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EFFECT OF REFINING PROCESSES ON THE DISSOLVED OXYGEN CONTENT OF VEGETABLE OILS

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This paper reports results obtained in an oil factory during a survey of the refining process of vegetable oils. The aim of our investigations was to study the effect of the main technological steps on the dissolved oxygen content of sunflower and rapeseed oils, which is of great importance regarding storability.

Improvement of the oxidative stability of edible fats and oils also in preserved foods is a growing concern of the food industry. The protection of lipids against oxidation is not merely an economic problem. Apart from the loss caused by rancidification, the nutritional value of the products also decreases as a result of the destruction of essential fatty acids and vitamins.

In the vegetable oil industry, the up-to-date study of oil-processing and complete quality control include also the measurement of the dissolved oxygen content of intermediate and final products. A simple, fast and reliable direct method is provided by the use of membrane-covered polarographic sensors. This type of oxygen sensors was developed by Clark and coworkers in the early fifties [4-6], their various modifications have since widely spread, mainly used for water quality control and the determination of oxygen in aqueous media. Their successful application in fat chemistry and also in the vegetable oil industry has been reported since the mid-sixties [1—3, 7—10, 12, 13].

In our investigation, the technological steps of the refining process of sunflower and rapeseed oils were studied by measuring the amount of physically dissolved oxygen in different intermediate and final products. The effect of neutralization, bleaching, deodorization, winterization was studied and the bottled products were examined.

Measurements were carried out by means of a Radelkis dissolved oxygen meter, type OH-501. The scheme of the measuring cell is shown in Fig. 1. The cell consists of a silver cathode and a zinc anode. The electrodes and the supporting electrolyte — KCl gel — are protected by a teflon membrane. The selectively permeable membrane permits oxygen and other gases to pass through, but excludes the oil, consequently, no chemically bound oxygen can be detected. Oxygen reduction produces a current directly proportional to the partial pressure of oxygen in the sample [11]. The electrons needed in the process are provided by the electrolytic solution of the anode. Thus, the sensor works without any external source of current. The instrument has automatic temperature compensation, the cell can be used for measurement in solutions up to 50°C. The response time of the sensor is about 1 min., reproducibility of the measurements is ± 1%.

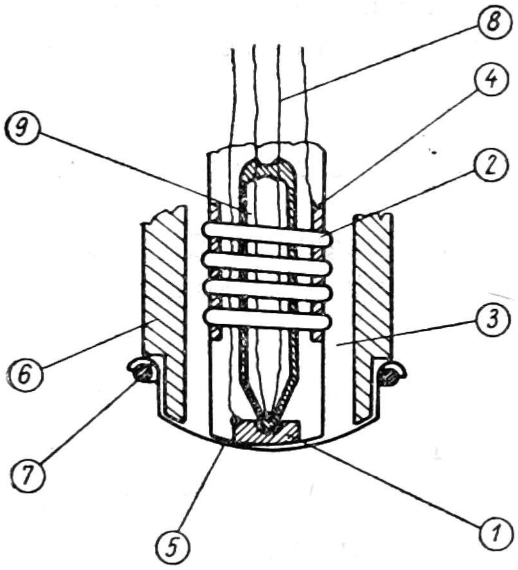

Fig. 1. Line diagram of the Radelskis oxygen sensor: *1* — silver cathode, *2* — zinc anode, *3* — electrolyte gel (KCL), *4* — silver contact of the anode, *5* — teflon membrane, *6* — gel holder, *7* — O — ring, *8* — electric terminal, *9* — thermistor

Figures 2 and 3 show the summarized results of our survey carried out in a three-week period under regular technological conditions. At all sampling places two parallel samples were drawn 10—15 times both from sunflower and rapeseed oils. Dissolved oxygen content of the samples was calculated as per cent air saturation.

Figure 2 shows a simplified scheme of the raffination process of sunflower oil. The dissolved oxygen content of the intermediate and

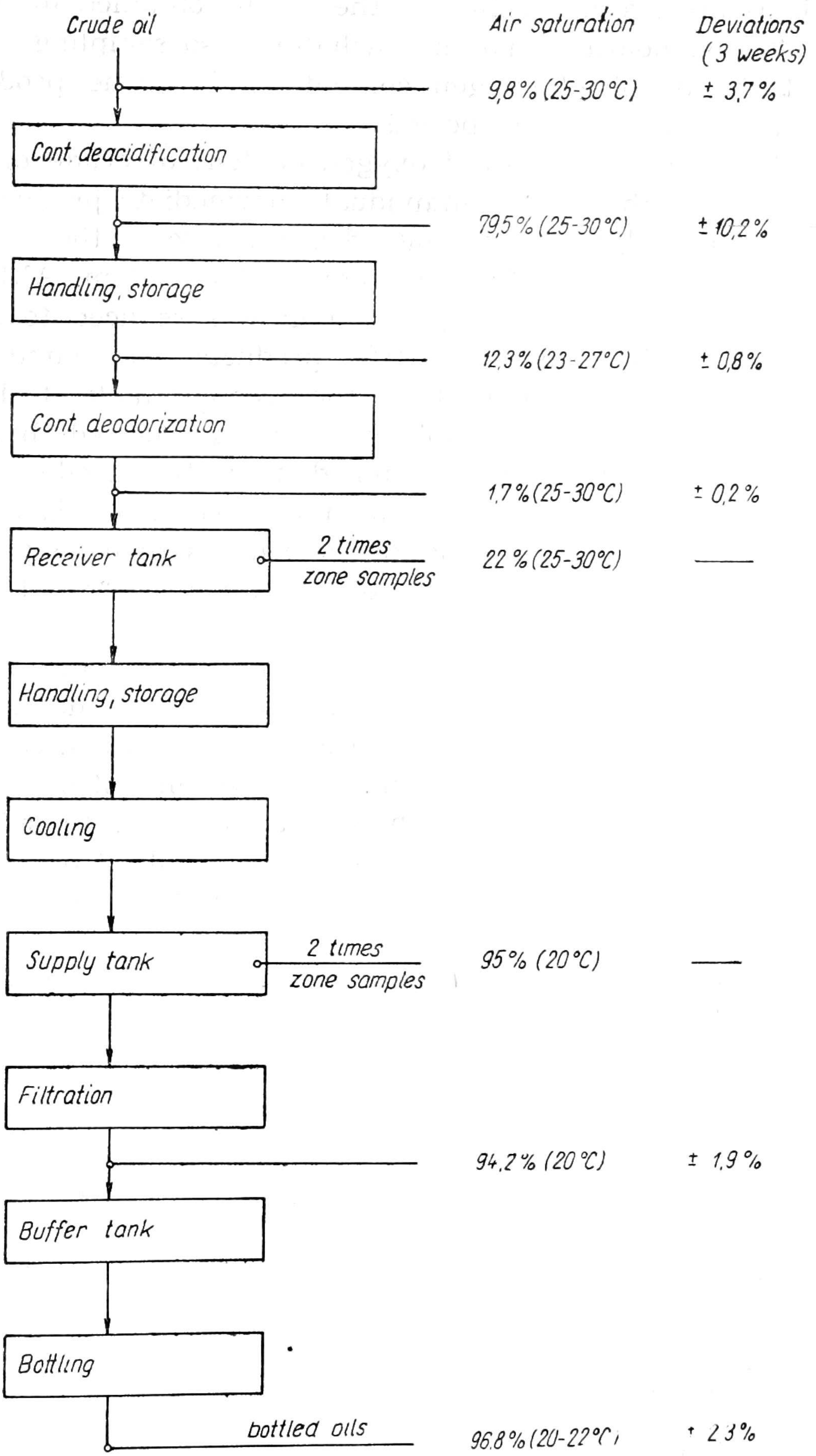

Fig. 2. Sunflower oil. Effect of technological steps of the refining process on dissolved oxygen content (summarized results of 3 weeks)

final products are average values of the results obtained, in the period examined. The standard deviations, including also sampling errors, indicate that the dissolved oxygen content of the same products was fairly constant within a longer period.

As can be seen, the dissolved oxygen content of crude oil was relatively low, while that of the individual intermediate products varied It increased considerably during deacidification, the reason of which may be clarified by further study of the system. Although, on deodorization, the dissolved oxygen content was reduced to a negligible amount, both winterized and bottled products were found to be saturated with air. Zone samples from the receiver tank of the deodorized oil and from the supply tank of the filters showed that the dissolution of oxygen from air starts immediately after deodorization and the high amount of dissolved oxygen in winterized oils is not due to filtration but to storage and handling procedures preceding winterization. The samples drawn from the different zones showed the same oxygen content.

Figure 3 gives the scheme of the refining process of rapeseed oil with results of the period studied. According to these data, the same changes occurred during deacidification and deodorization. Rapeseed oil was bleached in a batch- type system. No great amount of oxygen was dissolved during bleaching and subsequent filtration. In spite of the fact that rapeseed oil was not winterized, the dissolved oxygen of bottled products was high, presumably due to handling and storing operations.

The table summarizes the changes in air saturation, occurring du-

Table

Dissolved oxygen content of intermediate and final products of oil raffination (average values obtained during 3 weeks)

		Sunflower oil			Rapeseed oil		
		air saturation %	deviations %		air saturation %	deviations %	
			one day	3 weeks		one day	3 weeks
Deacidification	before	9.8 (25—30 °C)	±1.6	±3.7	18.7 25—30 °C		±3.3
	after	79.5 (25—30 °C)	±7.5	±10.2	83.5 25—30 °C		±4.8
Bleaching	before	na bleaching			2.9 25—30 °C		±0.9
	after				17.6 25—30 °C		±3.6
Deodorization	before	12.3 (23—27 °C)	±0.4	±0.8	8.8 23—27 °C		±4.5
	after	1.7 (25—30 °C)	±0.4	±0.2	1.8 25—30 °C		±0.3
Winterized, filtered oil		94.2 (20—22 °C)	±2.6	±1.9	no winterization		
Bottled oils		96.8 (20—22 °C)	±0.4	±2.3	87.7 20—22 °C	±2.7	±3.5

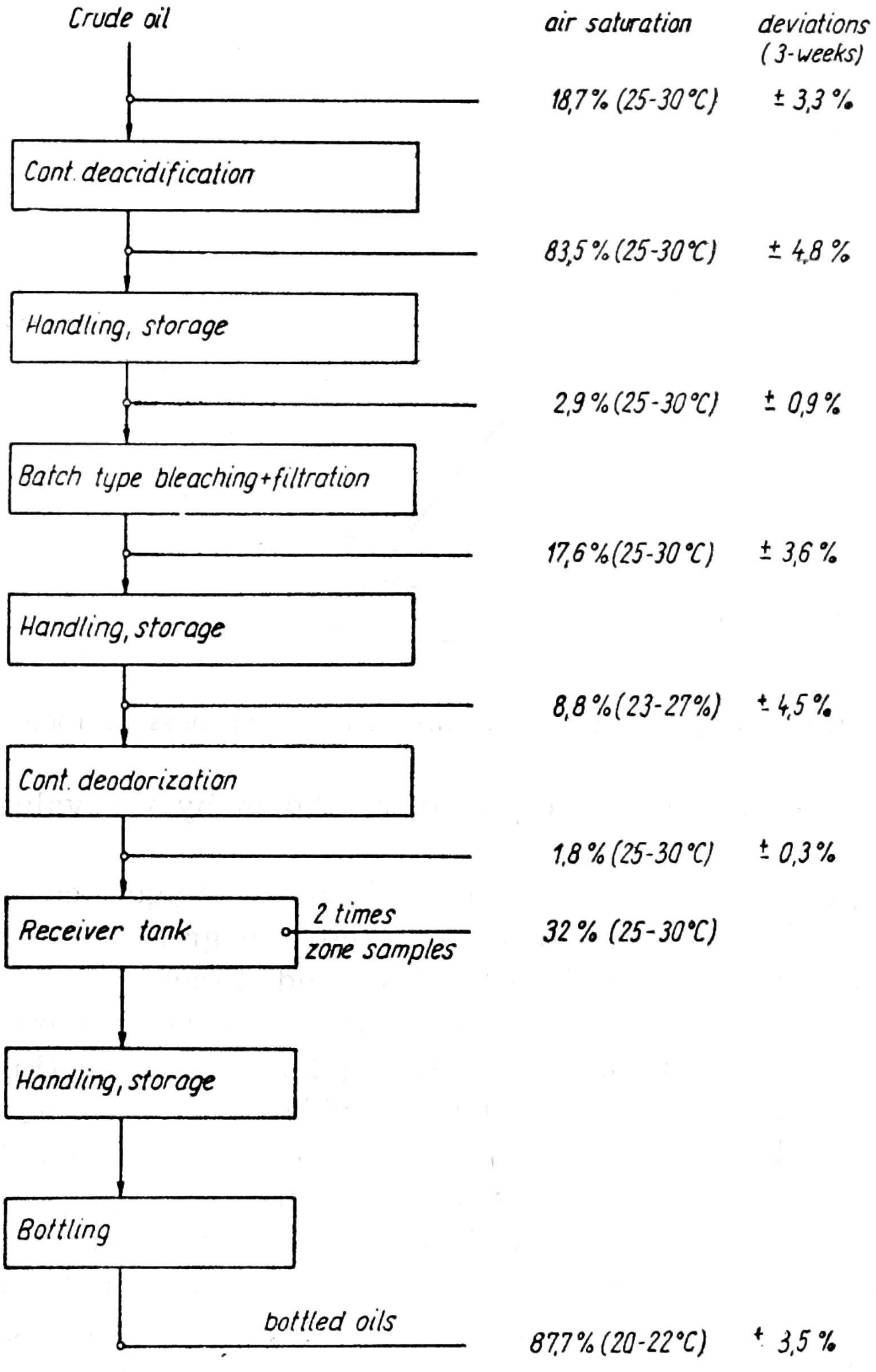

Fig. 3. **Rapeseed oil. Effect of technological steps of the refining process on dissolved oxygen content (summarized results of 3 weeks)**

ring the main technological operations in the raffination process of both kinds of oils. The deviations for one day were calculated from 5 measurements made at different times.

According to our results, it can be stated that:

1) under constant technological conditions, the dissolved oxygen content of the intermediate and final products is constant during one

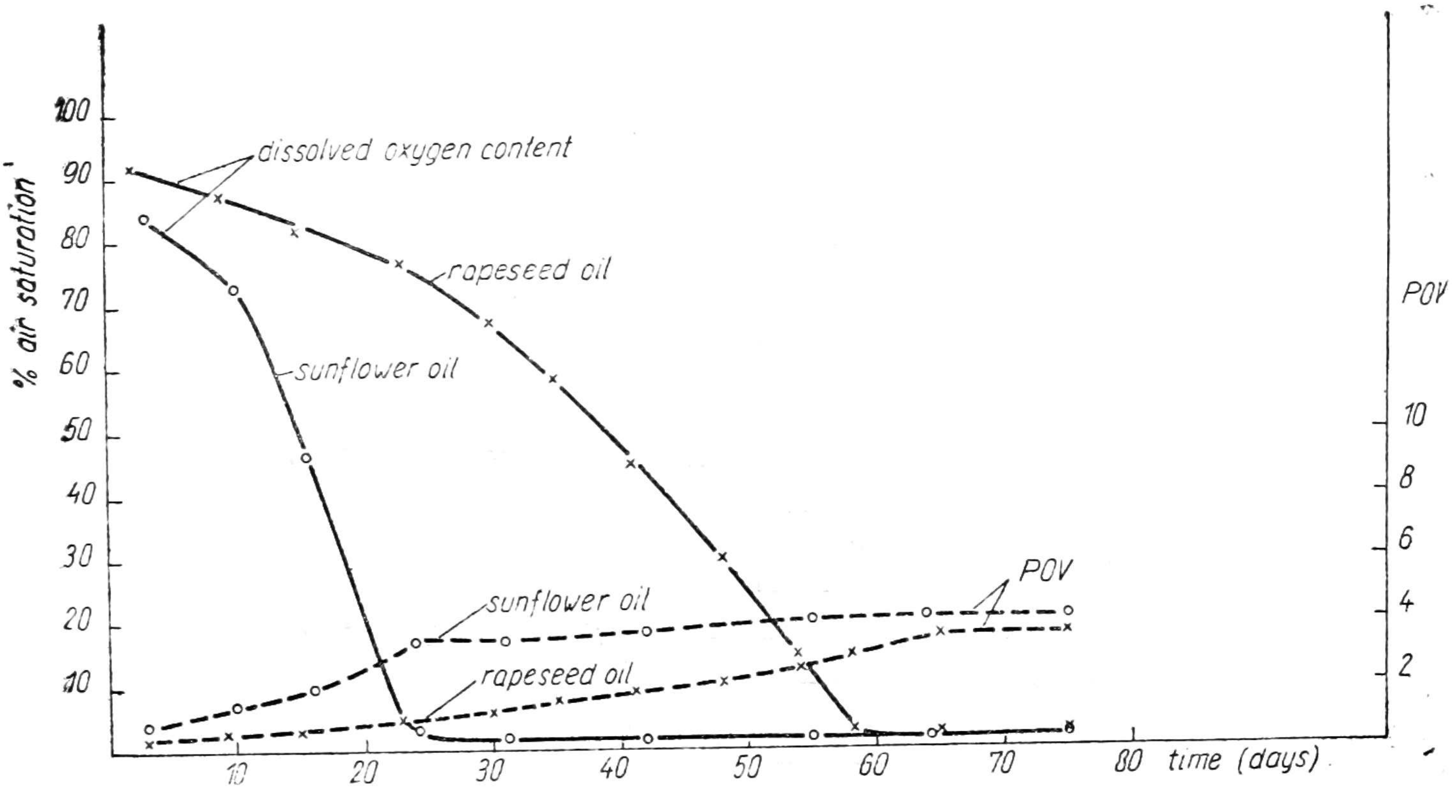

Fig. 4. Oxygen consumption of bottled oils held in darkness at room temperature

day as well as over a longer period, as shown by the values of standard deviations;

2) except for deodorization, the dissolved oxygen content of the oils increases during each raffination step, the greatest change occurs, however, during relatively short handling and storage.

We also studied the oxygen consumption of bottled products held in the dark at room temperature during longer storage (Fig. 4). Sunflower oil, which is less resistant to oxidation due to its fatty acid composition, consumed physically dissolved oxygen faster than rapeseed oil. 100% air saturation is about 40 ppm oxygen [3, 14], which is equivalent to approx. 5 POV. The change in the peroxide values of both kinds of oils proves that in the initial stage of autoxidation, the chemically bound oxygen arises from physically dissolved oxygen and the oxygen in the headspace gas as well as that possibly diffusing through the plastic bottle is presumably of less importance.

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WPŁYW PROCESU RAFINACJI OLEJÓW ROŚLINNYCH NA ZAWARTOŚĆ ROZPUSZCZONEGO W NICH TLENU

Postęp procesu rafinacji oleju słonecznikowego i rzepakowego śledzono przez pomiar fizycznie rozpuszczonego tlenu w poszczególnych produktach przejściowych, jak i w produktach końcowych. Próbki pobierano podczas neutralizacji, bielenia, dezodoryzacji, winteryzacji i z oleju butelkowanego. Pomiary przeprowadzano za pomocą polarograficznego czujnika tlenu Radelkisa, wyposażonego w katodę ze srebra i cynkową anodę pokrytą membraną teflonową w celu odizolowania elektrolitu do próby. Czujnik ten pozwala na szybki i bezpośredni odczyt ciśnienia parcjalnego tlenu. Stwarza to możliwość zastosowania go w przemysłowych laboratoriach kontroli jakości.

Wyniki pracy wykazują, że ilość rozpuszczonego tlenu jest różna w różnych próbach, nieznaczna po dezodoryzacji, wzrastająca podczas przechowywania i największa w oleju butelkowanym. Zbadano również zużycie tlenu przez olej butelkowany.

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ВЛИЯНИЕ ПРОЦЕССА РАФИНАЦИИ РАСТЕЛЬНЫХ МАСЕЛ НА СОДЕРЖАНИЕ РАСТВОРЕННОГО В НИХ КИСЛОРОДА

Резюме

Продвижение процесса рафинации подсолнечникового и рапсового масла следили путем измерения физически растворенного кислорода в отдельных пероходных и в конечных продуктах. Образцы отбирали во время нейтрализации, отбелки, дезодорации и винтеризации. Отбирали также образцы масла разлитого в бутылки. Измерения проводились с помощью полярографического датчика кислорода Раделькиса, оснащенного серебрянной катодой и цинковой анодой покрытой тефлоновой мембраной с целью изолирования электролита от образца. Указанный датчик позволяет быстро и непосредственно отсчитывать давление парциального кислорода. Это делает возможным его использование в промышленные лабораториях контроля качества.

Полученные результаты показывают, что количество растворенного кислорода является различным в разных образцах — назначительное после дезодорации, повышенное во время хранения и самое высокое в масле разлитом в бутылки. Исследовали также потребление кислорода разлитым в бутылки маслом.