Utilization of spent bleaching earth from vegetable oil processing

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ABSTRACT

Introduction. The tests of Bulgarian bentonite, which is bleaching agent for vegetable oils, were conducted in industrial environments. The purpose is the compliance of standards to colouration vegetable oils.

Materials and methods. Sunflower oil which was prepared by hot pressing method. The colouration was determined by spectrophotometric methods. Colour number, refraction coefficient, acidity, peroxide number and phospholipid determined by standard methods.

Results and discussion. The results of the research carried out under industrial conditions provide the basis for the following main conclusions. A decrease in the carotenoids in bleached oils in comparison with unbleached oils, estimated according to their optical density was established by the spectra in the visible region at λ from 400 to 700 nm. During oil bleaching, a process of positional isomerisation and the formation of dienes at 235 nm and trienes at 258, 268 and 278 nm occurred with regard to the unsaturated olefins in the oil triglycerides. The enrichment of the grist with 5, 10 and 15% of SBE did not increase the moisture content because the bleaching process was carried out at 105-110^{o}C and 17 mm HgS residual pressure. The increasing in the total oil and mineral (ash) content depended on the percentage of grist enrichment. During the storage of the enriched grist, their acid and peroxide values increased slightly compared to the initial grist. It is preferable to apply 10% addition of spent bleaching earth to enrich grist or feed blends with differentiated function.

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Утилізація відбілювального пилу при переробці рослинних олій

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Introduction

Vegetable oils, such as sunflower, rapeseed, soybean, cotton, etc., contain pigments which belong to the group of unsaponifiables. The quantity of pigments in different oils varies widely. The most typical pigments are chlorophylls, carotenoids, gossypol in cottonseed oil, etc. Their presence in the oil depends on the characteristics of the variety, the oilseed growing conditions - and the technological methods of plant oil extraction. The degree of colouration of edible vegetable oils is one of the quality parameters regulated by the relevant standard (*BSS 1-77. Sunflower oil, BSS 14779-79. Soybean oil for food*).

To meet the quality requirements for vegetable oils, especially when the oils are intended for catalytic modification by hydrogenation, hydro re-esterification and for technical oils, they are submitted to bleaching with designated bleaching earth (bentonite), activated by heat and acid treatment [7].

In the Bulgarian vegetable oil industry, mainly bleaching earth produced by the Bentonote industrial plant for non-metallic minerals in the town of Kardzhali is used in the stage of oil bleaching during the refining process. After the vegetable oil bleaching, the spent bleaching earth (SBE) is separated from the oil by filtration and discharged as a waste product which is commonly disposed in solid waste landfill. As is well known, SBE saturated with oil from the refining process is susceptible to rapid oxidation and in the extreme, may even spontaneously ignite. This results in discharge of various toxic gases into the atmosphere, and strong odour because of oxidation. A lot of investigations have been carried out on SBE utilisation and recovery, mainly under laboratory conditions, including hexane extraction, sodium hydroxide or carbonate treatment, supercritical CO_2 extraction, high-temperature wet oxidative regeneration, etc. [13, 15].

A number of strategies for handling SBE have been reported, such as direct disposal at landfill or farmland, blending with oilseed/re-extract oil, use as animal feed supplement and as low-grade fuel for power/heat generation, preparation of graphitic sorbents for waste organics, biogas generation and etc. Which strategy any given plant might adopt will depend on a number of factors related to the location and operations of the plant, local environmental regulations, and economic considerations [14, 15, 16].

In this research we aim to investigate the changes in the oil during the bleaching process, the characteristics of the spent bleaching earth, and the possibilities for SBE utilisation by using it as a supplement to enrich the grist for animal feed production.

Materials and methods

The experiments were conducted on the vegetable oil refining line at the Debar Ltd. industrial plant, town of Parvomay, Bulgaria. For our research purposes, we used a batch of 1000 kg bleaching earth. The chemical composition (*BSS 6732-78. Finger bleach for mineral oils)*, particle size and pH of the aqueous suspension [10] were determined on the average sample taken from this batch. The sunflower oil obtained by final pressing was subjected to bleaching. The heat-moisture treatment of the oil material prior to pressing was carried out at a temperature within the 125-130^{o}C range. The 40 t batch of pressed sunflower oil was given preliminary treatment using a technology introduced by us. It involved the following steps: hydration, free fatty acid neutralisation in an aqueous salt solution, trace alkali removal to neutral reaction with phenolphthalein, drying, bleaching and filtration. The oil bleaching process and removal of spent bleaching earth were carried out on the Dutch Amafilter line. The parameters of the individual technological steps during the oil refining and preparation for bleaching as well as the bleaching conditions with 0.5 % bleaching earth in relation to the used oil weight have been described in detail in the literature [11]. Average samples of SBE were taken and its oil adsorption capacity, phospholipids, alkali content, acidity of the absorbed oil, insolubility in diethyl ether, moisture content and volatile substances were determined as described in [6]. Analyses of the obtained bleaching oil were carried out for determination of the colour number, coefficient of refraction, acidity, peroxide value and phospholipids using standard methods (*Aratyunyan N.S, Arisheva E.A (1979). Laboratory practicum on the chemistry of fats, Moskow*). The change of the pigments in the sunflower oil during bleaching was evaluated at λ = 400-700 nm in the visible region of the spectrum. By means of the UV spectrum and the catalytic isomerisation ability of bentonite with regard to olefins during bleaching, the quantities of conjugated dienes and trienes formed in the oil were also determined [9]. For this research, regular grist produced by the oil extraction plant in the town of Stara Zagora, Bulgaria was used. All samples were prepared according to the forepressing/extraction technology used in oilseed processing worldwide. The physicochemical characterisation of the grist was carried out by determination of the following parameters: moisture content, oil content, crude ash and crude protein content, using standard methods [6]. The content of phospholipids as phosphorus and stearooleoletsitin was determined as described in [8]. The acidity of the residual oil in the grist was determined by cold extraction with ethyl ether (via 24-hour soaking), filtering and titration with alcoholic solution of KOH.

Results and Discussion

The results of the evaluation of the physicochemical and grain size composition of the initial bleaching earth are presented in Tables 1 and 2.

Table 1
Physicochemical composition of bleaching earth

Composition	Content
K_2O, %	0.85
Na_2O, %	0.46
Fe_2O_3, %	3.85
SiO_2, %	59.98
Al_2O_3, %	16.95
CaO, %	3.92
MgO, %	2.89
Moisture, %	11.20
Bulk density, kg/dm^3	54.50
pH of aqueous suspension	4.52

Table 2
Particle size of bleaching earth

Sieve diameter, mm	0.2	0.16	0.09	0.071	0.063
Fractional composition, residue on the sieve, %	-	0.12	0.83	7.04	0.01
Fractional composition, passed through the sieve, %	-	-	-	-	92.00

The analytical results of the bleached oil batches and the change in the pigments are shown in Figure 1 and Table 3.

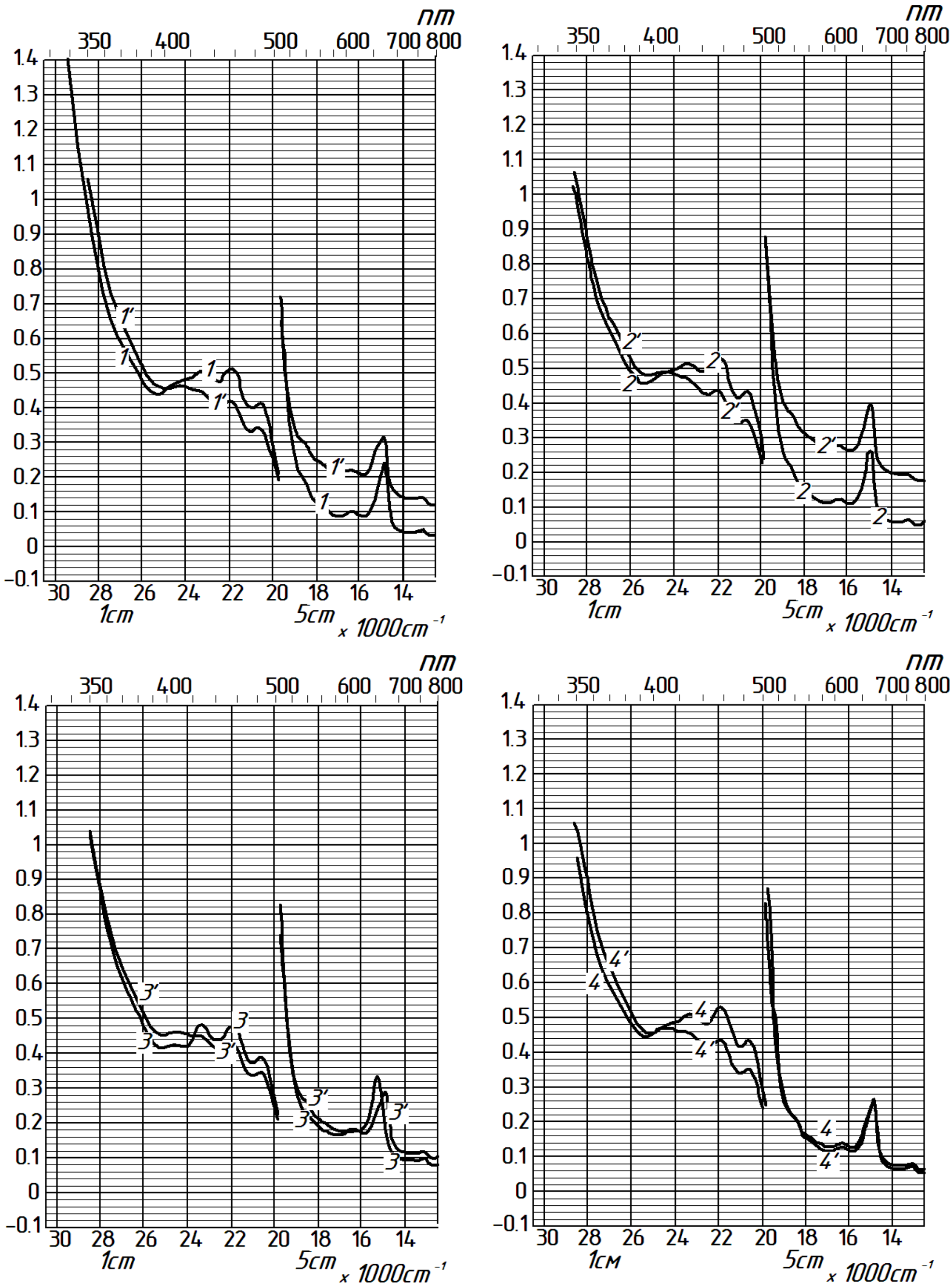

Fig. 1 (*a*). Change in the pigments in bleached pressed sunflower oils at λ = 400-700 nm:
unbleached – 1, 2, 3, 4; bleached – 1', 2', 3', 4'

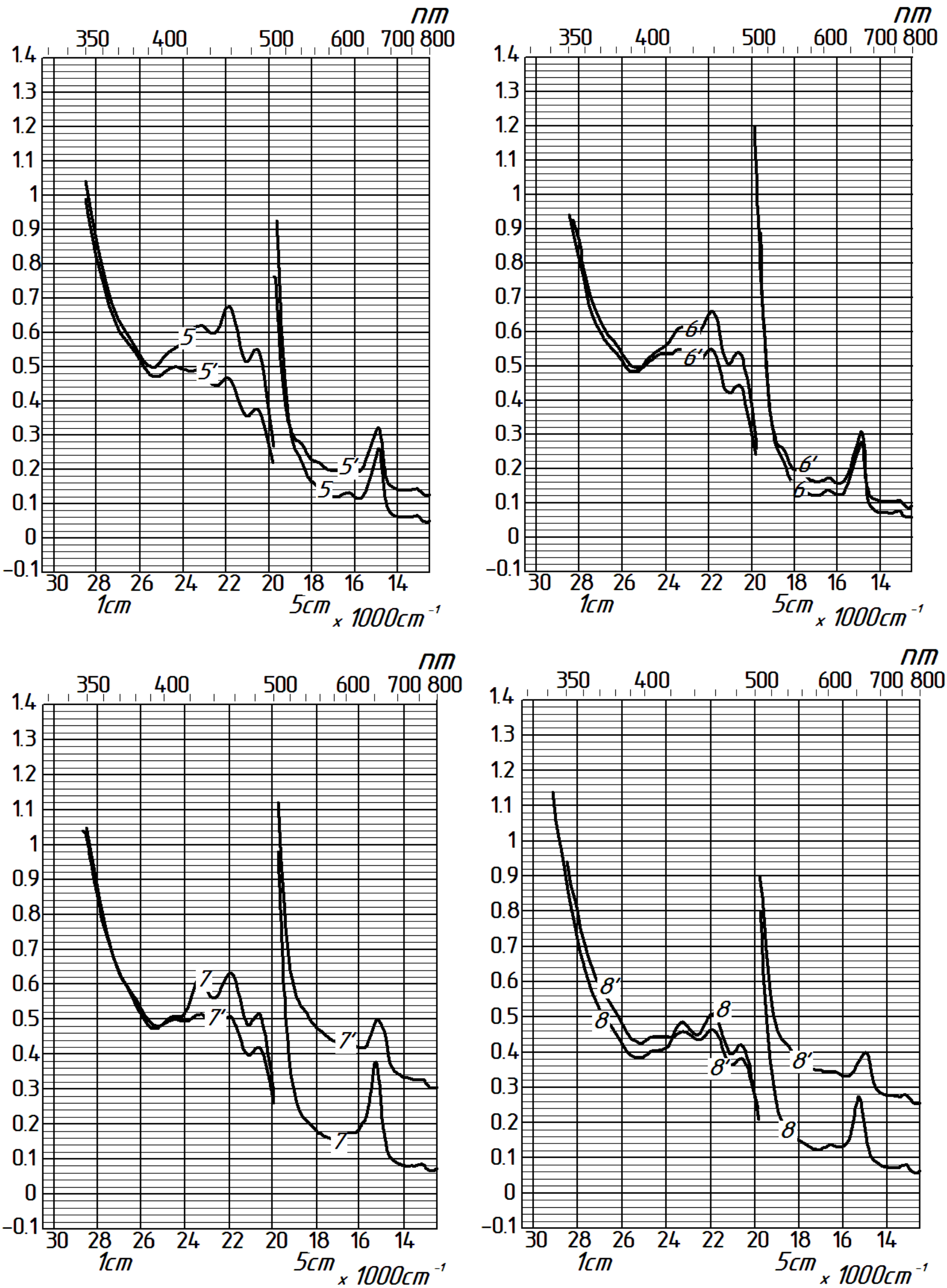

Fig. 1 (*b*). Change in the pigments in bleached pressed sunflower oils at λ = 400-700 nm:
unbleached – 5, 6, 7, 8; bleached – 5', 6', 7', 8'

Table 3

Physicochemical characteristics of bleached pressed sunflower oils

Series of bleaching	Parameter					Content	
	Colour number, *mg/J_2*	Coefficient of refraction $n_D^{20°C}$	Acid value, *mg/$_{KOH}$*	Peroxide value, *% J_2*	Phospholipids, %	Dienes at 235 *nm*	Trienes, at 258, 268,278 *nm*
Unbleached	25.5	1.4740	0.32	0.23	0.146	0.6	0.4
Bleached 1	7.5	1.4745	0.28	0.10	0.095	3.2	2.2
Bleached 2	8.0	1.4746	0.28	0.10	0.102	3.6	2.6
Bleached 3	7.5	1.4746	0.26	0.13	0.097	3.4	2.8
Bleached 4	7.0	1.4746	0.26	0.13	0.090	3.6	2.4
Bleached 5	7.5	1.4746	0.26	0.10	0.108	3.8	2.2
Bleached 6	7.5	1.4746	0.24	0.13	0.103	3.8	2.2
Bleached 7	7.5	1.4746	0.24	0.16	0.098	4.0	2.0
Bleached 8	8.0	1.4746	0.26	0.13	0.102	2.2	2.5
Bleached 9	7.5	1.4746	0.28	0.14	0.085	3.5	2.8
Bleached10	7.5	1.4746	0.24	0.16	0.090	3.2	2.5

After filtration of the individual series of bleached sunflower oil, the separated bleaching earth was discarded. The main aim of this study, as noted above, was the utilisation of SBE by using it as supplement to enrich animal feedstuff. Therefore we used bleaching earth separated from all bleaching series. After that, an average sample was taken and its composition was investigated. The results obtained are presented in Table 4.

Table 4

Physicochemical characteristics of spent bleaching earth

Series number	Moisture and volatile substances at 105 °C, %	Adsorbed oil at absolute dry matter, %	Acid value, *mg KOH*	Phospholipids, %	Alkali, by phenolphtalein	Insoluble substances at absolute dry matter, %
1	7.51	31.65	0.99	0.113	0.00	60.84
2	7.37	34.90	0.98	0.107	0.00	57.72
3	7.12	30.98	0.43	0.103	0.00	61.90
4	7.41	33.64	0.34	0.105	0.00	58.92
5	7.24	31.41	0.44	0.107	0.00	61.35
6	7.28	31.93	0.65	0.115	0.00	60.79
7	2.24	31.23	0.58	0.125	0.00	61.53
8	7.19	31.48	0.72	0.107	0.00	61.33
9	7.04	31.33	0.82	0.124	0.00	61.63
10	7.01	31.16	0.66	0.105	0.00	61.83

The main results of the investigation of SBE used in sunflower oil bleaching showed that SBE had absorbed some oil and phospholipids but no alkali was present, which was a favourable factor for its use as a component in grist enrichment.

The characteristics of the initial grist used are presented in Table 5.

For the development of the SBE utilisation method we used selected industrial grist models and created mixtures with the addition of SBE in 5, 10 and 15% amounts in relation to the cake weight. A key criterion in the blend creation was the SBE residual moisture and oil content. During the mixing, the uniform SBE distribution in the grist was observed. In order to obtain good homogeneity, the blends were passed repeatedly through a 3 mm sieve. The analytical data are reported in Table 6.

Table 5

Physicochemical characteristics of initial grist

No	Parameter	Sunflower grist	Soybean grist
1	Moisture and volatile substances at 105 °C, *%*	7.45	6.85
2	Oil content at absolute dry matter, *%*	2.56	3.45
3	Acid value, *mg KOH*	9.45	12.55
4	Crude ash at absolute dry matter, *%*	7.71	5.78
5	Phosphorus at absolute dry matter, *%*	0.004	0.006
6	Phosphatides as stearooleoletsitin, *%*	0.102	0.126
7	Crude protein at absolute dry matter, *%*	42.25	46.40

Table 6

Physicochemical characteristics of grist enriched with SBE

Type of grist	Added SBE, %	Moisture and volatile substances at 105 °C, %	Acid value, *mg KOH*	For absolute dry matter			
				Oil content,%	Phosphatides, %	Crude ash,%	Crude protein,%
Sunflower grist							
Initial	-	7.45	9.45	2.56	0.102	7.71	42.25
Enriched	5	7.52	9.65	3.20	0.108	7.85	42.05
Enriched	10	7.65	9.75	3.80	0.112	7.98	41.85
Enriched	15	7.65	9.70	4.10	0.116	8.05	41.70
Soybean grist							
Initial	-	6.85	12.55	3.45	0.126	5.78	46.40
Enriched	5	6.92	12.45	4.10	0.122	6.05	46.10
Enriched	10	7.10	13.18	4.42	0.118	6.20	46.00
Enriched	15	7.15	13.20	4.85	0.125	6.20	45.90

To monitor the changes that would occur during the storage of the enriched grist, we performed a periodic analysis of the acidity and peroxide content of the oil contained in the grist, for a total of three and a half months at 15-day intervals. An average samples were taken from each grist using the approved standard methods *(BSS 1552-86. Rules for acceptance and testing)*. The changes in the main properties of the grist enriched with SBE are presented in Figures 2, 3, 4 and 5.

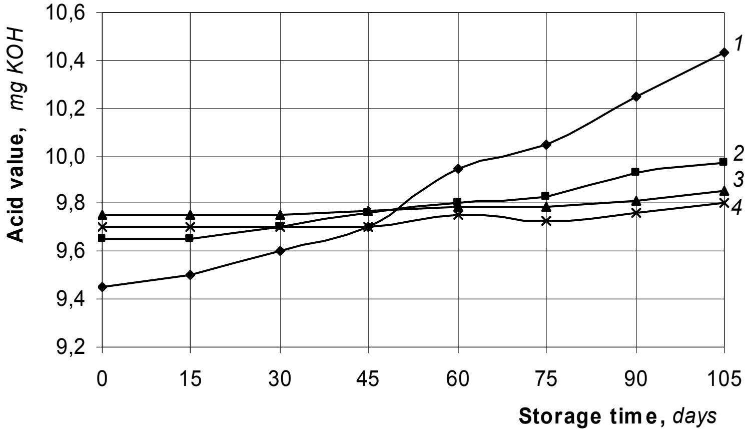

Fig. 2. Change in acidity during storage of sunflower grist enriched with SBE:
1 - Initial grist, Enriched with: 2 - 5% SBE, 3 - 10% SBE, 4 - 15% SBE

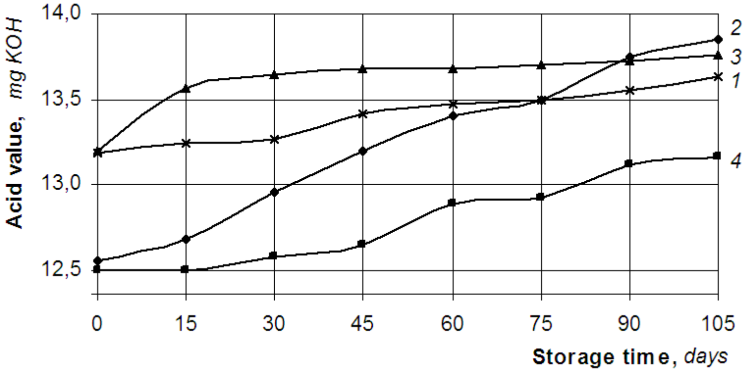

Fig. 3. Change in acidity during storage of soybean grist enriched with SBE

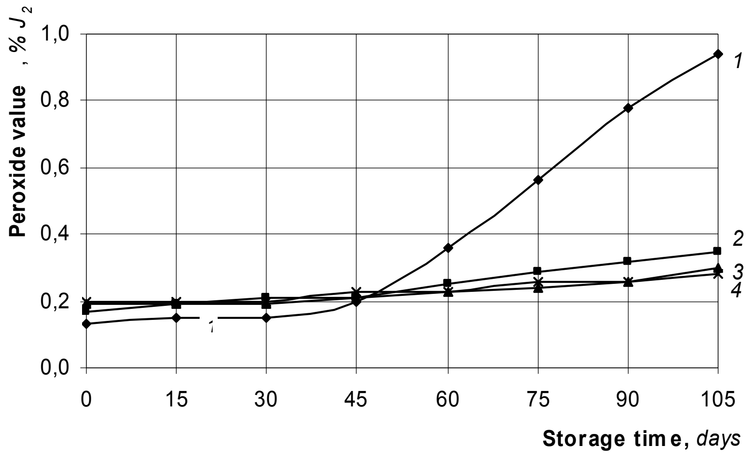

Fig. 4. Change in oxidation degree during storage of sunflower grist enriched with SBE

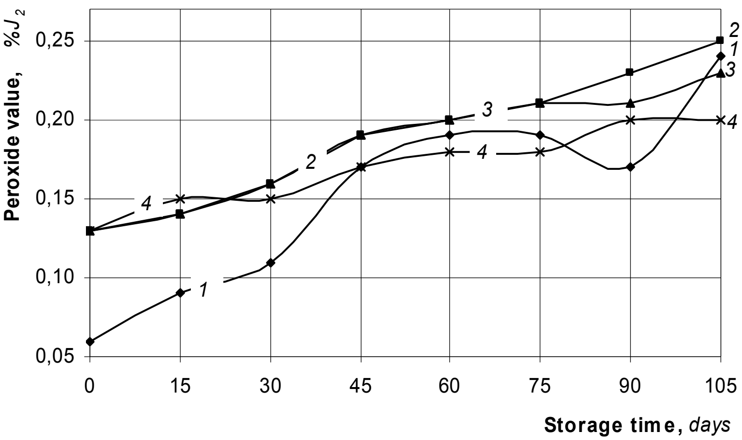

Fig. 5. Change in oxidation degree during storage of soybean grist enriched with SBE

1 **- Initial grist, Enriched with:** ***2*** **- 5% SBE,** ***3*** **- 10% SBE,** ***4*** **- 15% SBE**

Conclusions

The results of the research carried out under industrial conditions provide the basis for the following main conclusions. A decrease in the carotenoids in bleached oils in comparison with unbleached oils, estimated according to their optical density was established by the spectra in the visible region at λ from 400 to 700 nm. During oil bleaching, a process of positional isomerisation and the formation of dienes at 235 nm and trienes at 258, 268 and 278 nm occurred with regard to the unsaturated olefins in the oil triglycerides. The enrichment of the grist with 5, 10 and 15% of SBE did not increase the moisture content because the bleaching process was carried out at 105-110°C and 17 mm HgS residual pressure. The increasing in the total oil and mineral (ash) content depended on the percentage of grist enrichment. During the storage of the enriched grist, their acid and peroxide values increased slightly compared to the initial grist. It is preferable to apply 10% addition of spent bleaching earth to enrich grist or feed blends with differentiated function.

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