | |
| III | 15.20 abc | 83.40 bc | 1.40 b | | | |
| IV | 15.25 abc | 83.30 c | 1.45 a | | | |
| V | 15.33 ab | 83.30 c | 1.37 c | | | |
| VI | 15.40 a | 83.25 c | 1.35 e | | | |

* a, b and c: means with the same letter among the treatments are not significantly different (p<0.01).

Treatment I: sweet cow's butter stored at -20 °C served as control.

Treatment II: sweet cow's butter stored at 5 °C.

Treatment III: sour cow's butter stored at 5 °C.

Treatment IV: sweet buffaloe's butter stored at -20 °C served as control.

Treatment V: sweet buffaloe's butter stored at 5 °C.

Treatment VI: sour buffaloe's butter stored at 5 °C.

Peroxide value:

Table (2) illustrates the changes in the peroxide values expressed as meq oxygen /kg butter of samples as affected by using sweet or sour of cow's and buffaloe's cream to make butter during storage at 5 °C and -20 °C. Peroxide value is an index of the initial stages of oxidative changes for butter referring to concentration of hydroperoxide (Riuz *et al.*, 2001). It is

found that storage of butter at 5 °C (treatments II and V) increased significantly (p<0.01) the peroxide values than those of treatments I and IV stored at -20 °C. Several researches have shown that the oxidation rate increases with increased storage temperature. The stored butter at 10 °C increased the peroxide values above 2 meq oxygen/kg are considered unacceptable (Wade *et al.* 1986; Chehade *et al.* 1990). So, increasing the

storage temperature to 5 $^{\circ}$ C significantly shortened the shelf-life of butter to less than 60 days instead of 150 days.

Butter made from sour cream (treatments III and VI) had significantly higher (p<0.01) peroxide values during the storage period than those made from sweet cream stored at 5 °C (treatments II and V). Similar finding for higher oxidation parameters of butter made from sour cream by Mehanna, 1973. Walstra *et al.* (2005) reported that butter from sour cream exhibited higher autoxidation rate than that from sweet cream.

Butter made from cow's cream had significantly higher peroxide values than those values of butter made from buffaloe's (Table 2). This may be due to the higher unsaturated fatty acids of cow's fat which causes a higher oxidation rate. Soliman and Mohamed (1979) reported that buffaloe's milk fat had lower contents of unsaturated fatty acids especially, polyunstrated fatty acids than the cow's milk fat.

Thiobarbaturic acid reactive substances values (TBARS):

The changes in the thiobarbaturic acid reactive substances (TBARS) values expressed as mg malonaldehyde /kg butter of samples as affected by using sweet or sour of cow's and buffaloe's cream to make butter during storage at 5 °C and -20 °C are shown in Table (2). TBARS measures the concentration of secondary oxidation products such as aldehydes, mainly malondialdehyde and ketones (Farag *et al.*, 1990).

It was noticed that increasing the storage temperature to 5 °C (treatments II and V) increased significantly (p<0.01) its TBARS values than those of control which stored at -20 °C (treatments I and IV). Prasad and Gupta (1982) found that as higher storage temperature of butter as more oxidized the fat rapidly causing higher TBARS values. Similar findings were noticed by Ozturk and Cakmakci (2006). So, increasing the storage temperature of butter to 5 °C significantly shortened the shelf-life of butter sample to less than 60 days instead of 150 days.

Butter made from sour cream (treatments III and VI) had significantly higher (p<0.01) TBARS values during the storage period than those treatments made from sweet cream stored at 5 °C (treatments II and V). Similar finding were reported by Mehanna (1973) and Walstra *et al.* (2005). Butter made from cow's cream had significantly higher TBARS than those treatments of butter made from buffaloe's cream. This may be due to the higher unsaturated fatty acids of cow's fat which causes a higher oxidation rate.

| Description | Treatment | Storage periods (days) | | | | | LCD | |
|---|-----------|------------------------|-------|-------|-------|-------|-------|-------|
| Parameters | | 1 | 30 | 60 | 90 | 120 | 150 | - LSD |
| Peroxide value (expressed as mleq. O ₂ /kg butter) | Ι | 0.102 | 0.124 | 0.150 | 0.181 | 0.213 | 0.255 | C* |
| | II | 0.105 | 0.479 | 0.843 | - | - | - | А |
| | III | 0.115 | 0.575 | - | - | - | - | Е |
| | IV | 0.096 | 0.119 | 0.141 | 0.166 | 0.198 | 0.236 | D |
| | V | 0.100 | 0.439 | 0.799 | - | - | - | В |
| | VI | 0.108 | 0.507 | - | - | - | - | F |
| | LSD | С | А | В | F | Е | D | |
| TBARS (mg malonaldehyde /kg butter fat) | Ι | 0.09 | 0.11 | 0.13 | 0.16 | 0.19 | 0.23 | А |
| | II | 0.09 | 0. 23 | 0.44 | - | - | - | С |
| | III | 0.13 | 0.46 | - | - | - | - | Е |
| | IV | 0.08 | 0.10 | 0.12 | 0.14 | 0.17 | 0.20 | В |
| | V | 0.08 | 0. 22 | 0.40 | - | - | - | D |
| | VI | 0.13 | 0.44 | - | - | - | - | F |
| | LSD | С | А | В | F | Е | D | |

Table (2): Effect of using cow's and buffaloe's sweet or sour cream to make butter on peroxide values and thiobarbaturic reactive substances (TBARS) during storage at different temperatures (average of three replicates)

* A, B, C, D, E and F: means with the same letter among the treatments or ripening period are not significantly different (p<0.01)

Milk fat acidity as acid degree values:

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The changes in acid degree values of butter samples as affected by using sweet or sour of cow's and buffaloe's cream to make butter during storage at 5 °C and -20 °C are illustrated in Figure (1). Acid degree values of all treatments showed a gradual increase during butter storage may be due to the growth of psychrophilic lipolytic microorganisms in butter stored at 5 °C and activity of lipolytic enzymes which causes a gradual hydrolysis of milk fat (Nadeem *et al.*, 2013).

Results referred to that frozen butter (treatments I and IV) had significantly lower acid degree values than those stored at 5 °C (treatments II and V). This may be due to the bacterial lipase which causes a gradual

lipolysis of triglycerides. Also, suitability of butter stored at 5 °C to psychrophilic lipolytic microorganisms (Nadeem *et al.*, 2013). Similar findings were reported for increasing acid degree of butter with increasing the storage temperature (Shaheen *et al.*, 2010).

Butter made from sour cream (treatments III and VI) had significantly higher acid degree than those made from sweet cream (treatments II and V) during storage at 5 °C. Walstra *et al.* (2005) said that the lower pH of butter caused less disassociation of the free fatty acids; the acidity of fat is somewhat increased by churning at lower pH value. So, butter from sour cream will contain higher acid degree values.

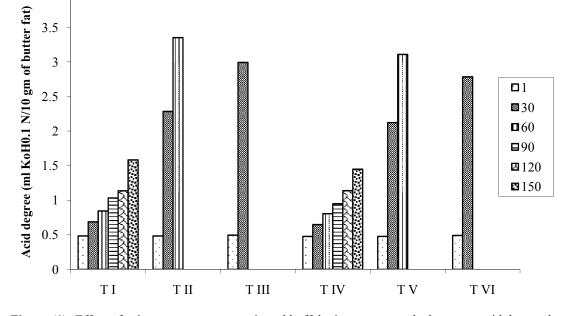


Figure (1): Effect of using sweet or sour cow's and buffaloe's cream to make butter on acid degree during storage at different temperatures (average of three replicates)

The pH of butter serum:

The changes in the pH of butter serum of samples as affected by using sweet or sour of cow's and buffaloe's cream to make butter during storage at 5 °C and -20 °C are presented in Figure (2). The pH of butter serum indicates that total acidity presented mainly by microbial growth and activity. Generally, the pH of butter serum for all treatments gradually decreased during storage. This decrease can be attributed mainly to the changes of lactose to lactate by the microbial fermentation process. These results are in accordance with the results reported by Najgebauer-Lejko *et al.* (2009).

Frozen storage at -20 °C (treatments I and IV) of butter had significantly (p<0.01) higher pH of butter serum than those stored at 5 °C (treatments II and V) during the same storage period. This may be due to the suitability of butter stored at 5 °C to psychrophilic microorganism growth (Nadeem *et al.*, 2013).

Butter made from sour cream (treatments III and VI) had significantly (p<0.01) lower pH of butter serum than that made from sweet cream (treatments II and V) may be due the ripening step of cream which increased

the bacterial growth and consequently initiated the fat lipolysis.

Refractive index:

Table (3) illustrates the changes in the refractive index values of butter samples as affected by using sweet or sour of cow's and buffaloe's cream to make butter during storage at different temperatures. Refractive index is a traditional test of milk fat in order to assess their authenticity. ESO (2005) for buffaloe's butter specify that the refractive index should be within the range of 1.4525-1.4552. All the obtained results were in accordance with the standards. Generally, all values of refractive indices were tended to increase during storage due to autoxidation. This may be due to both hydroperoxide formations in the secondary stage, and polymerization of partially oxidized fats in the tertiary state of autoxidation (Schultz *et al.*, 1962).

Refractive index of butter stored at 5°C (treatments II and V) were higher than that frozen butter stored at -20 °C (treatments I and IV). Similar results were found by Flavia *et al.* (2014). This may be due to the effect of storage temperature on oxidation rate.

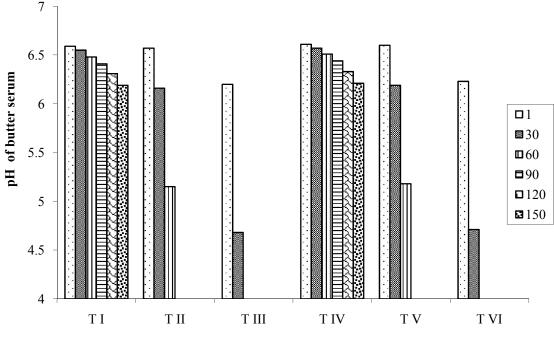


Figure (2): Effect of using sweet or sour cow's and buffaloe's cream to make butter on pH values of butter serum during storage at different temperatures (average of three replicates

Butter made from sour cream (treatments III and VI) had significantly higher refractive indices during the storage period than those made from sweet cream stored at 5 °C (treatments II and V). This may be correlated to higher oxidation rate of sour butter which presented in Table (2) for peroxide value and thiobarbaturic acid reactive substances. Walstra *et al.* (2005) reported that butter from sour cream is much more affected by autoxidation than that from sweet cream.

Generally, cow's butter had lower refractive index values than that of buffaloe's butter. Soliman and Mohamed (1979) reported that buffaloe's milk fat has lower contents of unsaturated fatty acids especially, polyunsaturated fatty acids than the cow's milk fat, which may be explain the previous finding.

The obtained results showed a direct relationship between refractive index and deterioration of fats and oil. Also, refractive indices of fats and oils have been reported to increase on autoxidation (Ayra *et al.*, 1969). Comparatively changes in refractive indices were not significant during the induction period. Thereafter in all the samples there was a sharp increase for these values with progressing the storage period.

Iodine number values:

Table (3) shows that iodine value of all treatments decreased during the storage period. The decline in iodine value may be due to the saturation of some double and triple bonds with oxygen, which resulted in lower iodine absorption sites on the fatty acid moiety (Nadeem *et al.*, 2013). Hussain *et al.* (2011) characterised the samples of butter collected from the market of Lahore and found iodine value in the range of 34-42. The iodine value of rancid fats is lower than that of fresh fats.

ESO (2005) for buffaloe's butter specify that iodine value ranged from 24.1 to 42 while the

comparable iodine value for cow's butter ranged between 26.4-43.1. All the obtained results were in accordance with the standards. It was noticed that the iodine value decreased with oxidation. This gave rise to the belief that oxygen was adding to the double bond and forming moloxides or dioxetane rings (Hammond and White, 2011). In addition to that, many of these observations were undoubtedly caused by conjugation of the double bonds of polyunsaturated fatty acid during oxidation.

From the obtained results, it was found that sweet butter stored at 5 °C (treatments II and V) as well as butter made from sour cream (treatments III and VI) significantly decreased the iodine values during the storage period as compared to control one which stored at -20 °C (treatments I and IV). This can be explained by storage temperature and sour butter had significant effect on primary oxidation process expressed as peroxide values as well as secondary oxidation process expressed as thiobarbaturic acid reactive substances (TBARS) consequently the iodine values will decrease.

Generally, it was noticed that iodine values of cow's butter were significantly higher than that of buffalo's butter. Similar findings were reported by Kumar *et al.* (2014) for ghee made from cow's or buffaloe's butter.

From the foregoing results, the keeping quality butter is dependent on the chemical changes that would take place during chilled or frozen storage. It can be concluded that the oxidation rate increased by storage at 5°C than that traditionally stored at -20 °C. Butter made from sour cream increased both acid degree and oxidation indices. Also, milk fat type had a significant effect on the rate of hydrolysis, oxidation and decreasing the shelf life of cold stored butter to 30 days only while the freeze stored butter has a good keeping quality through 150 days of storage.

| D (| | Storage periods (days) | | | | | LCD | |
|------------------|-----------|------------------------|--------|--------|--------|--------|--------|-------|
| Parameters | Treatment | 1 | 30 | 60 | 90 | 120 | 150 | - LSD |
| Refractive index | Ι | 1.4529 | 1.4530 | 1.4532 | 1.4534 | 1.4535 | 1.4536 | B* |
| | II | 1.4529 | 1.4533 | 1.4539 | - | - | - | D |
| | III | 1.4530 | 1.4542 | - | - | - | - | F |
| | IV | 1.4532 | 1.4533 | 1.4535 | 1.4537 | 1.4538 | 1.4539 | А |
| | V | 1.4532 | 1.4535 | 1.4543 | - | - | - | С |
| | VI | 1.4531 | 1.4548 | - | - | - | - | Е |
| | LSD | С | А | В | F | Е | D | |
| Iodine values | Ι | 39.95 | 39.68 | 39.04 | 38.34 | 37.51 | 36.61 | А |
| | П | 39.95 | 34.78 | 28.53 | - | - | - | С |
| | Ш | 39.81 | 29.85 | - | - | - | - | Е |
| | IV | 38.67 | 38.40 | 37.93 | 37.35 | 36.67 | 35.90 | В |
| | V | 38.67 | 34.37 | 28.21 | - | - | - | D |
| | VI | 38.72 | 29.50 | - | - | - | - | F |
| | LSD | А | В | С | D | Е | F | |

 Table (3): Effect of using cow's and buffaloe's sweet or sour cream to make butter on refractive index value and iodine value during storage at different temperatures (average of three replicates)

* A, B, C, D, E and F: means with the same letter among the treatments or ripening period are not significantly different (p<0.01).

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التغيرات في جودة ودلائل أكسدة كلاً من الزبد البقري و الجاموسي المخزنة تحت ظروف التبريد

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يتعرض دهن اللبن خلال عملية الأكسدة إلى مجموعة من التغيرات الغير مرغوبة مثل انخفاض الجودة الحسية وكذلك القيمة الغذائية للمنتج. تتعدد العوامل التي تؤثر على جودة الزبد مثل ظروف التخزين من حيث درجة الحرارة والمدة، حموضة القشدة المستخدمة في الصناعة ونوع دهن اللبن المستخدم. تهدف هذه الدراسة إلى المقارنة بين مدى ثبات كلا من الزبد البقرى والزبد الجاموسى سواء المتخمر وغير المتخمر وغير المتخمر وغور المتخمر وغير المتخمر وغير المتخمر تفوع دهن اللبن المستخدم. تهدف هذه الدراسة إلى المقارنة بين مدى ثبات كلا من الزبد البقرى والزبد الجاموسى سواء المتخمر وغير المتخمر وغير المتخمر وغير المتخمر ونوع دهن اللبن المستخدم. تهدف هذه الدراسة إلى المقارنة بين مدى ثبات كلا من الزبد البقرى والزبد الجاموسى سواء المتخمر وغير المتخمر لمعلية الأكسدة تحت تأثير الحفظ المبرد على ٥ م مع عينة المقارنة المخزنة على – ٢٠م. أوضحت النتائج أن حفظ الزبد مبردا على ٥ م مع كم له تأثير معنوي كبير في رفع معدلات أكسدة الدهن مقدرة كرقم بيروكسيد، قيم التفاعل مع حمض الثيوبارياتيوريك Thiobarbaturic acid ونج مع معنه المالمع معدور كرف مع معنه المالم معنويا مقدرة كرقم بيروكسيد، قيم التفاعل مع حمض الثيوبارياتيوريك الجموسي المالمي كان م كان لله للبني المنتجر وي معدلات أكسدة الدهن مقدرة كرقم بيروكسيد، قيم التفاعل مع حمض الثيوبارباتيوريك المن الزبين وانخفاض قيم الما للمن علي معار والذي والغاض قيم المالي وانخفاض قيم الرقم اليودي والاس الهيدروجيني لسيرم الزبد بمعدلات اكبر من تلك المخزنة على درجة حرارة – ٢٠ م. أسارت النتائج أيضا إلى أن الزبد الرقم اليودي والاس الهيدروجيني لسيرم الزبد بمعدلات اكبر من تلك المخزنة على درجة حرارة – ٢٠ م. أسارت النتائج أيضا إلى أن الزبد مالوي اليودي والاس الهيدروجيني لمالي معدلات اكبر من تلك المخزنة على درجة حرارة – ٢٠ م. أسارت النارت النوي المويني الماليودي والالم الوردي والاس القيدة مال الذي الزبي من الزبي والاس الهيدروجيني لسيرم الزبد بمعدلات اكبر من تلك المخرة على درجة حرارة معرارة أول الارت الزبي والزبي ماليو الرقم اليودي والاس الهيدروجيني لسيرم الزبد بمعدل الدهن مالم ولدي على درجة حرارة – ٢٠ م. أسارت النائج أيضا إلى أن الزب