A.N. Mironova,
T.B. Morozova,
F.B. Estrina, USSR

INFLUENCE OF SOME COMPONENTS OF SUNFLOWER OIL

A high-quality edible sunflower oil must have an optimum quantity of biologically active components and the least possible quantity of oxidation products, while retaining good taste and oxidation-resistance both when it is produced and stored. So, some regularities of oxygen and oil components interaction are close objects of industrial research.

The amount of oxygen dissolved in oil and the speed of its interaction with oil components were measured by means of electrochemistry. The former parameter was measured by measuring the force of electric current produced by the eduction of oxygen on the cathode of the testing unit. The unit consisted of a silver cathode and a chlorine-silver anode dipped in an electrolyte (0.1n KCl or a mixture of 0.1 M HCl with 0.05 M Na_2BO_7, pH=9.0) and was separated from the working compartment by an oxygen-penetrable diaphragm. Benzol was used as a standard liquid with a known solubility of oxygen (when mixed with oil, benzol provides a homogeneous liquid). We gradually put oil into oxygen-free benzol until it made 20% of the liquid, gauging the force of the electric current, by which the oxygen concentration was calculated.

The maximum solubility of oxygen in soya, sunflower, olive and cotton oils with the maximum peroxide number being 0.15% J_2 (at the temperature of 20°C) fluctuated in the narrow range of $(5.4-6.3) \times 10^{-3}$ mole per litre, in spite of their different fatty acid composition. When up to 5% of free fatty acids, 1% of phosphatides and up

to 25% J_2 PN of hydroperoxide ethyl-linoleate were added to refined sunflower oil, the solubility of oxygen remained stable at the temperature of 20°C. With the temperature rising above 50°C the concentration of oxygen dissolved in oil reduced drastically not only due to a change in its solubility but also to the increased speed of oxidation. This was borne out by a rise in oxidation products concentration in oil samples under study.

An analysis of raw and refined oils demonstrated that oxygen concentration varied widely, up to the maximum saturation (at 20°C). Deodorized oil kept in closed bottles and containing $2.6 \cdot 10^{-3}$ mole per litre of oxygen was compared to a similar oil maximally saturated with oxygen, also at 20°C. The analysis proved such an increase in oxygen concentration to be of much importance. In two months the taste of the oil with a higher concentration of oxygen was evaluated 2 points less than that of industrial oil, and in five months, 10 points less, with much more carbonyl compounds.

When oxygen was constantly added to the oil, at a certain moment the amount of free oxygen contained in the oil was equal to that of reacting oxygen, and the more the oil's peroxide number, the sooner the equilibrium was reached and the less free oxygen was found in the oil. At 20°C the quantity of free oxygen is roughly equal to that of maximum saturation, so the oil-oxygen interaction is very slow, with peroxide number of up to 0.25% J_2. Its speed rises sharply with peroxide number above 0.25% J_2, and when it exceeds 1% J_2, the oxygen contained in the oil reacts with its components within some minutes.

Linoleic acid concentration also strongly influenced the oxidation speed. Linoleic acid making 40% of the overall acid composition proved, from the point of view of their stability, to be maximal for mixtures of sunflower and olive oils

and for a mixture of their glycerides.

Iron and copper contained in oil also make for an increase in oxidation speed. With oxygen constantly supplied to the oil at 20°C; and iron chloride being added to it containing $4 \cdot 10^{-4}$% of 3-valency iron, concentration of free oxygen was 38% less 20 minutes later, and 8% less when stearate was added, containing a similar quantity of iron, whereas 2-valency iron provided but a negligible reduction of oxygen concentration. $5 \cdot 10^{-5}$% of copper lessened oxygen concentration in oil by 11%.

α-tocopherol, with its pronounced aniti-radical characteristics, is one of the physiologically most important components involved in the process of oxidation. A study of its interaction with peroxide radicals demonstrated that at the beginning of the oxidation process its quantity did not virtually change, as an analysis according to the Emmery-Engel method showed, with the peroxide number no more than 0.5% J_2; then a drastic decrease was observed. With the peroxide number of 1% J_2, about 15% of tocopherols were present in the oil.

In certain conditions, α-tocopherol can demonstrate pro-oxidant properties. We saw, during an analysis of deodorized oils with differing concentrations of α-tocopherol, from 10 to 120 mg%, that the speed of oxidation rises sharply and the oil stability decreases with the tocopherol concentration exceeding 80-90 mg%.

While in storage at 20°C, raw oils have the greatest speed of oxygen eduction, then come the neutralized oils, and then the deodorized ones. To explain this, we studied the speeds of oxygen eduction in 1% benzol solutions of triglycerides, phosphatides, sterols, carotinoids and chlorophyls, always at 20°C. These speeds were $0.09 \cdot 10^{-6}$ for sterols, $0.9 \cdot 10^{-6}$ for triglycerides, $5.4 \cdot 10^{-6}$ for phosphatides,

$5.9 \cdot 10^{-6}$ for chlorophyls, and $6.2 \cdot 10^{-6}$ mole per litre/hour for carotinoids, which proves that the most characteristic components of raw oils are most active in oxidation.

The analysis showed that oxygen dissolved in oil educes during chemical reaction with oil components on a zero level. When the oil is heated, the speed of the process increases in accordance with Arrenius' equation. Our experiments showed the energy of the activization of this process to be 10 kcal/mole for sunflower oil.