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ACIDITY CHANGES IN RAPESEED OIL DURING STORAGE UNDER DIVERSIFIED CONDITIONS

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Changes in free fatty acids content in different kinds of pressed, extracted non-hydrated and hydrated rapeseed oil were studied. The same phenomena were studied in rapeseed oil composed of partially deacidified pressed and extracted batches. Oil produced by pressing was most resistant to changes in acidity while the most susceptible to such changes were the partially deacidified mixtures of pressed and extracted oils, which showed a double content of acids after one month storage in +20° and +37°C.

INTRODUCTION

An excessive content of free fatty acids (ffa) in vegetable oils may derive from hydrolytic processes and from advanced autooxidation reactions. It is influenced by the seed quality and the technology of oil rendering (pressing, extraction) and also by the refining treatment (hydration, neutralization, drying, filtration) as well as oil transportation and storage. During processing some hydrolysis enhancing substances may be removed (water, phospholipids and other hydrated substances), also the hydrolyzing and oxidating substances may be destroyed. They are particularly abundant in oil obtained from low-quality seeds. On the other hand, technological processing may destroy natural oil stabilizers and introduce emulsyfying agents conducive to hydrolysis. The latter may take place when fatty acid soaps formed during oil neutralization have not been washed out. The ffa content is one of the most important quality criteria in commercial operations with vegetable oils, this being next to the content of volatile and polluting substances. It seems, therefore, quite justi-

fied to examine the effect of temperature and mixing on oil acidity, taking into account all the previous stages of the technological process.

THE EXPERIMENT

SAMPLING

The investigations were carried out on the following samples from each kind of oil, taken at two different production dates:

1) raw rapeseed oil, produced by pressing and nonhydrated. The samples were marked T1 and T2.

2) raw extracted non-hydrated oil. The samples were marked EN1 and EN2.

3) raw extracted hydrated oil. Hydration was made with an addition of ca 2% hot water, centrifuged, and dried; The samples were marked EH1 and EH2.

4) raw rapeseed oil, a mixture of pressed and extracted oils, partially neutralized and meeting the industry's standard. The samples were marked EX1 and EX2.

Samples EX1 and EX2 were collected from railway cisterns prior to tanker-loading, other samples were taken during production of oil either from pipleines by gauge cocks (EN 1 and EN 2) or from oil tanks (P1, P2, EH1 and EH2). Samples from cisterns and tanks were collected with a zone sampler from three zones (bottom, center, top). The sample volume was ca. 5 litres.

Three samples of seeds were collected from different lots to estimate the raw material used in the regular oil production cycle.

CHEMICAL CHARACTERISTICS OF THE OIL AND SEED SAMPLES

Oil samples were analyzed chemically. Results of the analysis are presented in Table 1. The phospholipid content was determined by the AOCS method [2]. Other determinations followed the Polish standards [1]. The content of ffa is reported in units of oleic acid.

From sample III, 2 fractions were isolated: undamaged whole seeds and fragments of seeds penetrating a sieve of lmm mesh. The content of ffa was determined in both fractions.

EXPERIMENTAL CONDITIONS

Each sample of oil was divided into 7 sub-samples (0,7 l each): 1 for chemical characteristics, 3 for investigations at −4°C to +20°C and +37°C, with periodical aeration by shaking, and three for investigations in the same temperatures but without shaking.

Table 1. Chemical characteristics of oil samples

	Pressed oils		Extracted nonhydratable oils		Extracted hydratable oils		Commercial oils	
	P1	P2	EN1	EN2	EH1	EH2	C1	C2
FFA as the oleic acid %	2.57	2.66	2.66	2.53	2.71	2.49	1.67	1.69
Acid value	5.11	5.29	5.29	5.03	5.39	4.95	3.32	3.36
Moisture (%)	0.12	0.06	2.5	0.8	0.18	0.18	0.18	0.18
Impurities (%)	0.20	0.22	0.03	0.02	0.01	0.01	0.01	0.02
Phospholipids as phosphorous (mg/100 g)	24.7	31.7	44.5	43.7	14.3	13.2	11.1	27.4
Saponification value	176.5	172.7	174.0	174.0	174.1	174.0	174.5	173.0
Iodine value	104.7	109.6	108.3	107.5	108.3	105.8	103.0	105.2

The methodology provided 48 samples (4 types of oil × 2 production batches × 6 variants of the study), in which the ffa content was determined every day in the first week, and then every 1 to 4 days over 1 month. On the days when determinations of ffa were carried out, the subsamples to be aerated, were shaken over 30 min. with a wrist-shaker and placed in an appropriate temperature. The ffa determinations were used in outlining the acidity changes in different types of oil under diversified storage conditions (Fig. Fig. 1-4). The initial and final acidities in all samples are given in Table 2.

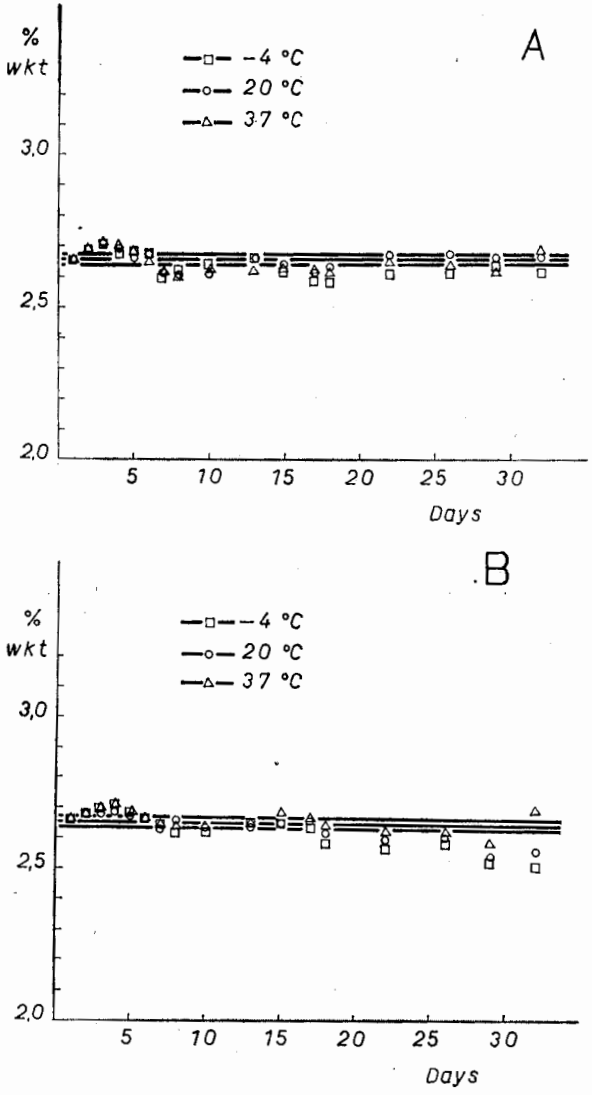

Fig. 1. Acidity of pressed rapeseed oil during storage (A) without and (B) with occasional shaking, wkt — free fatty acids (ffa)

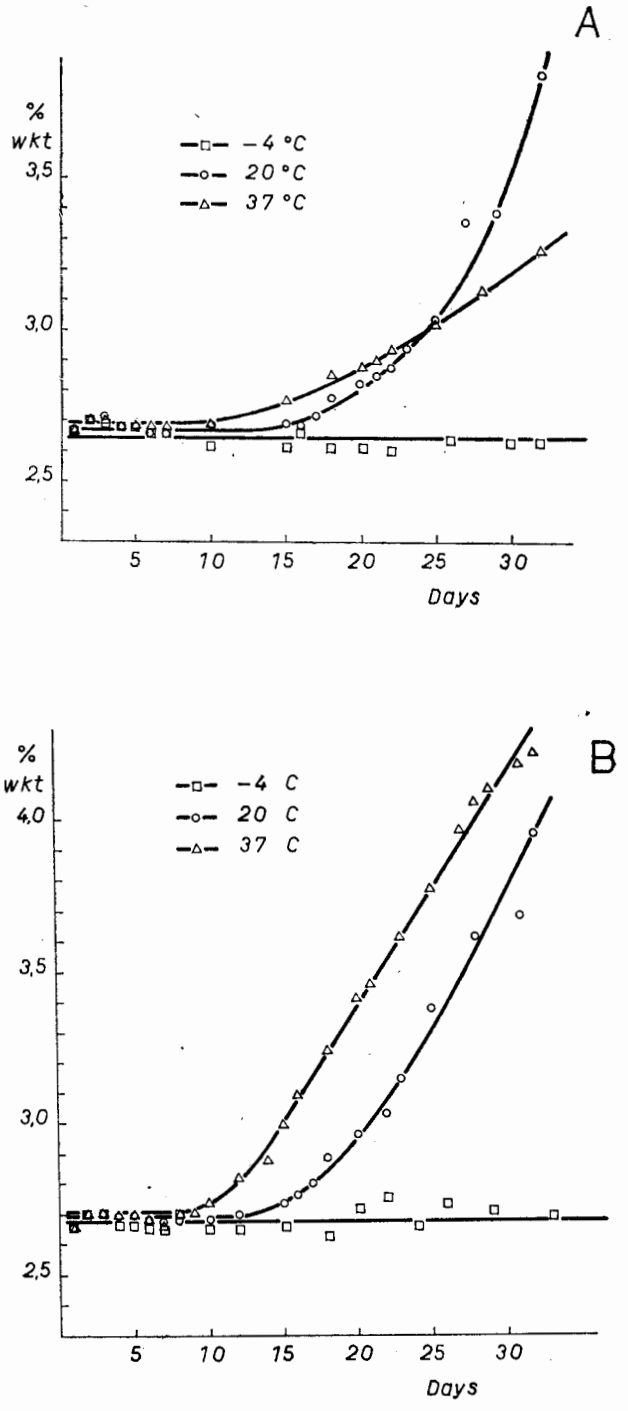

Fig. 2. Acidity of extracted non-hydrated rapeseed oil during storage (A) without and (B) with occasional shaking, wkt — free fatty acids (ffa).

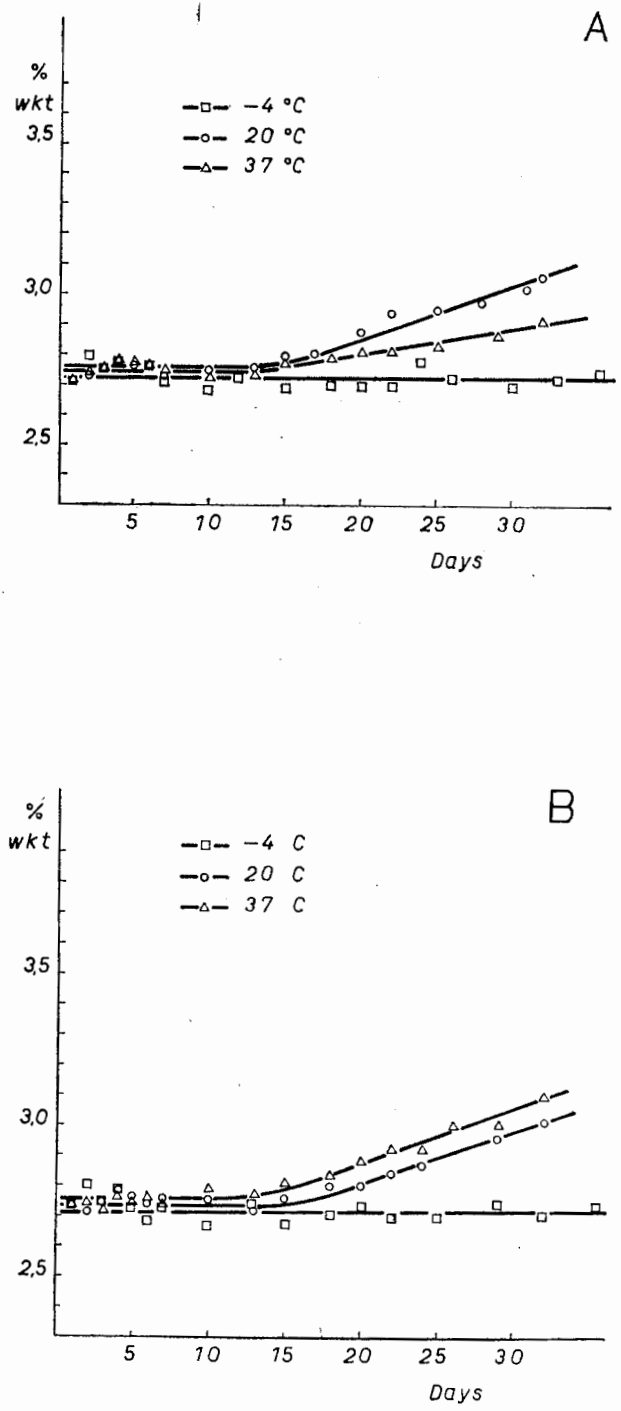

Fig. 3. Acidity of extracted hydrated rapeseed oil during storage (A) without and (B) with occasional shaking, wkt — free fatty acids (ffa)

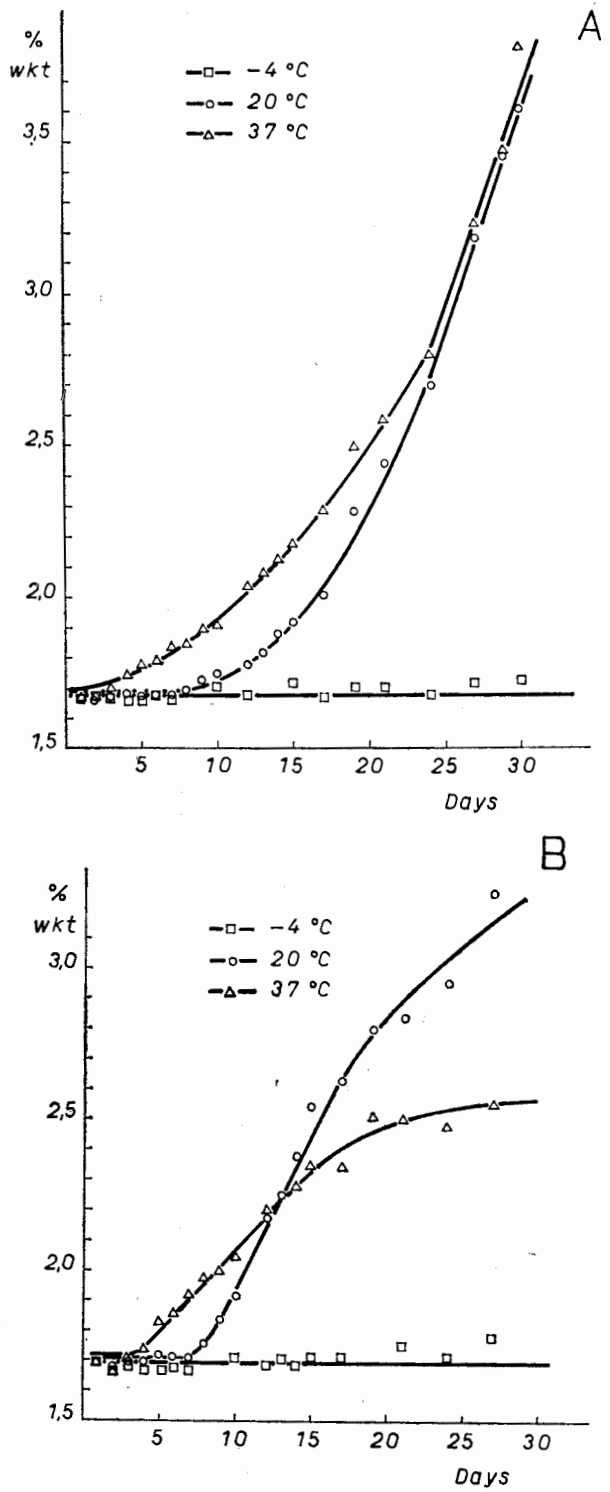

Fig. 4. Acidity of commercial raw rapeseed oil during storage (A) without and (B) with occasional shaking, wkt — free fatty acids (ffa)

Table 2. Initial and final FFA content of various rapeseed oil samples

Kind of oil		Initial FFA content %	Final*) FFA content %					
			non-shaken			shaken		
			−4°	+20°	+37°	−4°	+20°	+37°
Pressed oils	P1	2.57	2.58 38*)	2.60 34	2.61 34	2.48 24	2.60 33	2.61 33
	P2	2.66	2.61 36	2.67 36	2.68 32	2.51 36	2.68 36	2.70 32
Extracted non-hydrated oils	EN1	2.66	2.60 36	3.84 32	3.26 32	2.71 36	3.96 32	4.22 32
	EN2	2.53	2.40 30	3.45 26	3.14 26	2.51 30	3.75 26	3.87 26
Extracted hydrated oils	EH1	2.71	2.74 36	3.06 32	2.92 32	2.73 36	3.01 32	3.10 32
	EH2	2.49	2.40 30	2.64 26	2.60 26	2.40 30	2.83 26	2.77 26
Commercial oils	C1	1.67	1.73 30	3.61 30	3.82 30	1.77 27	3.25 27	2.54 27
	C2	1.69	1.70 27	3.67 32	3.94 32	1.67 27	3.30 24	2.53 27

*) lower figures present days of storage

RESULTS

RAPESEED

The fat content in the investigated rapeseed was 43.1% on the average, water — 5.7%. The seeds had a high — 2.7 to 3.9% content of ffa. The samples contained substantial amounts of broken seeds (5-10%), which were more susceptible to decomposition than the undamaged seeds. It is illustrated by the fact that oil from undamaged seeds has an average ffa content of 0.89%, and in broken ones — 28.40%. Damage of seeds can be regarded one of the major reasons for production of poor quality oils with higher ffa levels and greater susceptibility to changes during storage and transportation.

PRESSED RAPESEED OIL

Both samples have an initial ffa content higher than allowed by the standard. The comparison of initial and final accidities (Table 2) as well as the corresponding graphs (Fig. 1) prove that pressed rapeseed oil does not change its acidity in any significant way during storage over 1 month at −4°C, +20°C and +37°C, both in the case of additional aeration by shaking and without it. The chemical characteristics (Table 1) indicate that the oils do not contain positive levels of phospholipids, impurities, water and initial acifity as compared with other investigated oils. Lack of growing acidity in pressed oil is an evidence that they are stable on account of the activity of chemical and enzymatic factors.

EXTRACTED RAPESEED OIL

Initial acidity of oils produced by extraction is similar to that of pressed oils and exceeds the allowances for raw commercial oils. Samples of non-hydrated oil show the phospholipid content about 4 times higher than in hydrated oils. Considerable water content in no-hydrated oils may be caused by the use of steam in distillation of miscellas. No significant changes of acidity have been observed in −4°C. The growth of acidity for hydrated oils in +20°C and +37°C is not important and amounts to about 10% of the initial values, while for non-hydrated oils it is about 50% for the occasionally shaken samples and ca 40% in +20°C as well as ca 20% in +37°C in the case of non-shaken ones.

MIXED (COMMERCIAL) RAW RAPESEED OILS

The initial ffa content is below 2% and it complies with the standard. The same goes for volatiles and impurities. Oil samples are stable at −4°C but at +20°C the growth of acidity is about 95% (shaken samples) and 120% (non-shaken samples); at +37°C the figures are: 50% (shaken) and ca 130% (non-shaken). This is an evidence of exceptionally low resistance of mixed rapeseed oil to decomposition of triglycerides.

The graphs of acidity changes in the non-shaken samples of oil keep similar courses for +20°C and +37°C. In the case of shaken ones they differ. After some 20 days of storage acidity was observed to slow its increase at +37°C. This may prove the dominance of enzymatic over chemical factors in the mechanism of decomposition of triglycerides in such oil. At a higher temperature and an increased contact with air oxygen (aeration) possibly there occurs desactivation or weakening of enzymes. Poor aeration of a sample (non-shaken oil) does not lead to desactivation of enzymes splitting glycerides.

The very low stability of mixed oils results from partial neutralization. Such a treatment, as it turned out, induced the destruction of the natural

stabilizing system in raw oil and, consequently, a rapidly progressing decomposition of fats. In view of this fact, partial refining during production of oil should be dropped entirely.

CONCLUSIONS

1. The rapeseed oil used in the investigation had a significant level of acidity, exceeding 2% (in terms of oleic acid). It seems that this is largely due to excessively high level of damaged seeds.

2. Pressed rapeseed oils do not manifest major changes in acidity during storage for 1 month at +20°C and +37°C. Extracted rapeseed oils show less resistance to hydrolysis of glycerides in comparison with that of pressed oil.

3. It was observed that non-hydrated extracted rapessed oils stored for 1 month at +20°C and +37°C and subjected to aeration, show acidity increases greater than in the case of hydrated rapeseed oils stored under the same conditions. For the investigated samples the growth was ca 50% and 10%, respectively.

Raw rapeseed oils resulting from mixing partially neutralized pressed and the extracted oils reveal very low resistance to hydrolysis of glycerides. Acidity of such oils may double after storage for 1 month in +20°C and +37°C.

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ZMIANY KWASOWOŚCI OLEJU RZEPAKOWEGO W RÓŻNYCH WARUNKACH PRZECHOWYWANIA

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Streszczenie

Zawartość WKT jest w obrocie handlowym jednym z najistotniejszych kryteriów oceny jakości olejów roślinnych, oprócz zawartości substancji lotnych i zanieczyszczeń. Można przypuszczać, że trwałość oleju w czasie przechowywania i transportu w aspekcie możliwości wzrostu WKT uzależniona jest od historii oleju i jego składu, od kontaktu z powietrzem i temperaturą.

W pracy badano wpływ temperatury i mieszania na przechowywanie olejów z uwzględnieniem uprzednich etapów przerobu technologicznego. Badaniom poddano następujące próby oleju pobrane dla każdego rodzaju z dwóch różnych dat produkcji:

— tłoczony olej rzepakowy niehydratowany próbki T1 i T2,

— ekstrahowany olej rzepakowy niehydratowany próbki EN1 i EN2,

— ekstrahowany olej rzepakowy hydratowany z dodatkiem ok. 2% gorącej wody, a następnie odwirowany i suszony EH1 i EH2,

— olej rzepakowy surowy, otrzymany przez zmieszanie oleju tłoczonego i ekstrakcyjnego, częściowo odkwaszony odpowiadający normie branżowej, próbki EX1 i EX2.

Badania doprowadziły do następujących wniosków: Stosowane do produkcji olejów rzepakowych nasiona posiadają znaczną kwasowość przekraczającą 2%. Wydaje się, że jest ona w dużym stopniu wynikiem nadmiernego uszkodzenia nasion. Pobrane próbki surowych olejów rzepakowych tłoczonych i ekstrakcyjnych posiadają kwasowość 2,5-2,7%, tj. powyżej tolerancji normy. Przechowywanie oleju rzepakowego przez miesiąc w temperaturze −4°C nie powoduje wzrostu zawartości WKT. Oleje rzepakowe tłoczone nie wykazują istotnych zmian zawartości WKT podczas przechowywania przez miesiąc w temperaturze +20° i +37°. Oleje rzepakowe ekstrakcyjne wykazują mniejszą odporność na hydrolizę glicerydów niż oleje tłoczone.

Stwierdzono, że oleje rzepakowe ekstrakcyjne niehydratowane przechowywane przez miesiąc w temperaturze +20° i +37°, poddawane wytrząsaniu, wykazują wzrost kwasowości większy niż oleje rzepakowe hydratowane przechowywane w tych samych warunkach. Dla badanych próbek olejów wzrost ten wynosił odpowiednio ok. 50 i ok. 10%.

Kwasowość surowych olejów rzepakowych produkowanych przez zmieszanie częściowo odkwaszonych olejów tłoczonych i ekstrakcyjnych po ok. 1-miesięcznym przechowywaniu w temp. +20° i +37° może przekroczyć o ponad 100% początkową zawartość WKT.

Stosowana aktualnie technologia produkcji surowych olejów rzepakowych z nasion rzepaku o zawartości WKT uniemożliwiającej uzyskanie bezpośrednio, zarówno wskutek tłoczenia, jak i ekstrakcji olejów o kwasowości zgodnej z wymaganiami normy i w związku z tym obejmująca obróbkę oleju przez częściowe odkwaszanie jest niewskazana ze względu na znaczne osłabienie stabilności oleju i w konsekwencji, przyspieszenie jego rozkładu.