Physical Refining of Sunflower Oil Using Nitrogen as the Stripping Gas

Etelka DIMIĆ, Jovan TURKULOV, Đerđ KARLOVIĆ, Vladimir PUŠKAŠ, Vjera VUKŠA,
University of Novi Sad, Faculty of Technology
21000 Novi Sad, Bul. Cara Lazara 1 (Yugoslavia)

Abstract

Physical refining of sunflower oil was performed according to a simplified technological process in laboratory conditions and nitrogen was used for the deacidification. The change of quality, oxidative state and stability of oil was followed during the refining. The kinetics of free fatty acids and degradated oxidation products removal was followed during the deacidification. The obtained refined oil was of very good sensory characteristics and stability. However, it was found that the degradation and removal of the oxidation products is slower when nitrogen is used instead of water vapour.

Key words: sunflower oil, physical refining, nitrogen as stripping gas, quality, stability

Introduction

The replacement of water vapour with an inert gas for the distillation of evaporable components during deodorization became recently very interesting for the investigation. Bailey (1) considered that any inert gas, hydrogen or nitrogen can replace the water vapour, under the condition that it is cheap, that it can be condensed and easily removed from the system.

The use of nitrogen for oil deodorisation is justified by the quality of final product (condensate) as well as by the decreased environment pollution (2). However, several factors limitate the application of nitrogen. Namely, this gas cannot be condensed under the usual working conditions of the deodorizer. Therefore, certain technical solutions are necessary for the achievement of appropriate vacuum and the system for recuperation. Besides, the nitrogen has to be of certain purity for the use in the edible industry.

The results of semi-industrial application of nitrogen for oil deodorization are encouraging. Graciani et al. (2) obtained a rather good agreement between the effect degree e.g. distillation efficiency of free fatty acids (using nitrogen in the semiindustrial discontinuous deodorizer, with built in pumps maintaining the absolute pressure at 147 Pa), and the theoretical values. Cheng (3) established that the use of nitrogen for edible oil deodorization may be even more economic then of water vapour under certain conditions. The experiments were performed in a 150 t/day capacity deodorizer.

This paper presents the physical refining of sunflower oil with nitrogen, according to a simplified technology.

Material and technics

The crude oil used in the experiments was obtained by usual process from the oil processing plant.

Oil refining

The oil pretreatment was performed applying the multistep acid degumming with 50% citric acid solution, 0,3%/oil mass, according to the "Superdegumming" process, Unilever (4). A portion of the degummed oil was treated with amorphous silica gel - Trisyl (Grace & Co. - Germany) to complete the removal of undesirable components. The amounts of added Trisyl were 0,3 and 2,0% per mass of oil. The other part was treated with active bleaching earth - Tonsil standard FF, 1,5%/mass of oil.
A laboratory apparatus was used for the physical refining using water vapour e.g. nitrogen as the stripping agent (5, 6). When applying water vapour the vacuum was achieved with mercury diffusion pump and a two-stage vacuum pump. A rotometer was added to the system when nitrogen was used, while the necessary gas flow rate was regulated with a reducing valve on the nitrogen containing bottle and appropriate vacuum.
The parameters of physical refining were: temperature 240°C, absolute pressure 400 Pa, time 2h, condensation temperature -17°C. The nitrogen flow rate was 96-100 l/h e.g. the amount of water vapour 2,5%/h.
The applied low temperature (-17°C) was insufficient for the condensation of nitrogen, so it was removed from the system with the vacuum pump.

Investigation methods

The ISO methods were used for quality and oxidative state determination. The oxidative stability of the oil samples was determined using the Rancimat apparatus, at 100°C (8).
The sensory oil determination was performed according to the methodology proposed by the International quality control organization ISO (9).

Results and discussion

A. Quality and oxidative stability of sunflower oil samples prepared for physical refining.

All undesirable components, except the FFA, should be removed by the pre-treatment process. Due to the fact that the temperatures of physical refining are higher (230-250°C) than for "normal" deodorization (10), the removal of phosphatides, metal traces and oxidation products should be more complete than in case of classical refining. The change of quality, oxidative state and stability of oil samples during pretreatment for physical refining is presented in Table 1.

Table 1.

It is obvious that the phosphatides removal efficiency depends on the oil pretreatment way. The best phosphatides removal, this being one of the pretreatment goals, was achieved in sample A_1, which was degummed by the multistep acid degumming and treated with 2% of

Trisyl. The residual phosphorous content was 3 mg/kg and this is even less than the recommendation given in the literature. Namely, according to the latest literature data, the residual phosphatides content of the oil prepared for physical refining should not exceed 10 mg/kg (11).
The treatment of oil with smaller amounts of Trisyl (0,3%) and/or higher amounts of active earth (1,5%) did not result in expected residual phosphorous content (below 10 mg/kg). The phosphatides composition could be the explanation for this.
The applied sorbent affected also the oxidative stability of pretreated oil samples. Trisyl caused an insignificant increase of oxidative value (though its initial value was rather high) while the specific absorbances remained unchanged. However, the use of active earth resulted in the degradation of primary and increase of secondary oxidation products content, as well as in significant increase of absorbance at 270 nm. Trisyl had no effect on the colour of oil, but the active earth treatment yielded an appropriate bleaching degree. Similar effects were reported by Kővári et al. (12).

B. Quality and oxidative stability of oil after the physical refining

The characteristics of quality and oxidative state of samples after the physical refining with water vapour e.g. nitrogen are presented in Tables 2 and 3. Trisyl was used in the pretreatment process.

Table 2.

Table 3.

The quality of oil obtained using both stripping agents for the physical refining meet the basic quality demands (FFA, moisture content, peroxide value, colour) prescribed by the Roolebook for edible oil at the market (13).
The physical refining with nitrogen, like with water vapour, results in gradual decrease of FFA and degradation products content of the oil. After about 90 min of physical refining with nitrogen the FFA content dropped from 1% to 0,3%.
It is interesting that the colour of oil obtained after nitrogen stripping was lighter than of the oil obtained by water vapour. The A sample is especially interesting (Table 2) where high transparency of oil was achieved (83% with H_2O and 86% with N_2), though the phosphorous content was the highest, 25 mg/kg.
Table 4 presents the results of oil quality determination after physical refining (active earth was used in the pretreatment process).

Table 4

The overall quality of this oil is very similar to the one pretreated with amorphous silicagel. However, in this case, the high amount of conjugated compounds, as the result of pretreatment with active earth, remained in the oil after physical refining.
The sensory evaluation and stability are of special importance for the quality analyses of edible oils. The obtained oils were of very good sensory characteristics and stability (Table 5). The stripping agent has no influence on the sensory characteristics.

Table 5

The A_1 oil sample is outstanding again, since it was given the highest scores, and in the same time, its stability was the best. It should be underlined that the residual phosphorous content was the lowest (3 mg/kg), however, it was achieved with a rather high amount of Trisyl (2%). It is also interesting that sample A was also graded with rather high scores and is of good stability, though the phosphorous content was the highest (25 mg/kg).
On the bases of these, as well as of the results of our earlier investigations (14), we consider that 10 mg/kg of residual phosphorous in the sunflower oil for the physical refining as the limiting content (according to some authors) (11) is to severe, and practically unnecessary.
The stability of oil samples treated with active earth during the pretreatment for the physical refining is lower. Thus, higher amounts of active earth should not be used for the removal of nonhydratable phosphatides before physical refining.

References

1. Bailey, A.E., Industrial oil and fat products, Interscience Publishers Inc. New York, 1951

2. Graciani C.E., F.R. Berbel, A.P. Torrenteras, J.H. Lope, Deacidification by distillation using nitrogen as stripper. Possible application to the refining of edible fats, Grasas y Aceites, 42: 286 (1991)

3. Cheng A.T.Y., Deodorization of edible oil with nitrogen, 82nd AOCS Annual Meeting and Exposition, Chicago, USA, 1991

4. Segers J.C., R.L.K.M. van de Sande, Degumming- Theory and practice, World Conference Proceedings, Edible Fats and Oils Processing: Basic Principle and Modern Practices, edited by D.R. Erickson, AOCS, Champaign, Illinois, 1990

5. Turkulov J., Determination of optimal conditions of deodorization of oils with different peroxide value, on the bases of secondary products of autoxidation, components important for the evaluation of edible oil quality and stability, Ph.D. Thesis, Faculty of Technology, Novi Sad, 1974

6. Turkulov J., Đ. Karlović, Ž. Vrbaški, Laboratory deodorization, DGF Congress, Munster, 1992.

7. Pacquot C., J. Mercier, D. Lefort, A. Mathieu, R. Perron, Lipid analysis, Beograd, 1967

8. Karlović Đ., J. Turkulov, E. Dimić, Investigation of edible oils stability with Rancimat 617, Journal of Edible Oil Industry - Uljarstvo 25: 157 (1988)

9. ISO/TC 34/Sc 12, Secretariat 139/180E, Sensory Analysis DC, 1985

10. Young F.V.K., Physical refining, World Conference Proceedings, Edible Fats and Oils Processing: Basic Principle and Modern Practices, edited by D.R. Erickson, AOCS, Champaign, Illinois, 1990

11. Cleenewerk B., A.J. Dijkstra, The total degumming process - Theory and industrial application in refining and hydrogenation, Fat Sci. Technol, 94: 317 (1992)

12. Kővári K., Kis Lajosné, Tabajdi Miklosné, Refining of vegetable oils with synthetic silica adsorbent, Olaj Szappan kozmetika, 42: 1 (1993)

13. Roolebook on quality of edible oils, fats of plant and animal origin, margarine and related products, Yugoslav Official Journal Register 25/1992

14. Dimić E., Physical Refining of Sunflower Oil, Ph. D. Thesis, Faculty of Technology, Novi Sad, 1995.

Table 1. Quality and oxidative stability changes of sunflower oil during the pretreatment for physical refining

Characteristic	Oil sample			
	crude	pretreated*		
		A	A_1	B
FFA (% oleic kis.)	1.14	1.00	0.94	0.98
Moisture content (%)	0.15	0.08	0.08	0.08
Colour ($T_{455\ nm}$)	28	33	34	81
Total P/content (mg/kg)	84	25	3	18
% of removed phosphatides (compared to crude oil)	-	71	96	79
Peroxide value (mmol/kg)	5.18	5.24	5.53	0.37
Anisidine value (100 $A^{1\%}_{350\ nm}$)	0.88	1.19	1.00	6.53
Oxidation value	11.24	11.67	12.06	7.27
Specific absorbances				
$A^{1\%}_{232}$	1.76	1.76	-	0.59
$A^{1\%}_{270}$	0.22	0.20	-	1.93
Stability (h)				
Induction period at 100°C	8.3	7.1	6.9	8.4

* oil prepared for physical refining

A degummed oil treated with 0,3% of amorphous silica gel
A_1 degummed oil treated with 2% of amorphous silica gel
B degummed oil treated with 1.5% of active earth

Table 2. Quality and oxidative state of oil after physical refining with nitrogen e.g. water vapour sample A_1 - oil treated with 0,3% of Trisyl)

Analytical parameter	Physical refining with nitrogen Time (min)				water vapour
	30	60	90	120	120
FFA (% oleic kis.)	0.37	0.31	0.18	0.15	0.30
Moisture (%)	-	-	-	0.08	0.09
Colour (T%, 455 nm)	88.	84	85	86	83
Peroxide value (mmol/kg)	1.18	0.46	0.46	0	0
Anisidine value (100 $A^{1\%}_{350\ nm}$)	5.84	5.42	5.32	4.98	1.77
Oxidation value (2Pbr+Abr)	8.20	6.34	6.24	4.98	1.77
Specific absorbances					
$A^{1\%}_{232\ nm}$	-	-	-	2.1	1.58
$A^{1\%}_{270\ nm}$	-	-	-	.0.44	0.32

Table 3. Quality and oxidative state of oil after physical refining with nitrogen e.g. water vapour sample A_1 - oil treated with 2,0% of Trisyl

Analytical parameter	Physical refining with nitrogen Time (min) 30	60	90	120	water vapour 120
FFA (% oleic kis.)	0.47	0.31	0.27	0.25	0.30
Moisture (%)	-	-	-	0.08	0.04
Colour (T%, 455 nm)	90	89	88	88	86
Peroxide value (mmol/kg)	0.76	0.44	0.57	0	0
Anisidine value (100 $A^{1\%}_{350\ nm}$)	4.81	4.63	3.84	3.25	3.16
Oxidation value OV (2Pbr+Abr)	6.33	5.51	4.98	3.25	3.16
Specific absorbances					
$A^{1\%}_{232\ nm}$	-	-	-	1.77	-
$A^{1\%}_{270\ nm}$	-	-	-	0.48	-

Table 4. Quality of sunflower ol (treated with active earth) after physical refining applying nitrogen e.g. water vapour

Analytical parameter	Physical refining with nitrogen Time (min) 30	60	90	120	water vapour 120
FFA (% oleic acid)	0.50	0.30	0.19	0.09	0.30
Moisture(%)	-	-	-	0.08	0.09
Colour (T%, 455 nm)	87	84	86	88	85
Peroxide value (mmol/kg)	0.51	0.37	0.25	0	0
Anisidine value (100 $A^{1\%}_{350\ nm}$)	-	-	-	-	2.86
Oxidation value (2Pbr+Abr)	-	-	-	-	2.86
Specific absorbances					
$A^{1\%}_{232\ nm}$	-	-	-	2.07	2.50
$A^{1\%}_{270\ nm}$	-	-	-	1.42	1.34

Table 5. Sensory scores and stability of sunflower oil after physical refining

Characteristic	Oil sample A		A_1		B	
	Physical refining N_2	H_2O	N_2	H_2O	N_2	H_2O
Sensory scores (points)	19.7	19.6	20	20	19.5	19.5
Stability $IP_{100°C}$ (h)	9.3	9.5	10	9.6	8.0	8.6