Palm Olein Quality Parameter Changes During Industrial Production of Potato Chips

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ABSTRACT: New legislation introduced in South Africa for the quality of used frying oils has resulted in the need to identify quicker, more suitable methods that correlate well with results from two official methods, namely, total polymerized glycerides and total polar components. Oil and product samples were taken at regular intervals during a commercial frying process in palm olein. Oil samples were analyzed for a number of different quality parameters viz. tocopherol content, dielectric constant, total polymerized glycerides, total polar components, tertiary butylhydroquinone (TBHQ) content, anisidine value, Rancimat induction period, and free fatty acid content, and the results statistically compared to results from official methods. Oil was expressed from product stored under accelerated conditions and analyzed for the same quality parameters. Fried product was also subjected to sensory evaluation to measure the degree of oil deterioration and sensory preference. The frying trial was successfully executed with refined, bleached, and deodorized palm olein and the frying oil used to a free fatty acid (FFA) content of 0.41%. Oil and product sampling were done at different FFA value levels. Frying oil quality was verified at the onset of the trial and at regular intervals. The frying oil total polar component value increased to approximately half of the limit set by the official regulation. This point was reached mainly due to the high starting value of the fresh oil. Frying oil total polymerized glycerides increased from below 1% to 2.1%. This increase is negligible when compared to the general trend for polyunsaturated oils. The alternative laboratory methods used for predicting oil quality can be rated as follows: total tocopherol content > dielectric constant > FFA > TBHQ content > anisidine value > Rancimat induction period. The first three methods correlated well with total polar component levels and it is recommended that the dielectric constant and FFA measurements be applied for monitoring oil condition during frying. It is possible that viscosity changes could be used for the monitoring of polyunsaturated frying oils. Evaluation of oil extracted from product revealed a negligible effect of non-oil components on oil quality parameters. The same was observed when product was stored at -10°C and at 37°C.

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KEY WORDS: Frying, oxidation, palm olein, potato chips, quality parameters, shelf life.

Palm olein is preferred for industrial deep frying of snack products in South Africa either in pure form or combined with other oils. Although several locally produced oils are available, at competitive prices, the main deciding factor in selecting frying oil is based on the shelf life requirements of the fried products. Another deciding factor is the recent introduction of regulations for controlling the quality of used frying oil in South Africa (1). The Department of Health selected two oil quality evaluation parameters, total polymerized glycerides (2) and total polar component contents (3). The two official methods proved to be adequate for regulatory purposes but a need for quick laboratory monitoring methods still remained. The National Brands Limited, Snack Division, research and development staff also expressed the need to determine the effect of storage on the quality of the oil absorbed by the product. It was postulated that the used oil could undergo oxidative deterioration during storage, with negative effects on the nutritional properties of the chips. National Brands management was convinced that the frying test should be based on a typical industrial protocol. The objectives were: (i) to conduct a chip frying test with specified palm olein (specified stability and quality as determined by National Brands incoming oil specification) and to conduct the sampling during the industrial run, (ii) to analyze frying oils by means of the two official methods (2,3) and by laboratory methods such as dielectric constant, anisidine value, viscosity, color and free fatty acid (FFA) values, (iii) to evaluate the nutritional quality of the frying oils by means of tocopherol (natural antioxidants) analyses, with changes in tertiary butylhydroquinone (TBHQ) levels (synthetic antioxidant) to be monitored, (iv) to compare Rancimat induction period measurements for fresh oils, used frying oils and oils isolated from product, (v) to compare oil quality parameters by means of statistical analysis, and (vi) to subject the finished product to sensory analysis to evaluate the quality of fresh product and product under accelerated storage, attempting to link the frying oil's degree of deterioration and sensory preference.

EXPERIMENTAL PROCEDURES

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Frying methodology. The frying trial was conducted at the National Brands Limited snack factory, Rosslyn, South

Africa. The potato chip line was used. Pure fresh palm olein refined bleached and deodorized (RBD) grade, supplied by Nedan Oil Mills, Potgietersrus, with characteristics given as Fr-0 in Tables 1–5) was used to fill the multizone fryer. Different temperature zones ranging from 180 to 168° C were applied. The fryer capacity was 2000 kg per hour and oil uptake was approximately 620 kg per hour, at a constant rate. Replenishing was done with high-FFA oil (make-up oil) with a FFA value of 0.31%. Fryer turnover time was 9 h and during frying no filtration of frying oil took place. It was initially planned to conduct the trial until the frying oil reached a FFA of 0.5%. This value could not be reached during the trial, as the cooker throughput was high enough to prevent the build-up of FFA. The raw potato

TABLE 1

Rancimat Induction Period Data for Frying Oils Sampled from the Fryer (Rancimat temperature 120°C, airflow 16 L/h)

Oil sample ^a	Average (duplicate or triplicate runs)
Fr-0	17.0 h
Fr-2.0	17.7 h
Fr-3.0	17.6 h
Fr-7.5	16.5 h
Fr-11.75	16.0 h
Fr-13.5	16.7 h
Fr-26.5	17.1 h
Fr-30.5	16.6 h
Make-up oil	11.5 h

^aNumbers are hours in the fryer.

TABLE 2

Anisidine Value (AV) and Dielectric Constant for Oils

Oil sample ^a	AV	Dielectric constant
Fr-0	7.3	0.0
Fr-2.0	12.5	0.18
Fr-3.0	11.7	0.20
Fr-7.5	14.1	0.39
Fr-11.75	19.0	0.49
Fr-13.5	17.9	0.67
Fr-26.5	12.8	0.56
Fr-30.5	10.6	0.55
Make-up oil	33.0	0.79

^aNumbers are hours in the fryer.

TABLE 3

Color Measurements (Lovibond scale) on Frying Oil Sampled from	
Fryer	

	Color r	eading
Oil sample ^a	Yellow	Red
Fr-0	5.4	1.0
Fr-2.0	10.9	3.0
Fr-3.0	15.2	3.0
Fr-7.5	10.0	5.0
Fr-11.75	11.0	6.5
Fr-13.5	13.0	7.0
Fr-26.5	14.0	7.0
Fr-30.5	11.0	6.6
Make-up oil	18.0	6.1

^aNumbers are hours in the fryer.

Oil sample ^a	TPC (g/100 g oil)	TPG (g/100 g oil)	TBHQ (mg/1000 g oil)
Fr-0	7.0	<1.0	46.0
Fr-2.0	8.0	2.1	19.5
Fr-3.0	8.0	1.5	16.9
Fr-7.5	8.7	2.1	7.4
Fr-11.75	10.9	2.1	3.8
Fr-13.5	11.0	2.9	15.6
Fr-26.5	10.6	2.1	17.8
Fr-30.5	12.1	2.1	14.0
Make-up oil	13.2	2.9	13.0

^aNumbers are hours in the fryer.

used for chip production normally contains up to 80% moisture whereas the final product is packed at less than 2%. Production data, oil top up rate and relevant manufacturing details were recorded by production staff.

Sampling procedure. Sampling of frying oil included 11 oil samples, representing fresh oil (Fr-0), make up oil (make up), and oil from 2.0 to 30.5 h in the fryer (Fr-2.0 to Fr -30.5). Frying oil samples (approximately 500 g of each frying period) were collected in 5×100 g amber glass bottles, fitted with screw caps and stored at approximately -15° C, until subsampling was done for analysis. 180 packets (30 g each) of potato chips were sampled when frying oil reached FFA values of 0.16, 0.26, 0.36 and 0.41%. The samples were sealed in metallized, polypropylene-laminated film (40 micron) and packets were not flushed with nitrogen. All finished product samples were kept at -10° C.

Accelerated storage of finished product. Potato chips from frying oil with four FFA levels were kept for 30 d at 35°C and 80% relative humidity. During storage the packets were inspected to identify packets with leaks (air and moisture penetration). Sampling and sensory analysis sessions were conducted through the storage period.

Expelling of oil from product. Oil was isolated from product subjected to accelerated storage (stored at 35° C) and from controls (stored at -10° C). Chip samples were crumbled, heated to 60° C and the oil expelled by means of a hydraulic press. The press cyclinder and piston, made of stainless steel, were preheated to 60° C. Oil was filtered by passing through a 0.45 mm disc filter.

Sensory analysis. The National Brands-trained sensory panel (10–12 members) was used to evaluate overall freshness and particularly oil flavor. The chip flavor and texture were considered as attributes of the overall freshness. A fivepoint scale was applied ranging from 5, being very good, to 1, being very bad. The cut-off point was 3, being acceptable. Control samples were taken from the frozen lots. Overall freshness also included characteristics of flavor and texture. The pickup of moisture during storage adversely affects the texture, resulting in a lower score for overall freshness.

Analytical methods. Total polar component levels (TPC) were done by applying the International Union of Pure and

Oil sample ^a	α-Τ	α-Τ-3	γ-Τ	γ-T-3	δ-T-3	Total (mg/100 g)
Fr-0	13.9	14.2	0.8	16.3	4.2	49.4
Fr-2.0	12.5	11.3	0.3	12.4	2.3	38.8
Fr-3.0	12.4	11.9	0.3	12.3	2.4	39.1
Fr-7.5	11.0	10.7	0.5	10.3	2.0	34.5
Fr-11.75	10.1	9.5	0.3	8.6	1.9	30.4
Fr-13.5	10.2	9.5	0.3	8.7	1.6	30.3
Fr-26.5	10.0	9.5	0.3	9.5	1.8	31.1
Fr-30.5	10.2	9.6	0.3	9.9	1.8	31.8
Make-up oil	7.8	7.0	0.2	7.4	1.4	23.8

TABLE 5
Tocopherol (T) and Tocotrienol Content of Oils (mg/100 g)

^aNumbers are hours in the fryer.

Applied Chemistry (IUPAC)–(Association of Official Analytical Chemists) (AOAC) method (3). Total polymerized glycerides (TPG) were quantified by using the method of Beljaars *et al.* (2). Dielectric constant measurements were obtained by using the Foodoil Sensor instrument (Northern Technologies International Corporation, Lino Lanes, MN) (4). Fresh oil was used to zero the instrument. Anisidine values (AV) were determined according to the International Standards Organization (ISO) method (5).

Viscosity measurements were made using a Cannon Fenske type viscometer (Cannon Fenske Instrument Company, State College, PA), bath temperature 37°C and flow time approximately 60 s. Color measurements of frying oil and oil extracted from chips was obtained with a Lovibond Model E Tintometer (White light cabinet, The Tintometer Ltd., Salisbury, England). Oil was isolated from chips by using a hydraulic press and ram arrangement. Solvent extraction was not used because of contamination of oils.

FFA determination was done according to the American Oil Chemists' Society (AOCS) method (6). Oil samples were dissolved in isopropanol/toluene (1:1) and the FFA value expressed as percent oleic acid. Tocopherol concentration was measured by applying a Council for Scientific and Industrial Research (CSIR) accredited method (7) based on a high-performance liquid chromatography (HPLC) method using fluorescence detection (8, 9).

TBHQ concentration was analyzed by applying an accredited method (10) based on a published method (11). Peroxide value (PV) was determined by means of the AOCS method (12).

Solvents and reagents were of analytical grade and mobile phases, HPLC-grade. The following suppliers were used: E. Merck, Darmstadt, Germany; BDH Chemicals Limited, Poole, England; Burdick and Jackson Inc., Muskegon, MI.

Statistical analysis. Frying oil quality parameters were graphically plotted by means of a computer program used by the Food Quality Programme of the CSIR for calibration curve plotting.

In addition to the visual plot (showing degree of scatter), the correlation coefficient for the variables were obtained. The correlation coefficient data were used to evaluate the ability of the monitoring methods (quick methods) to predict oil condition and discard point.

RESULTS AND DISCUSSION

Specifications of fresh oil. Specifications for fresh oil included Rancimat induction period of fresh oil to exceed 16 h at 120°C, FFA value <0.1% and PV 2 meq/kg or less. Legal limit of TBHQ in South Africa is 200 mg/kg.

The fresh oil (Fr-0) had an induction period of 17 h (Table 1) which met the specification. The FFA and PV were also within specification. AV of 7.3 units (Table 2) seemed to be high. A totox value $(2 \times PV + AV = TOTOX)$ for RBD palm oil was suggested as 10 maximum (13,14). The totox value for the fresh palm olein was 9.1 units and this implied that the oil was not of the best quality. Augustin et al. (15) reported an AV of 1.0 for fresh RBD palm olein. The fresh oil recorded a TPC value of 7.0 (Table 4) that was higher than expected. Augustin et al. (15) reported a TPC value of 5.5% for fresh palm olein whereas Marquez-Ruiz et al. (16) indicated that fresh palm olein contained 7.7% and Arroyo et al. (17) reported 9.27% TPC before frying. The high TPC was explained by the high concentration of diglycerides present in the starting oil. The sunflower seed and high oleic sunflower seed oils used by the authors (16) contained 2.8 and 3.1% TPC respectively. The palm olein used in the present study probably also contained high levels of diglycerides reflecting the condition of the crude oil.

FFA changes. If the FFA data is plotted against frying time (Fr-0 to Fr 30.5), a linear function ($R^2 = 0.91$; Fig. 1) or polynomic function ($R^2 = 0.97$) for the factory measurements is possible. The nonlinear curve suggested that the FFA values plateaued after about 25 h of frying.

Color changes. The frying oil color darkened swiftly within the first hours and plateaued after about 8 h. Both yellow and red increased significantly (Table 3).

Rancimat induction periods. The induction periods of samples from the fryer varied between 17.7 and 16.0 h (Table 1). The induction periods showed no trend and were therefore of little use to indicate oil quality changes. The make-up oil had a shorter induction period of 11.5 h.

Peroxide, anisidine, dielectric constant and viscosity values. PV changes of frying oils were of little help to indicate oil quality. It is known that PV is useful during initial stages of oxidation, but during frying the peroxide breakdown is so fast that it is useless as a monitoring method (13,14).

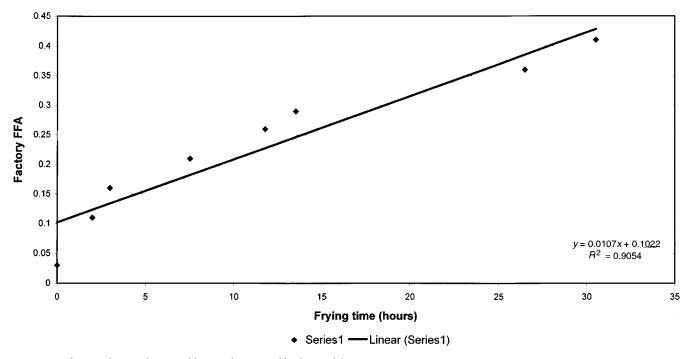


FIG. 1. Free fatty acid (FFA) changes of frying oil measured by factory laboratory.

The AV on the other hand is a more reliable parameter to measure oil quality changes against exposure time (14). The AV data in Table 2 is difficult to interpret. Maximum values were obtained at 11.75 h followed by a downward trend. It is difficult to understand how the AV could decrease while make-up oil, with three times higher AV, was used to replenish frying oil.

Viscosity changes in frying oil were minimal and also showed no pattern. Values ranged from 81 to 87 s. The increase in viscosity during the first 2 h leveled off to a constant value slightly lower than that of the make-up oil. The slight variation in viscosity values can be explained by the small variation in total polymerized glycerides. Viscosity changes correlated very well in the case of polyunsaturated oils (18) but the present study confirmed that palm olein formed very little total polymerized glycerides. The variation in viscosity values was not sufficient to indicate any trend.

TPC and TPG. The frying oil had a relatively high TPC level at the beginning of the trial (Table 4). The TPC increased during the frying period at a moderate rate (Fig. 2). A linear fit ($R^2 = 0.77$; Fig. 2) or parabolic function ($R^2 = 0.88$) is possible. The latter would suggest that TPC levels plateaued after 12 h of frying.

TPG values increased slightly during the first 3 h and remained constant above 2% for the rest of the period (Table 4). The TPG content of the make-up oil was also low and the addition of this oil therefore contributed little to the TPG of the frying oil.

TBHQ. The TBHQ content of the frying oil dropped sharply during the first 12 h of frying from 46.0 to 7.4 mg/1000 g oil (Table 4). Between 11.75 and 13.5 h a sharp increase occurred to a level slightly higher than that of the

make-up oil. A parabolic function fitted relatively well to the TBHQ values plotted against time (Fig. 3).

Total tocopherol. Table 5 presents the changes in individual tocopherols as well as the total tocopherols. If the total tocopherol values are plotted against frying time, a parabolic function fits well to the data (Fig. 4) with a correlation coefficient of 0.91. Tocopherol changes followed the same general trend as the TBHQ values but the sharp dip that occurred in the TBHQ curve did not show in the tocopherol curve. A previous industrial frying test with cottonseed oil (19) showed the same initial loss in tocopherols and TBHQ, followed by a steady increase.

It is of nutritional significance that the α -tocopherol level of the frying oil only dropped from 13.9 to 10.2 mg/100 g oil. The vitamin E activity of the oil absorbed in chips is therefore not seriously affected by the frying process. It has been shown (20) that the total tocopherol level of the frying oil is a valuable predictor of general oil quality.

Table 6 provides further confirmation that oil absorbed by the product retained its tocopherol level. Products made after 3 h frying (frying oil FFA = 0.16) retained more than 14 mg α -tocopherol per 100 g oil (46.5 mg total tocopherols). Products made after 30.5 h frying (frying oil FFA = 0.41) still contained 13 mg per 100 g oil (42.9 mg total tocopherols). Storage of the packed product at 35°C for up to 30 d did not lead to a pronounced reduction in vitamin E levels.

Correlation between oil quality parameters. Table 7 lists the correlation coefficients obtained when the different oil quality parameters are compared. In the majority of comparisons nine data pairs were used. The nine pairs represented the eight frying oils sampled during frying as well as the make-up oil data. The nine data sets revealed a very good to good correlation between total tocopherol values and six

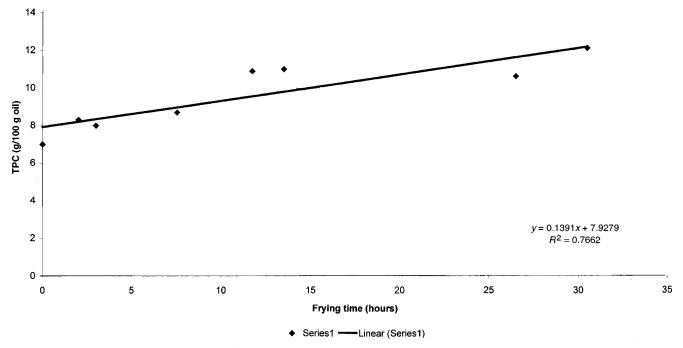


FIG. 2. Total polar component (TPC) changes of frying oil over time.

other oil quality parameters (Table 7). These results suggest that the tocopherol content of the palm olein is the best predictor of overall oil quality. The tocopherol level is also valuable as indicator of frying oil condition for legal purposes. It correlated very well with both official (TPC and TPG) parameters. This study further confirmed that FFA value is a reliable laboratory method for monitoring frying oil quality. The dielectric constant reading was even more reliable than FFA value for monitoring oil quality. Both quick methods, FFA and dielectric constant correlated very well with the TPC values.

Rancimat induction period data of the frying oils did not correlate well with the two regulatory methods, or with the quick laboratory methods. The exception is the AV which correlated well (R = -0.92) with the Rancimat data.

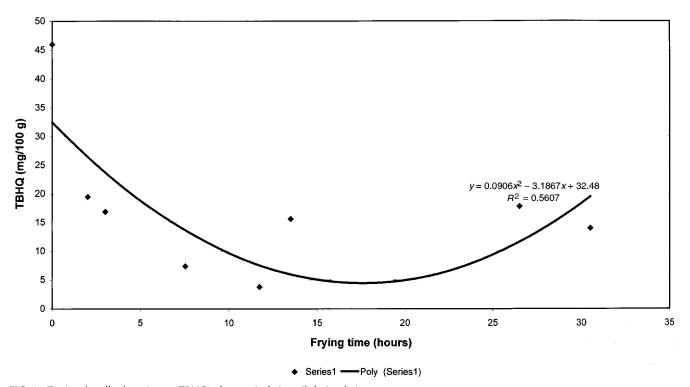


FIG. 3. Tertiary butylhydroquinone (TBHQ) changes in frying oil during frying run.

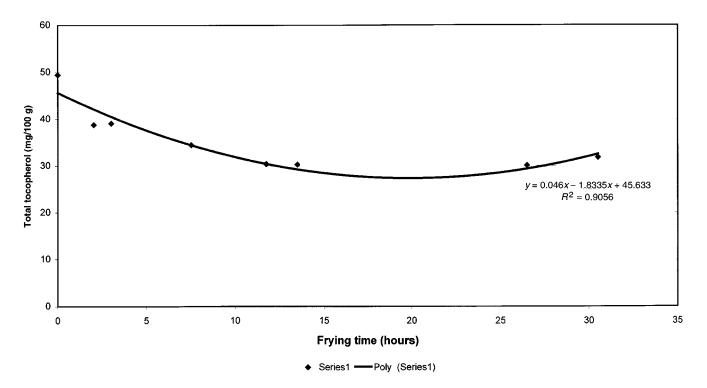


FIG. 4. Total tocopherol changes in frying oil during frying run.

Quality of oil from product. TPC values of oil expelled from stored potato chips showed that the polar components increased slightly. Chips produced from frying oil Fr-3.0 (FFA = 0.16) gave an oil with approximately 2% higher TPC than the original oil. Chips produced from frying oil Fr-30.5 (FFA = 0.41) yielded an oil with about 1% higher TPC (Table 6). The stored product, both low and high FFA, did not show a tendency to increase TPC on storage.

TPG values from expelled oil did not supply a clear pattern. The Fr-3.0 oil-produced chips showed a small increase in TPG in the expelled oil. In the case of the Fr-30.5 chips a lower TPG value was observed. It is also impossible to determine if TPG did increase during chip storage. (Table 6 data

TABLE 6

compared to Table 4 data). The small changes that occurred during storage at 35° C were also present in the control samples stored at -10° C.

TBHQ levels were affected by chip storage at 35°C. A reduction of 2.8 mg/kg TBHQ took place during storage of Fr- 30.5 chip. The Fr-3.0 chip did not show a similar downward trend (Table 6). Total tocopherol levels of stored product showed minimal changes (Table 6). This observation is important if it is accepted that tocopherol content is the quality parameter with the best overall correlation with other quality parameters (18,20).

Sensory evaluation. The storage of product was maintained until it appeared that overall freshness dropped to 3.0 or below (Table 8). The panel could not differentiate between

Frying oil used ^a	Product storage period and conditions	TPC (g/100 g oil)	TPG (g/100 g oil)	TBHQ) (mg/1000 g oil)	Total tocopherols (mg/100 g)
	At 35°C				
Fr-3.0	19 d	10.6	2.1	11.6	46.5
(FFA = 0.16)	24 d	9.2	2.3	11.9	46.2
	30 d	9.7	2.4	11.7	45.9
FR-30.5	3 d	13.1	1.2	15.4	42.9
(FFA = 0.41)	16 d	10.3	1.2	13.0	42.5
	24 d	12.6	0.9	13.6	44.7
	30 d	10.3	1.1	12.6	42.7
	At -10°C				
	(Controls)				
	14 d	15.3	1.5	14.1	41.0
	24 d	9.2	1.2	14.0	38.9
	30 d	11.8	1.7	14.0	44.4

TPC, TPG, TBHQ, and Total Tocopherol Content of Oil Mechanically Expelled from Product

^aFFA, free fatty acid. See Table 4 for other abbreviations.

	Total	Diel.				
	toc.	const.	TPC	AV	Ran. IP	FFA
Total toc.						
Diel. const.	-0.96					
TPC	-0.91	0.94		0.72	-0.69	0.95
TPG	-0.89	0.89	0.79		-0.56	
TBHQ	0.79	0.63		-0.64	0.24	
AV	-0.78	0.75			-0.92	
Ran. IP	0.63	-0.64				
FFA		0.96				

Correlation Coefficients Determined by Using Frying Oil Quality Parameters (8 frying oil
samples and make-up oil)

^aTotal toc., total tocopherol; diel. const., dielectric constant; Ran. IP, Rancimat Induction Period. See Tables 2, 4, and 6 for abbreviations.

TABLE 8 Sensory Evaluation Results—Overall Freshness Rating on a 1 to 5 Point Scale Followed by Oil Taste Rating Also on a 1 to 5 Point Scale

TABLE 7

		Overall free	shness score	
Day	0.16 FFA	0.26 FFA	0.36 FFA	0.41 FFA
3	4.0	3.8	4.0	3.8
7	4.4	4.2	4.4	4.4
10	4.2	4.2	4.2	4.2
14	4.3	3.7	3.8	3.8
17	4.0	4.2	4.2	3.7
19	3.2	3.8	3.3	3.7
21	3.7	3.3	3.4	3.3
24	3.3	3.3	3.0	3.3
26	3.4	3.4	3.3	3.2
30	2.9	3.0	3.0	3.3
		Oil flav	or score	
3	4.3	4.0	3.8	4.1
7	4.6	4.4	4.6	4.6
10	4.4	4.4	4.4	4.4
14	4.3	4.0	4.2	4.2
17	4.3	4.3	4.3	4.0
19	3.7	3.8	3.7	3.8
21	3.9	3.7	3.6	3.7
24	4.3	4.3	4.3	4.3
26	4.2	3.9	3.6	3.7
30	3.6	3.6	3.2	4.0

^aProduct stored at 35°C, 80% relative humidity, for 30 d period. For abbreviation see Table 6.

the lower (FFA = 0.16) and higher (FFA = 0.41) oil quality product. In the case of oil flavor the high FFA product scored a consistently higher rating up to the end of the 30 d storage period. It must be noted that good tasting chips are generally produced in oils with a moderately increased FFA level (21).

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