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Effects of using whey and maltodextrin in white cheese powder production on free fatty acid content, nonenzymatic browning and oxidation degree during storage

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A B S T R A C T

Use of maltodextrin and whey improves the physical properties of spray-dried cheese powder and, as cheese replacers, they decrease the raw material costs. However, it is necessary to evaluate their effects on the chemical quality and sensory properties of the product. Three powders, control (CON), whey-added cheese powder (WACP), and maltodextrin-added cheese powder (MACP) were produced to determine free fatty acid (FFA) content, degree of nonenzymatic browning, oxidation, and sensory (flavour) changes during 12 months' storage. In the emulsion preparation and drying process, total volatile FFAs decreased up to 9% and 53.5%, respectively, with higher decrease in CON than in WACP or MACP. Although whey increased oxidation degree of powder, oxidised flavour could not be perceived until the ninth month of storage. Maltodextrin slightly decreased cheese flavour and overall impression scores. There was no difference detected in the powders for scorched flavour.

1. Introduction

The use of cheese as an ingredient to enhance flavour and to improve mouthfeel properties of foods is widely applied (Guinee, 2011a; Guinee & Kilcawley, 2004). One of the most common ways to use cheese as an ingredient is to convert it into powder, which has improved shelf-life and stability. Powdered cheese also facilitates its direct use in industrial applications such as surface applications, incorporation into dry or wet mixes, etc. (Guinee, 2011b; Missel, 1996). Thus, industrial availability and applicability of cheeses as an ingredient are enhanced and, as recently noted, there is an increasing trend in the use of cheese powders (Guinee, 2011a).

One important advantage of cheese powder is its general stability during extended storage, because of its low moisture content and low water activity. However, there can be changes in the quality of the powder during storage. Some of these changes are variations in fat hydrolysis and oxidation, and nonenzymatic browning reactions such as the Maillard reaction (Stapelfeldt, Nielsen, & Skibsted, 1997; Thomas, Scher, Desorby-Banon, & Desorby, 2004).

Cheese powder is a high-fat dairy powder and the distribution of fat plays important role in flavour. Both hydrolytic and oxidative degradation of milk fat may take place during processing and storage of cheese powder (Collins, McSweeney, & Wilkinson, 2003; McSweeney & Sousa, 2000). Free fatty acids (FFAs), the main product of enzymatic hydrolysis of triacylglycerides, have a direct influence on the cheese flavour. Specifically, short chain fatty acids are very important because of their low perception thresholds. Additionally, FFAs may participate in catabolic reactions and cause an increase in the amount of aroma compounds such as methyl ketones, esters, alkanes, lactones, aldehydes, and secondary alcohols (Collins et al., 2003; Park & Drake, 2014). Therefore, variation in FFAs should be examined to gain insight into the quality of the dairy product (Collins et al., 2003; McSweeney & Sousa, 2000). To summarise, FFAs have a critical role in flavour development and characteristics of cheese. Specifically, it is also important to minimise the variation in FFAs during cheese powder production.

Lipid oxidation is one of the most dominant reasons for flavour deterioration of high fat powders during storage, especially if there is a high amount of free fat on the surface of powder particles (Kelly, Kelly, & Harrington, 2002; Schuck, 2007). Polyunsaturated fatty acids are the principal source for oxidation if they undergo catabolic reactions that produce various unsaturated and strongly flavour-active aldehydes resulting in the flavour defect referred to as oxidative rancidity (Collins et al., 2003).

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Another important reaction in dairy powders is nonenzymatic browning. Generally, nonenzymatic browning in dairy powders is a result of Maillard reactions; these reactions can have positive/negative effects on nutritional value and health (Tamanna & Mahmood, 2015). While nonenzymatic browning may occur during processing, it may continue or develop during storage (Schuck, 2011; Thomas et al., 2004). Although the reaction rate is not high in powder products, it causes the formation of nutritionally unavailable and chemically stable compounds which are not desired (Kilic, Muthukumarappan, & Gunasekaran, 1997; Palombo, Gertler, & Saguy, 1984).

Even though an increase in cheese powder production has been reported, there are limited studies on cheese powders, especially on powder quality. Since spray drying is one of the most energy-intensive and expensive processes in food processing, we have previously studied ways to improve the cost-effectiveness of the spray drying process and use in cheese powder production (Erbay & Koca, 2014) and also analysed the exergy efficiency of the process (Erbay & Koca, 2012a,b). Further, optimisation of cheese powder production has been studied to improve the physical and storage properties, as well as process efficiency (Erbay, Koca, Kaymak-Ertekin, & Ucuncu, 2015). Effects of spray drying process parameters and uses of different multilayer packages during storage on white cheese powder properties and the nonenzymatic browning of Cheddar cheese powder have been investigated (Ceylan Sahin, Erbay, & Koca, 2018; Kilic et al., 1997; Koca, Erbay, & Kaymak-Ertekin, 2015). Furthermore, volatile compounds and descriptive sensory characteristics of different cheese powders have been evaluated (Hunutlu, Karagül-Yüceer, & Koca, 2016; Varming, Andersen, Petersen, & Ardö, 2013; Varming, Beck, Petersen, & Ardö, 2010). In addition, decreased amount of volatile compounds in Edam and Danbo cheese powders were determined because of spray drying process (Varming, Beck, Petersen, & Ardö, 2011).

Studies to increase the stability of the cheese emulsions and decrease the use of emulsifying salt in cheese emulsion preparation have been conducted (Hougaard, Sijbrandij, Varming, Ardö, & Ipsen, 2015; Kelimu, da Silva, Geng, Ipsen, & Hougaard, 2017; Ray, Gholamhosseinpour, Ipsen, & Hougaard, 2016; Varming, Hougaard, Ardö, & Ipsen, 2014). It was also reported that the characteristics of cheese emulsification depend on the emulsifying salt, cheese types and fat reduction, which affect particle structure (da Silva, Ahrné, Larsen, Hougaard, & Ipsen, 2018; da Silva, Larsen, Hougaard, & Ipsen, 2017; Urgu, Unluturk, & Koca, 2018).

The major problems in the production and quality of cheese powder were found to be powder sticking on the dryer wall during production and poor flowability. Using carriers or fillers is the easiest way to improve the physical properties of the powders. Another advantage of using carriers or fillers is the reduction of cost by decreasing the amount of cheese needed. In fact, in a previous study, we improved the physical properties of white cheese powder during storage using carriers such as whey and maltodextrin, with about a 13% reduction in matured cheese amount and 30% reduction of cheese dry matter, respectively (Erbay & Koca, 2015). However, changes in the chemical and sensory properties of powders during storage are also very important. Therefore, the present paper describes the effects of using maltodextrin and whey on nonenzymatic browning, oxidation degree and free fatty acid content, and flavour of white cheese powder during a one year period of storage.

2. Materials and methods

2.1. Materials

Seven months old ripened white brined cheeses were supplied by Sütaş Dairy Company (Bursa, Turkey) with 51.96 ± 0.64, 18.40 ± 0.27, 24.44 ± 0.34, and 4.34 ± 0.12% water, protein, fat, and salt content, respectively. Moisture, fat, protein, and salt contents were determined by gravimetric (AOAC, 2012c), Gerber (AOAC, 2012b), Kjeldahl (AOAC, 2012a), and Mohr (ISO-IDF, 2006) methods, respectively. Shredded white cheese was transferred to air- and water-tight durable polypropylene plastic containers and stored at 4 ± 1 °C. The cheese samples were processed within 48 h. Joha emulsifying salts (S 85 including combination of phosphate salts) obtained from Kipa Chemical Company (Istanbul, Turkey) were used to prepare cheese emulsions. Sweet whey from Kashar cheese production was supplied by Pınar Dairy Company (İzmir, Turkey) with 93.64 ± 0.01, 0.64 ± 0.02, 0.40 ± 0.00, 4,89 ± 0.02 and 0.42 ± 0.01% water, protein, fat, carbohydrate and ash content, respectively. To prevent acidity changes, the whey was pasteurised, and stored at refrigerated temperature up to 3 days. Although whey is used in industry in powder form as an additive, we used fluid whey to substitute both cheese dry matter and water. Maltodextrin having dextrose equivalent value of 20 and moisture content of 5.45% ± 0.14 was purchased from Qimhuangdao Starch Co. (Hebei, China).

2.2. Production procedure

Cheese powders were produced by spray drying of cheese emulsions with 25% dry matter (DM) coming from the cheese, maltodextrin and whey. Three different cheese emulsions (cheese emulsion, whey-added cheese emulsion and maltodextrin-added cheese emulsion) were used to produce the control powder without using any carrier (CON), whey-added cheese powder (WACP), and maltodextrin-added cheese powder (MACP). Whey was used in place of water in the production of whey-added cheese emulsion, and to keep the DM content of the whey-added cheese emulsion constant, 13% of white cheese was removed. Maltodextrin was added instead of 30% of cheese dry matter to produce maltodextrin-added cheese emulsion. Cheese powders for each formulation were produced twice. Drying conditions were chosen from the previous optimisation study on spray drying of white cheese; inlet drying air temperature of 174 °C, atomisation pressure of 354 kPa, and outlet drying air temperature of 68 °C (Erbay et al., 2015). The production procedures of emulsion preparation and spray drying were explained in detail in a previous study (Erbay & Koca, 2015). The cheese powder samples packaged in PET/Al-foil/LDPE were stored for 12 months at 20 °C and 40–50% relative humidity. The samples were analysed every three months of storage period.

2.3. Nonenzymatic browning

An enzymatic digestion method based on pronase proteolysis that releases the brown pigments was used to determine degree of nonenzymatic browning of white cheese powder samples according to Kilic et al. (1997) and Palombo et al. (1984). Pronase is a non-specific protease mixture that hydrolyses both denaturated and native proteins into individual amino acids. Thus, liberation of the brown pigments from the protein molecules is achieved and they can be measured spectrophotometrically (Labuza & Saltmarch, 1981; Palombo et al., 1984). Absorbance of the powders were quantified at 420 (A_{420}) and 550 (A_{550}) nm by using a UV–Vis spectrophotometer (Cary 50 Bio, Varian; Palo Alto, CA, USA). The following equation was used to calculate optical density (OD) of the samples and the nonenzymatic browning values for the powder samples were presented as OD per g DM of sample:

$$OD = A_{420} - A_{550} \quad (1)$$

2.4. Oxidation degree

Degree of lipid oxidation in the samples was determined by a thiobarbituric acid method used by Fenaille, Mottier, Turesky, Ali, and Guy (2001) with modifications as described by Ceylan Sahin et al. (2018). This method was used as a measure of secondary lipid oxidation products. Two different secondary oxidation product groups or thiobarbituric acid reactive substances (TBARS) can be measured at two different wavelengths. While secondary oxidation products such as malondialdehydes, which give a pink colour after TBARS derivatisation, can be measured at 532 nm, several other lipid oxidation products such as alkenals, alkadienals, other aldehydes, and ketones, which give a yellow colour with TBARs, can be detected at 450 nm (Fenaille et al., 2001; Kristensen & Skibsted, 1999).

However, there can be intense interfering peaks or the scale of the measured values may be too small in the analysis of dairy products and powders carried out at 532 nm. The interfering peaks may cause overestimations and/or imprecisions whereas small peaks may increase the uncertainties (Fenaille et al., 2001; Kristensen & Skibsted, 1999; Liang, 2000). Therefore, in this study, oxidation of the cheese powders was measured at both 450 and 532 nm. Lipid oxidation of powder samples was given as absorbance values at these two different wavelengths per 1 g of cheese powder. The blank of analysis was distilled water. Absorbance of maltodextrin and/or whey cannot be included as they were used as an ingredient in the cheese powder production. Therefore, the changes in oxidation because of the maltodextrin and whey addition to cheese powder were found compared to that of cheese powder with no addition.

2.5. Free fatty acid content

The amounts of the FFAs ($C_{4:0}$ to $C_{18:3}$) of white cheese, cheese emulsion and cheese powder samples were determined by a gas chromatographic method (De Jong & Badings, 1990; Deeth, Gerald, & Snow, 1983). FFAs in the samples were isolated using Bond Elut empty SPE columns (Agilent Technologies; Santa Clara, CA, USA) filled with neutral alumina deactivated with 10% water. Cheese, cheese emulsion and cheese powder samples of 1 g with 3, 4, and 0.5 g anhydrous Na_2SO_4 to hold the residual water from the sample, respectively, were mixed in a glass test tube. Afterwards, 0.3 mL 2.5 M H_2SO_4, 1 mL internal standard solution, including 0.5 mg mL^{-1} pentanoic and tridecanoic acids, and 3 mL solvent (diethyl ether:-hexane, 1:1, v/v) were added to the samples. Then, the mixtures in the test tubes were mixed with a vortex (Yellowline TTSE, Staufen, Germany) for 1 min. Thereafter, the samples were centrifuged at room conditions for 2 min at 700× *g* and the supernatant was collected. This extraction procedure was repeated three times. The SPE column, which contained 1 g of alumina, was used to filter the collected supernatant using a vacuum manifold system. Then, the alumina with the absorbed FFAs was dried under vacuum and transferred to an empty tube. FFAs were eluted using diethyl ether containing 3% formic acid. Finally, the mixture was centrifuged for 10 min at 450× *g* and 1 μL of the upper phase was injected to the GC (Hewlett Packard (HP) Series II, 5890; Palo Alto, CA, USA). In separation and detection of the FFAs, a DB-FFAP (30 m, 0.25 μm, 0.25 mm, Agilent Technologies) column and a flame ionisation detector (FID) were used, respectively. The oven temperature program started at 90 °C for 1 min, followed by a 7 °C min^{-1} increase up to 240 °C, and finished by holding at 240 °C for 15 min. The temperatures of the injection block and FID were 250 °C and 260 °C, respectively.

Identification of the FFAs was done by using analytical standards (butyric ($C_{4:0}$), pentanoic ($C_{5:0}$), caproic ($C_{6:0}$), caprylic ($C_{8:0}$), capric ($C_{10:0}$), lauric ($C_{12:0}$), tridecanoic ($C_{13:0}$), myristic ($C_{14:0}$), palmitic ($C_{16:0}$), stearic ($C_{18:0}$), oleic ($C_{18:1}$), linoleic ($C_{18:2}$), and linolenic ($C_{18:3}$) acids) with higher than 99.5% purities obtained from Sigma–Aldrich (Steinheim, Germany). Quantification of the FFAs were made using internal standards, pentanoic acid (for the FFAs from $C_{4:0}$ to $C_{8:0}$) and tridecanoic acid (for the FFAs from $C_{10:0}$ to $C_{18:3}$), and correction factors were calculated from curves drawn for standard peak area per internal standard peak area versus standard concentration per internal standard concentration were used. To account for FFAs differences due to the fat differences in the samples, results were expressed as mg 100 g^{-1} fat and all samples were analysed in duplicate.

2.6. Sensory evaluation

Cheese flavour, oxidised flavour, foreign flavour, and scorched flavour of the samples were determined by 10 trained panellists (age range of 24–50, 7 women and 3 men). For each sensory property, a unipolar scale ranging from 1 (none/absent) to 9 (highest intensity) was used. During training of panellists, cheese powder was kept in an open glass container at room temperature until oxidation was present. This powder was then was used as a reference of oxidised flavour. Cheese powder samples were also cooked at different temperatures for various times to evaluate scorched flavour. Further, ripened white cheese was used to represent cheese flavour (Koca et al., 2015). Panellists were required to take into account off-flavours except oxidised and scorched flavour for foreign flavour. They were asked to give the highest score to the least palatable one.

2.7. Statistical analysis

Data were analysed by ANOVA and Duncan post hoc test. A statistical package program (SPSS ver. 13.0, SPSS Inc.; Chicago, IL, USA) was used in the statistical analyses. Statistical significance was set at $P < 0.05$. As detailed in section 2.2 above, cheese powders for each formulation were produced twice on different days and each analysis was carried out in triplicate for each sample. Therefore, every result and its standard deviation were obtained from 6 data points.

3. Results and discussion

3.1. Differences in degree of nonenzymatic browning

Use of whey and maltodextrin in the formulation of the cheese powders had a significant impact on the nonenzymatic browning values ($P < 0.05$), which increased during storage for all powders (Fig. 1). Although the lowest nonenzymatic browning values were measured for MACP after production, the rise in nonenzymatic browning for this sample during storage was greater than those of other powders. Use of whey increased nonenzymatic browning values and the highest values for all samples were found in the first 6 months of storage. Results are in harmony with the literature. Kilic et al. (1997) observed an increase in nonenzymatic browning during storage of Cheddar powder under different storage conditions (Kilic et al., 1997). In addition, similar trends using whey and maltodextrin in cheese powder during storage were observed by objective colour measurements giving a browning index in our previous study (Erbay & Koca, 2015).

However, in the Erbay and Koca (2015) study, the increase in colour values was not detected by sensory evaluation, indicating the rate of browning was not high enough to impair the quality of powders. It is well-known that the rate of nonenzymatic browning reactions is affected by temperature, product moisture content and

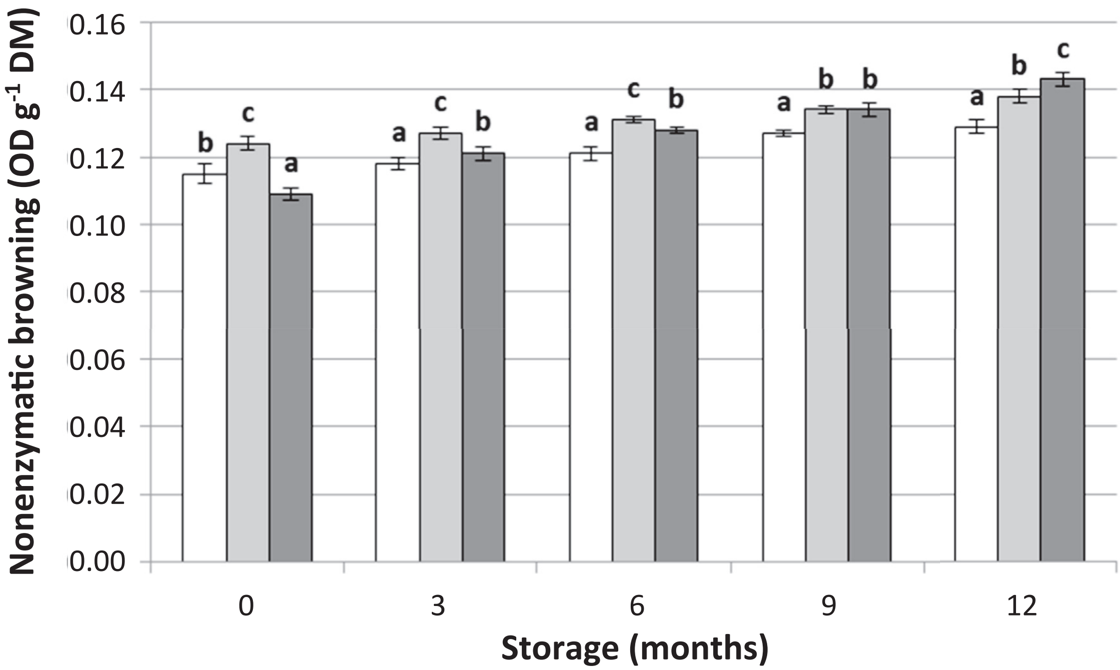

Fig. 1. Variation in non-enzymatic browning degree in cheese powders during 12 months' storage: □, control without using any carrier in the production; ■, whey-added cheese powder; ■, maltodextrin-added cheese powder). Error bars represent standard deviation, letters above the bars indicate statistical significant differences ($P < 0.05$) within powder formulation of each storage period.

protein type in the product. It was reported that the nonenzymatic browning reaction rate was very low at product moisture content of 2.3%, but increased above 5.4% (Guyomarc'h, Warin, Muir, & Leaver, 2000). Additionally, it was reported that a medium water activity value in the range of 0.5–0.7 favours the Maillard reaction (Thomas et al., 2004; Troyano, Olano, & Martínez-Castro, 1994) and it was reported in the literature that a rise in casein content, especially β-casein content, of the product causes a decrease in the reaction rate as it is less susceptible to relative humidity (Thomas et al., 2004). Cheese powders produced in the present study were in the low reaction rate range (with a moisture content range 2.13–2.72% and a water activity range 0.134–0.159).

Lactose, proteins and lipids may provide the carbonyl and amino compounds for the nonenzymatic browning reaction. Cheese powders contain higher amounts of fat and protein and much lower amounts of lactose compared with milk and whey powders (Kilic et al., 1997). It was reported that nonenzymatic browning reactions more easily occurred in lactose/whey protein model systems than lactose/casein model systems (Morales, Romero, & Jiménez-Pérez, 1995). In our present study, the nonenzymatic browning was higher in samples (WACP) with whey which had higher amounts of lactose than the control sample. Furthermore, the susceptibility of lactose to browning was reported to be higher than dextrose, but in the presence of amines, dextrose showed more browning than lactose (Kumar & Banker, 2005). The trend of increasing nonenzymatic browning during storage for cheese powders with added maltodextrin (MACP) can be attributed to higher amounts of dextrose in MACP samples.

3.2. Variation of oxidation degree

Use of whey and maltodextrin significantly affected the oxidation degree ($P < 0.05$) (Fig. 2). The highest values were detected in WACP, followed by MACP. In the production of WACP, liquid sweet

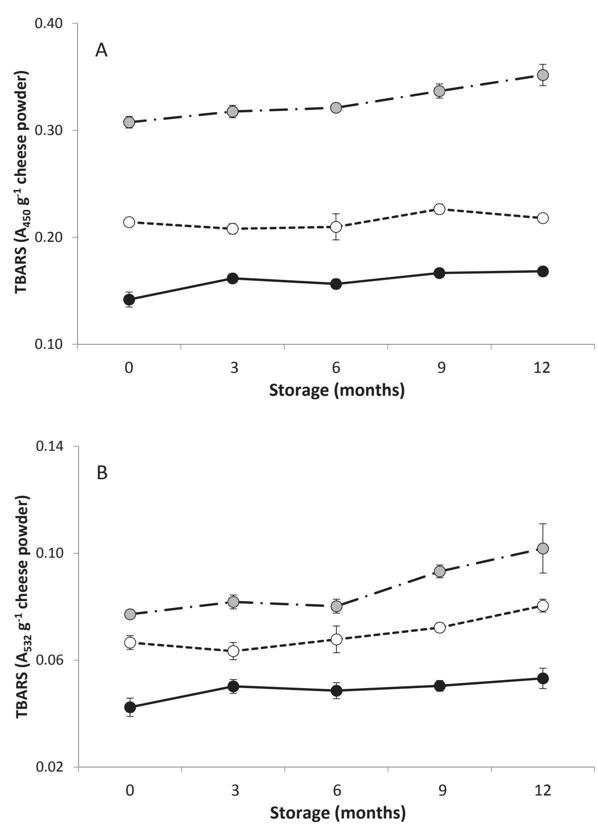

Fig. 2. Variation of oxidation degree in cheese powders determined by TBA method at (A) 450 nm and (B) 532 nm during 12 months' storage: ●, control without using any carrier in the production; ●, whey-added cheese powder; ○, maltodextrin-added cheese powder. Error bars represent standard deviation.

whey was obtained from kashar cheese production where thermophilic starter cultures were used to decrease the pH in the scalding process. Campbell, Miracle, Gerard and Drake (2011) proved that the fermentation process by starter cultures in liquid whey enhances lipid oxidation. Therefore, increasing oxidation in spray dried powders using liquid whey as ingredient is possible.

Before spray drying the cheese powder, a cheese emulsion is prepared. Hu, McClements, and Decker (2003) reported that casein has excellent physical and oxidative properties for oil in water emulsions compared with whey protein isolate. Although increased lipid oxidation can be due to the increased surface free fat was reported by Park and Drake (2014), surface free fat of WACP was lower compared with that in CON samples analysed in an earlier study by Erbay and Koca (2015). As a result, the higher oxidation in WACP during storage can be associated with using whey instead of water and thus having less casein compared to CON. As far as MACP is concerned, the products of nonenzymatic browning reactions may react with TBA, and influence the results of analysis (Papastergiadis, Mubiru, Van Langenhove, & De Meulenaer, 2012). There was an increase in nonenzymatic browning values in MACP during storage (Fig. 1). Using maltodextrin improved the physical properties such as bulk and tapped densities, wettability, dispersibility, solubility, and free fat content of cheese powder (Erbay & Koca, 2015). Maltodextrin, however, did not protect the cheese powder from oxidation.

The increase in oxidation for all samples after the ninth month of storage was significant ($P < 0.05$). This increase was greater for WACP and MACP. It has been reported that oxidation increases in whole milk powder significantly after the sixth month of storage (McCluskey et al., 1997; Thomas et al., 2004), which is in line with results obtained here for cheese powder samples. However, the oxidation of samples was not high enough to cause flavour deterioration as indicated by the oxidised flavour scores (maximum 2.55 for WACP at 12 months; Table 1). Oxidation values in whole milk powder higher than 0.1 (measured at 532 nm) may cause a distinct oxidised flavour (Sidwell, Salwin, & Mitchell, 1955). In the present study, the highest measured value for the cheese powders was 0.1 at the end of the storage for the WACP samples.

As expected, similar trends were observed for oxidation analyses performed at different wavelengths. However, the results measured at 532 nm were lower than the values obtained at 450 nm. Also, the differences in the values of MACP and WACP during storage were lower. In addition, compared with the measurements at 450 nm, the oxidation of MACP at the twelfth month of storage was significantly lower than that in the freshly produced WACP samples. These differences may be associated with the products of nonenzymatic browning reactions. These compounds may react with TBA, influence the results of analysis carried out at 532 nm (Papastergiadis et al., 2012) and according to the results of nonenzymatic browning, the rate of the increase of nonenzymatic browning for MACP was very high during storage (Fig. 1). These results were in harmony with the literature information about the risk of intense interfering peaks or the low scale problems of the analysis carried out at 532 nm for dairy products. In present study, use of 450 nm for determination of oxidation with the TBA method in cheese powder samples was also done.

3.3. Variation in free fatty acid content

From the earlier research (Erbay & Koca, 2015), addition of whey and maltodextrin decreased the fat content of samples. Therefore, the quantities of FFAs are given on a fat basis for processing steps.

The most abundant FFAs in white cheese were oleic acid, palmitic acid, myristic acid and stearic acid (Table 2). In white cheese 86.8% of FFAs were medium-long chain FFAs ($C_{12:0}$-$C_{18:3}$) and 61.1% of these were oleic and palmitic acids. These same FFAs were found to be the most abundant in white-brined cheeses in the literature (Akın, Aydemir, Koçak, & Yıldız, 2003; Atasoy & Türkoğlu, 2008; Cinbas & Kilic, 2006; Güler & Uraz, 2004; Özer, Kirmaci, Hayaloglu, Akçelik, & Akkoç, 2011; Yerlikaya & Karagozlu, 2014).

Table 1
Sensory evaluation of the flavour properties of cheese powders during storage.[a]

Item	Storage (months)	Sample		
		CON	WACP	MACP
Cheese flavour	0	7.50 ± 0.51^{a,A}	7.20 ± 0.62^{a,A}	5.80 ± 0.62^{b,A}
	3	7.35 ± 0.49^{a,A}	7.15 ± 0.75^{a,A}	5.85 ± 0.59^{b,A}
	6	7.60 ± 0.60^{a,A}	7.10 ± 0.72^{b,A}	5.85 ± 0.67^{c,A}
	9	7.50 ± 0.69^{a,A}	7.15 ± 0.59^{a,A}	5.80 ± 0.62^{b,A}
	12	7.20 ± 0.70^{a,A}	6.95 ± 0.69^{a,A}	5.70 ± 0.47^{b,A}
Scorched flavour	0	1.20 ± 0.41^{a,A}	1.25 ± 0.44^{a,A}	1.10 ± 0.31^{a,A}
	3	1.30 ± 0.47^{a,A}	1.45 ± 0.69^{a,A}	1.15 ± 0.37^{a,A}
	6	1.20 ± 0.41^{a,A}	1.40 ± 0.60^{a,A}	1.25 ± 0.44^{a,A}
	9	1.15 ± 0.37^{a,A}	1.30 ± 0.47^{a,A}	1.10 ± 0.31^{a,A}
	12	1.15 ± 0.37^{a,A}	1.30 ± 0.57^{a,A}	1.10 ± 0.31^{a,A}
Foreign flavour	0	1.10 ± 0.31^{a,A}	1.10 ± 0.31^{a,A}	2.10 ± 0.79^{b,A}
	3	1.15 ± 0.37^{a,A}	1.50 ± 0.61^{a,B}	2.45 ± 0.89^{b,AB}
	6	1.20 ± 0.41^{a,A}	1.35 ± 0.49^{a,AB}	2.05 ± 0.51^{b,A}
	9	1.10 ± 0.31^{a,A}	1.20 ± 0.41^{a,AB}	2.35 ± 0.81^{b,AB}
	12	1.15 ± 0.37^{a,A}	1.35 ± 0.49^{a,AB}	2.75 ± 0.79^{b,B}
Oxidised flavour	0	1.30 ± 0.47^{a,A}	1.65 ± 0.75^{a,A}	1.30 ± 0.47^{a,A}
	3	1.20 ± 0.41^{a,A}	1.70 ± 0.80^{b,A}	1.25 ± 0.44^{a,A}
	6	1.20 ± 0.41^{a,A}	1.70 ± 0.73^{b,A}	1.25 ± 0.44^{a,A}
	9	1.35 ± 0.49^{a,A}	2.00 ± 0.56^{b,A}	1.25 ± 0.44^{a,A}
	12	1.45 ± 0.51^{a,A}	2.55 ± 0.69^{b,B}	1.45 ± 0.51^{a,A}
Overall impression	0	7.60 ± 0.68^{a,A}	6.70 ± 0.73^{b,A}	5.55 ± 0.76^{c,AB}
	3	7.55 ± 0.76^{a,A}	6.60 ± 0.68^{b,A}	5.75 ± 0.79^{c,A}
	6	7.65 ± 0.67^{a,A}	6.55 ± 0.83^{b,A}	5.70 ± 0.80^{c,A}
	9	7.40 ± 0.75^{a,A}	6.55 ± 0.51^{b,A}	5.55 ± 0.69^{c,AB}
	12	7.25 ± 0.55^{a,A}	6.35 ± 0.75^{b,A}	5.15 ± 0.88^{c,B}

[a] Abbreviations are: CON, control cheese powder; WACP, whey-added cheese powder; MACP, maltodextrin-added cheese powder. A unipolar scale ranging between 1 and 9 was used. For all flavour properties, 1 was none/absent and 9 was highest intensity. Values are the mean ± SD; means within rows and columns with different superscript lowercase and uppercase letters, respectively, differ significantly ($P < 0.05$).

Table 2
Variation of free fatty acids in white cheese (raw material) and emulsions prepared with different formulations.[a]

Free fatty acids	WC	CE	WACE	MACE
Butyric acid ($C_{4:0}$)	44.5 ± 0.3^{a}	46.3 ± 0.3^{bc}	47.0 ± 0.4^{c}	46.0 ± 0.2^{b}
Caproic acid ($C_{6:0}$)	24.9 ± 0.4^{c}	22.9 ± 0.5^{ab}	21.9 ± 0.5^{a}	23.6 ± 0.1^{b}
Caprylic acid ($C_{8:0}$)	19.7 ± 2.0^{ab}	16.9 ± 0.4^{a}	20.7 ± 1.3^{b}	19.7 ± 0.1^{ab}
Capric acid ($C_{10:0}$)	31.8 ± 3.3^{b}	24.4 ± 3.7^{a}	27.6 ± 0.1^{ab}	26.8 ± 1.0^{ab}
Lauric acid ($C_{12:0}$)	36.9 ± 3.5^{a}	31.2 ± 3.0^{a}	32.9 ± 1.2^{a}	35.3 ± 0.5^{a}
Myristic acid ($C_{14:0}$)	108.6 ± 8.3^{b}	90.9 ± 2.2^{a}	104.5 ± 5.9^{ab}	101.4 ± 4.1^{bb}
Palmitic acid ($C_{16:0}$)	283.1 ± 19.1^{ab}	245.6 ± 29.0^{a}	311.1 ± 22.4^{b}	245.6 ± 2.2^{a}
Stearic acid ($C_{18:0}$)	93.3 ± 6.5^{ab}	87.5 ± 15.8^{ab}	114.8 ± 9.4^{b}	77.7 ± 7.8^{a}
Oleic acid ($C_{18:1}$)	450.5 ± 32.5^{ab}	409.8 ± 72.6^{a}	554.9 ± 45.6^{b}	363.2 ± 41.2^{a}
Linoleic acid ($C_{18:2}$)	54.8 ± 3.8^{ab}	50.3 ± 8.1^{a}	68.0 ± 6.0^{b}	44.9 ± 4.4^{a}
Linolenic acid ($C_{18:3}$)	13.3 ± 0.9^{ab}	12.6 ± 2.0^{ab}	16.6 ± 1.4^{b}	11.4 ± 1.2^{a}
TVFFA	120.9 ± 5.5^{b}	110.5 ± 2.5^{a}	117.1 ± 2.2^{ab}	116.1 ± 0.7^{ab}
TFFA	1161.3 ± 80.0^{ab}	1038.4 ± 124.2^{a}	1319.9 ± 94.0^{b}	995.5 ± 52.8^{a}

[a] Abbreviations are: WC, white cheese; CE, cheese emulsion; WACE, whey-added cheese emulsion; MACE, maltodextrin-added cheese emulsion; TVFFA, total volatile free fatty acids ($C_{4:0}$-$C_{10:0}$); TFFA, total free fatty acids. Values, in mg 100 g^{-1} fat, are the mean ± SD; means within emulsion formulation with different superscript letters differ ($P < 0.05$).

Heat treatments during processing of dairy products cause a decrease in the FFAs (Evers, Morris, Conaghan, & Palfreyman, 2000). The FFAs in cheese emulsion and maltodextrin added cheese emulsion decreased during emulsion preparation except for butyric acid (Table 2). The decrease in total volatile FFAs ($C_{4:0}$—$C_{10:0}$) in cheese emulsion was higher than that in other emulsions, especially for caprylic and capric acids. Decreases in volatile fatty acids were high during spray drying, compared with those in emulsion preparations. Although the amount of short and medium chain FFAs decreased in whey added cheese emulsion preparation, an increase was observed in the long chain FFAs. The reason for this may be FFAs present in liquid whey added during emulsion preparation.

Although it is certain that the most important process in powder production for variation in volatile compounds is spray drying, the effects of spray drying on FFAs is not clear in the literature. It was reported that volatile compounds were dramatically decreased during spray drying (Varming et al., 2011). There are similar results for variation of specific FFAs (Evers et al., 2000). Retention of FFAs changes depending on processing variables. Amundson, Ishino, and Lindsay (1980) reported increases in retention levels of FFAs with decreasing atomisation pressure, inlet air temperature and total solids, and with the use of emulsifying salt (Amundson et al., 1980). FFAs with high molecular weight also had higher retention levels under all drying conditions. On the other hand, some researchers asserted that spray drying may cause an increase in the FFA content of milk powder because of the possibility of an increase in lipase activity (Kim, Chang, & Kwak, 2010).

In the present study, the effect of spray drying on the FFAs contents were discussed with data shown in Tables 2–4. It is obvious that volatile FFAs significantly decreased. Decreases in TVFFAs during spray drying for CON, WACP and MACP were 53.5%, 47.0% and 47.5%, respectively. The changes in medium-long chain FFAs of CON and WAPC were almost negligible with small fluctuations, a significant rise was detected in total medium-long chain FFAs ($C_{12:0}$—$C_{18:3}$) of MACP during spray drying (Table 4).

The main reason for the decrease in the TVFFAs during spray drying may be explained by the effect of temperature. On the other hand, the formulation appeared to influence the variation of the FFAs, and this variation may be influenced by the physical structure of the powders. Using maltodextrin and whey may increase the emulsification efficiency and emulsion stability which may cause or increase the encapsulation efficiency of fat droplets. In the previous study, the highest free fat contents were detected in the CON samples with analytical measurements and the morphology of powders (analysed by scanning electron microscopy) supported these measurements (Erbay & Koca, 2015). Conversely, MACP and WACP samples had more and larger spherical structures with wrinkled surfaces which indicated that they had the lowest surface free fat (Kim, Chen, & Pearce, 2002; Thomas et al., 2004; Vignolles, Jeantet, Lopez, & Schuck, 2007). Results obtained from FFA analyses for TVFFAs are in line with these results. Because of the

Table 3
Variation of volatile free fatty acids in cheese powders from different formulations during storage.[a]

Sample	Storage (months)	Butyric acid ($C_{4:0}$)	Caproic acid ($C_{6:0}$)	Caprylic acid ($C_{8:0}$)	Capric acid ($C_{10:0}$)	TVFFA
CON	0	15.2 ± 0.2^{a,A}	9.0 ± 0.2^{a,A}	8.2 ± 0.2^{a,A}	19.0 ± 1.4^{a,A}	51.4 ± 1.9^{a,A}
	3	15.9 ± 0.3^{a,A}	9.4 ± 0.4^{a,AB}	8.7 ± 0.4^{a,AB}	19.8 ± 0.9^{a,A}	53.8 ± 1.6^{a,AB}
	6	16.1 ± 0.9^{a,A}	9.9 ± 0.5^{a,B}	9.3 ± 0.5^{a,BC}	21.6 ± 2.0^{a,AB}	56.9 ± 2.8^{a,B}
	9	18.3 ± 0.9^{a,B}	11.1 ± 0.4^{a,C}	10.3 ± 0.6^{a,C}	21.8 ± 2.4^{a,AB}	61.4 ± 2.7^{a,C}
	12	19.3 ± 0.4^{a,B}	11.3 ± 0.4^{a,C}	10.1 ± 1.0^{a,C}	23.4 ± 2.4^{a,B}	64.0 ± 2.2^{a,C}
WACP	0	17.9 ± 0.6^{b,A}	11.2 ± 0.2^{b,A}	10.6 ± 0.2^{b,A}	23.0 ± 0.9^{b,AB}	62.6 ± 0.9^{b,A}
	3	18.2 ± 0.7^{b,A}	11.4 ± 0.3^{c,A}	10.7 ± 0.5^{b,A}	21.0 ± 0.2^{b,A}	61.4 ± 1.4^{b,A}
	6	18.4 ± 0.5^{b,A}	11.5 ± 0.2^{b,A}	10.9 ± 0.4^{b,AB}	21.9 ± 1.7^{a,AB}	62.7 ± 1.1^{b,A}
	9	20.0 ± 0.6^{b,B}	12.4 ± 0.3^{b,B}	11.6 ± 0.8^{b,BC}	24.1 ± 2.5^{a,B}	68.2 ± 2.6^{b,B}
	12	21.2 ± 0.3^{b,C}	13.2 ± 0.2^{b,C}	12.2 ± 0.6^{b,C}	23.8 ± 1.8^{a,B}	70.5 ± 1.6^{b,B}
MACP	0	18.1 ± 0.5^{b,A}	10.4 ± 0.4^{b,A}	11.2 ± 0.5^{c,A}	22.2 ± 1.1^{b,A}	62.0 ± 1.7^{b,A}
	3	18.5 ± 0.8^{b,A}	10.4 ± 0.6^{b,A}	10.8 ± 0.6^{b,A}	20.9 ± 0.6^{ab,A}	60.6 ± 2.5^{b,A}
	6	19.1 ± 0.5^{b,A}	10.8 ± 0.6^{b,A}	11.3 ± 0.5^{b,A}	24.0 ± 3.1^{a,A}	65.3 ± 3.9^{b,AB}
	9	21.0 ± 1.3^{b,B}	12.0 ± 0.8^{b,B}	12.5 ± 1.0^{b,B}	24.1 ± 1.9^{a,A}	69.6 ± 3.1^{b,BC}
	12	21.9 ± 1.1^{b,B}	12.6 ± 0.8^{b,B}	13.1 ± 0.8^{b,B}	24.0 ± 3.6^{a,A}	71.6 ± 5.7^{b,C}

[a] Abbreviations are: WC, white cheese; CON, control cheese powder; WACP, whey-added cheese powder; MACP, maltodextrin-added cheese powder; TVFFA, total volatile free fatty acids. Values, in mg 100 g^{-1} fat, are the mean ± SD; means within powder formulation of each storage period and within storage period of each formulation with different superscript lowercase and uppercase letters, respectively, differ significantly ($P < 0.05$).

Table 4
Variation of free fatty acids in cheese powders from different formulations during storage.[a]

Sample	Storage (months)	Lauric acid ($C_{12:0}$)	Myristic acid ($C_{14:0}$)	Palmitic acid ($C_{16:0}$)	Stearic acid ($C_{18:0}$)	Oleic acid ($C_{18:1}$)	Linoleic acid ($C_{18:2}$)	Linolenic acid ($C_{18:3}$)	TFFA
CON	0	$29.3 \pm 1.7^{a,A}$	$90.7 \pm 6.2^{a,A}$	$245.2 \pm 26.7^{a,A}$	$81.8 \pm 11.6^{a,A}$	$383.1 \pm 57.2^{a,A}$	$46.1 \pm 6.0^{a,A}$	$10.9 \pm 1.1^{a,A}$	$938.4 \pm 107.0^{a,A}$
	3	$29.4 \pm 1.9^{a,A}$	$98.0 \pm 4.2^{a,ABC}$	$295.5 \pm 3.0^{a,B}$	$103.9 \pm 4.4^{a,B}$	$484.7 \pm 15.4^{a,B}$	$58.3 \pm 2.1^{a,B}$	$13.2 \pm 0.4^{a,B}$	$1136.9 \pm 23.9^{a,B}$
	6	$30.8 \pm 0.9^{a,AB}$	$93.6 \pm 1.6^{a,AB}$	$249.9 \pm 11.8^{a,A}$	$80.9 \pm 5.6^{a,A}$	$378.1 \pm 23.8^{a,A}$	$45.2 \pm 3.0^{a,A}$	$10.4 \pm 0.8^{a,A}$	$945.7 \pm 49.2^{a,A}$
	9	$32.7 \pm 3.3^{a,B}$	$106.5 \pm 8.3^{a,C}$	$303.6 \pm 13.45^{b,B}$	$104.1 \pm 8.4^{ab,B}$	$479.2 \pm 28.9^{a,B}$	$57.4 \pm 3.6^{a,B}$	$13.5 \pm 0.9^{a,B}$	$1158.4 \pm 42.9^{a,B}$
	12	$32.4 \pm 0.5^{a,AB}$	$101.3 \pm 6.5^{a,BC}$	$290.6 \pm 25.4^{a,B}$	$100.6 \pm 9.3^{a,B}$	$463.6 \pm 40.2^{a,B}$	$56.4 \pm 5.1^{a,B}$	$13.6 \pm 1.2^{a,B}$	$1122.4 \pm 85.3^{a,B}$
WACP	0	$33.4 \pm 0.9^{b,A}$	$109.0 \pm 3.7^{b,A}$	$316.5 \pm 13.6^{b,A}$	$108.8 \pm 13.6^{b,A}$	$511.5 \pm 60.4^{b,A}$	$64.5 \pm 7.3^{b,A}$	$14.0 \pm 1.7^{b,A}$	$1217.1 \pm 108.9^{b,A}$
	3	$33.0 \pm 0.7^{b,A}$	$111.1 \pm 3.4^{c,A}$	$348.2 \pm 4.6^{c,A}$	$121.6 \pm 4.6^{b,A}$	$569.7 \pm 19.7^{b,A}$	$68.6 \pm 2.7^{b,A}$	$15.8 \pm 0.6^{b,A}$	$1335.3 \pm 36.2^{b,A}$
	6	$33.4 \pm 1.3^{ab,A}$	$114.0 \pm 1.1^{b,A}$	$348.6 \pm 7.3^{c,A}$	$125.0 \pm 4.2^{c,A}$	$580.3 \pm 19.7^{c,A}$	$69.7 \pm 2.9^{c,A}$	$15.9 \pm 0.5^{c,A}$	$1349.8 \pm 33.0^{c,A}$
	9	$36.4 \pm 2.3^{a,B}$	$117.8 \pm 8.6^{ab,A}$	$324.2 \pm 39.9^{a,A}$	$105.4 \pm 16.5^{a,A}$	$490.5 \pm 76.3^{a,A}$	$59.1 \pm 9.1^{a,A}$	$14.0 \pm 2.1^{ab,A}$	$1215.6 \pm 141.2^{ab,A}$
	12	$34.5 \pm 1.7^{a,AB}$	$116.2 \pm 8.5^{b,A}$	$326.6 \pm 43.4^{a,A}$	$109.3 \pm 22.2^{a,A}$	$503.5 \pm 95.6^{a,A}$	$61.5 \pm 11.0^{a,A}$	$14.8 \pm 2.5^{a,A}$	$1236.9 \pm 177.9^{a,A}$
MACP	0	$32.9 \pm 0.6^{b,AB}$	$114.5 \pm 11.4^{b,A}$	$337.6 \pm 7.2^{b,A}$	$116.5 \pm 5.5^{b,A}$	$558.2 \pm 20.9^{b,A}$	$66.8 \pm 2.4^{b,A}$	$15.2 \pm 0.5^{b,A}$	$1303.8 \pm 20.8^{b,A}$
	3	$32.0 \pm 0.9^{b,A}$	$110.0 \pm 1.3^{b,A}$	$326.9 \pm 15.0^{b,A}$	$115.1 \pm 8.8^{b,A}$	$551.2 \pm 39.2^{b,A}$	$66.3 \pm 5.0^{b,A}$	$15.0 \pm 1.2^{b,A}$	$1277.2 \pm 69.8^{b,A}$
	6	$35.2 \pm 2.8^{b,BC}$	$115.6 \pm 8.9^{b,A}$	$326.0 \pm 19.3^{b,A}$	$112.2 \pm 7.6^{b,A}$	$538.5 \pm 32.9^{b,A}$	$64.2 \pm 3.8^{b,A}$	$14.4 \pm 0.7^{b,A}$	$1271.3 \pm 58.5^{b,A}$
	9	$36.2 \pm 1.8^{a,C}$	$119.8 \pm 6.2^{b,A}$	$346.3 \pm 29.3^{a,A}$	$121.4 \pm 12.9^{b,A}$	$568.4 \pm 64.6^{a,A}$	$68.6 \pm 7.6^{a,A}$	$16.3 \pm 1.5^{b,A}$	$1346.5 \pm 121.6^{b,A}$
	12	$34.2 \pm 1.6^{a,ABC}$	$112.5 \pm 4.7^{b,A}$	$334.8 \pm 33.3^{a,A}$	$120.3 \pm 17.0^{a,A}$	$564.1 \pm 82.2^{a,A}$	$68.3 \pm 9.8^{a,A}$	$16.4 \pm 2.1^{a,A}$	$1322.2 \pm 150.2^{a,A}$

[a] Abbreviations are: WC, white cheese; CON, control cheese powder; WACP, whey-added cheese powder; MACP, maltodextrin-added cheese powder; TFFA, total free fatty acids. Values, in mg 100 g^{-1} fat, are the mean ± SD; means within powder formulation of each storage period and within storage period of each formulation with different superscript lowercase and uppercase letters, respectively, differ significantly ($P < 0.05$).

encapsulating effect of the added materials, the decrease in TVFFAs in MACP and WACP were lower than CON.

Table 3 showed that volatile FFAs ($C_{4:0}$–$C_{10:0}$) were significantly increased for all powders during storage while the greatest variations were detected in CON ($P < 0.05$). The same trend was observed for medium-long chain FFAs ($C_{12:0}$–$C_{18:3}$) in CON (Table 4). However, their variation for WACP and MACP samples were not significant during storage ($P > 0.05$). At the end of the 12 months storage period, the differences among powder samples for long chain FFAs ($C_{16:0}$–$C_{18:3}$) became statistically insignificant ($P > 0.05$).

Although it is well-known that the FFA contents in cheeses during ripening generally increase (Akın et al., 2003; Andic, Tuncturk, & Javidipour, 2011; Atasoy & Türkoğlu, 2008; Kondyli, Katsiari, Masouras, & Voutsinas, 2002; Sousa, Balcão, & Malcata, 1997), an increase in FFA in dairy powders is generally not desired. Paez et al. (2006) observed the variation of FFAs in whole milk powders during storage and reported that the FFA contents generally fluctuated during storage. They explained the fluctuation in FFAs with regard to the oxidation development in the powders. Although the FFAs were produced in reactions during storage, they were used as substrate for oxidation as they are precursors for oxidation (Paez et al., 2006). Similarly, there was a negative relation between the oxidation rate and the FFA increase according to the results of the present study. The biggest increase in the volatile FFA content during storage was observed in CON which had the lowest oxidation rate, while the lowest increase was obtained in WACP which had the highest oxidation rate during storage.

3.4. Sensory evaluation of cheese powder samples

The effects of formulation and storage on the sensorial flavour properties of cheese powders are founds in Table 1. It is obvious that the highest cheese flavour with negligible scorched, foreign and/or oxidised flavour scores were CON samples. In addition, CON had the highest cheese flavour and overall impression scores by the panelists (7.25–7.65). The main reason is the amount of cheese used in the production of CON. In fact, while cheese content in CON is 13% higher than that of WACP and 30% of cheese dry matter was replaced with maltodextrin in MACP. Scorched flavour was negligible for all cheese powder samples.

Although an insignificant decrease was obtained in the cheese flavour scores because of using whey during cheese powder production, the overall impression scores of CON were followed by WACP (6.35–6.70) among cheese powders. Panellists defined those samples as "none or very slightly" oxidised during storage. This was determined to be significantly different at only the 12th month of storage ($P < 0.05$). These oxidised flavour scores for WACP were in harmony with the TBA results (Fig. 2). The use of maltodextrin resulted in a slight foreign flavour in cheese powders and the lowest cheese flavour intensity scores. The overall impression score for the MACP was the lowest between 5.15 and 5.75 (Table 1). The reason for foreign flavour in MACP may be the perception of maltodextrin presence as foreign flavour or the degradation of maltodextrin during processing. According to the nonenzymatic browning results (Fig. 1), the highest reaction rate was obtained in MACP during storage and the foreign flavour sensed by panellists may have come from the compounds produced during nonenzymatic browning. However, the degree of nonenzymatic browning was not high and the degree of foreign flavour for MACP samples was characterised as "between none and slightly".

4. Conclusions

White cheese powders were produced by addition of maltodextrin or whey during emulsion preparation. The cheese powders were stored for 12 months and differences in free fatty acid content, nonenzymatic browning degree and oxidation degree during storage were investigated. Additionally, the effects of formulation on the sensory properties were determined.

Nonenzymatic browning and oxidation of the cheese powders increased during storage. Although the most significant impact of oxidation was detected for WACP samples, the oxidised flavour could not be perceived before the 9th month of storage. Moreover, foreign flavour was detected in MACP samples just after production of powder and increased during storage. While the reason for the foreign flavour detected in the fresh powder may be associated with the perception of maltodextrin as a foreign flavour, the reason for the increase during storage may be associated with the degradation of the product during nonenzymatic browning reactions. Furthermore, the volatile FFAs in the white cheese decreased up to 9% and 53.5% during cheese emulsion preparation and spray drying, respectively. Finally, the control sample had the highest cheese flavour and total impression scores followed by WACP and MACP.

Results showed that although the nonenzymatic browning and oxidation behaviours of the WACP and MACP samples were varied, this variation did not cause a detectable scorched and/or foreign flavour for WACP and scorched and/or oxidised flavour for MACP according to the sensory analysis. On the other hand, to prevent unfair competition, the amount of maltodextrin, which is non-dairy product, should be used as required by the process and should be indicated correctly on the label. In this research, only one ratio was used for maltodextrin addition. The usage of different ratios of maltodextrin should be investigated to improve the sensory qualities.

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