Processing Effects on Oil Quality

J.S.R. OHLSON, Vice-President, Research Laboratory, AB Karlshamns Oljefabriker, Karlshamn, Sweden

ABSTRACT

Processing can have rather strong effects on oil quality. It is very important to avoid deleterious factors such as long processing times, contact with oxygen, high temperature, light, and other oxidation catalysts if high quality oils are to be obtained. The initial quality of the oil-bearing material should be very high, and the processing should be continuous and rapid.

INTRODUCTION

A method based on nuclear magnetic resonance gives a very accurate figure on a small seed sample (1-2 g). The disadvantage is the higher cost of the instrument.

Color

Color is normally determined in a filter colorimeter, e.g., Lovibond.

Metals

The metals of special interest are copper, manganese, iron, chromium, and nickel. Determination of these metals is today mostly done by using atomic absorption spectrometry.

Determination of Peroxides

The initially formed oxidation products are the peroxides. It is well known that the content can be determined by official methods, e.g., AOCS or IUPAC.

Determination of Secondary Oxidation Products

When oxidation proceeds, the peroxides are split into what we call secondary oxidation products, which are components probably containing an aldehyde group.

To determine the amount of these compounds, a considerable number of methods have been developed and tried, e.g., TBA-test, benzidine value, anisidine value.

EFFECTS

The processing of oilseeds and other oil-bearing materials can have rather strong effects upon the quality of the oil obtained. These influences can be on oxidative stability, color, or crystallization behavior of the oil. The effects on oxidative stability are very well known, but Figure 1 shows the effect of hydrolysis on the polymorphic behavior of shea butter (1). At a free fatty acid (FFA) level of >8%, the typical shape of the curve has changed drastically and the associated special behavior in a pastry margarine has vanished.

Other, more indirect effects of processing on oil quality are contamination with traces of metals from the equipment or with polycyclic hydrocarbons from drying with smoke. Evans et al. (2) found that oil from damaged soybeans was 2-10 times higher in iron than crude oil extracted from sound beans (Table I). The source of the increased iron appears to be both damaged beans and steel processing equipment.

TABLE I

Phosphorus and Metal Contents of Commercial Soybean Oil

Sample	Phosphorus (ppm)	Iron (ppm)	Copper (ppm)
Crude			
Normal			
Midwest	633	1.5	0.05
Midwest	673	1.2	0.03
Midwest	647	0.9	-
Southwest	799	2.8	0.04
Southwest	700	2.4	--
Southwest	570	2.9	0.05
Damaged			
Southeast	622	2.6	0.05
Southeast	616	3.9	0.04
Southeast	693	6.1	0.08
Southeast	312	4.5	0.06

PROCESSING

To start with, a high quality oil-bearing material as such is very important for the quality of the oil. This initial quality depends on growing, harvesting, and storage conditions. The seeds can be damaged, green, too wet or dry, or moldy. This has already been described by Mr. Spencer and Mr. Gustafson.

Harvesting

The whole process of efficient production of high quality palm oil, for example, must be integrated.

The formation of FFA in the fruit starts with the

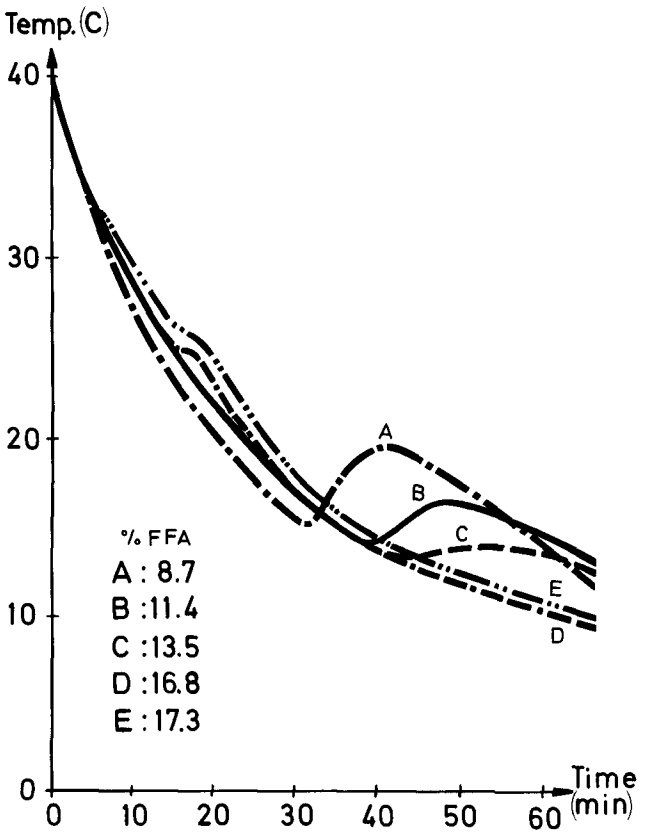

FIG. 1. Effect of hydrolysis on the cooling curve of sheanut oil. FFA = free fatty acid.

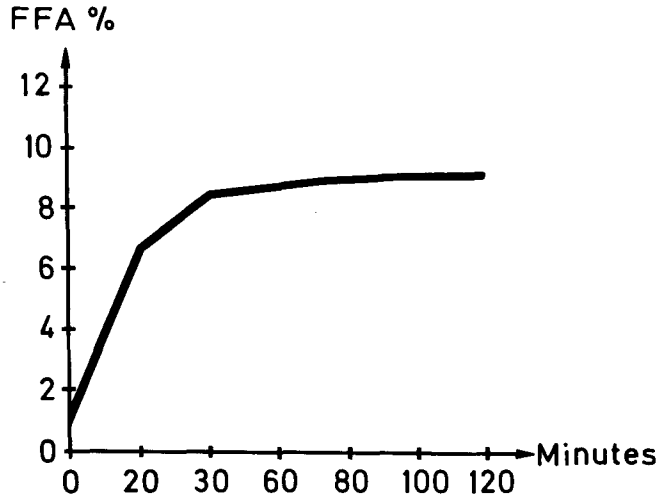

FIG. 2. Hydrolysis of palm oil in destroyed cells. FFA = free fatty acids.

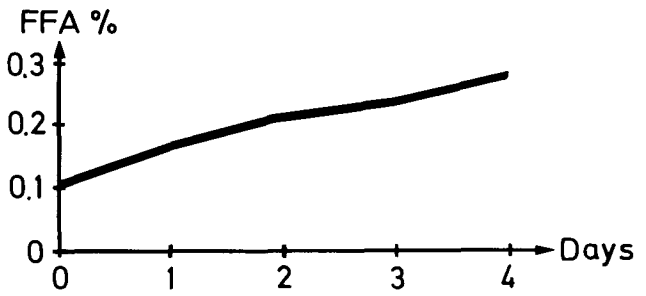

FIG. 3. Increase in free fatty acid of palm oil from unbruised fruit.

destruction of the cells which, in addition to oil, contain a protoplasm rich in lipolytic enzymes. The acidification is limited to the cells destroyed, and it is most rapid during the few minutes immediately following the breakage; the near maximum FFA content is reached within 40 min, as shown in Figure 2 (3).

The most important anti-FFA measure that can be taken under practical working conditions in an oil palm grove is to reduce handling and bruising of the fresh fruit bunches to the absolute minimum. The increase in FFA of the oil from unbruised fruits came to <0.2% in the course of 4 days, as shown in Figure 3 (3).

Seed Storage

The conditions that are most deleterious to the quality of an oil during storage of the oil-bearing material are a high moisture content, high temperature, and oxygen. Only the moisture content can be practically controlled. If this is not done, particularly the chemical lipolysis or microbiological degradation will lower the oil quality (Fig. 4) (4).

Seed Cleaning

It is important to remove any foreign material such as straw, sand, or stones before extraction. It is also of great importance to remove the "fines" and small weed seeds, since the quality of their oil is often very low. Besides having a high level of FFA, they very often contain oil with large amounts of chlorophyll and high peroxide values.

Extraction

As already pointed out, it is essential to start with well ripened, high quality seeds to get an oil of high quality. Further, it is essential to use optimal processing conditions and parameters throughout the processing. The earlier the oil is exposed to damage, the more serious it is for the end products. In other words, the basic quality of the oil is not

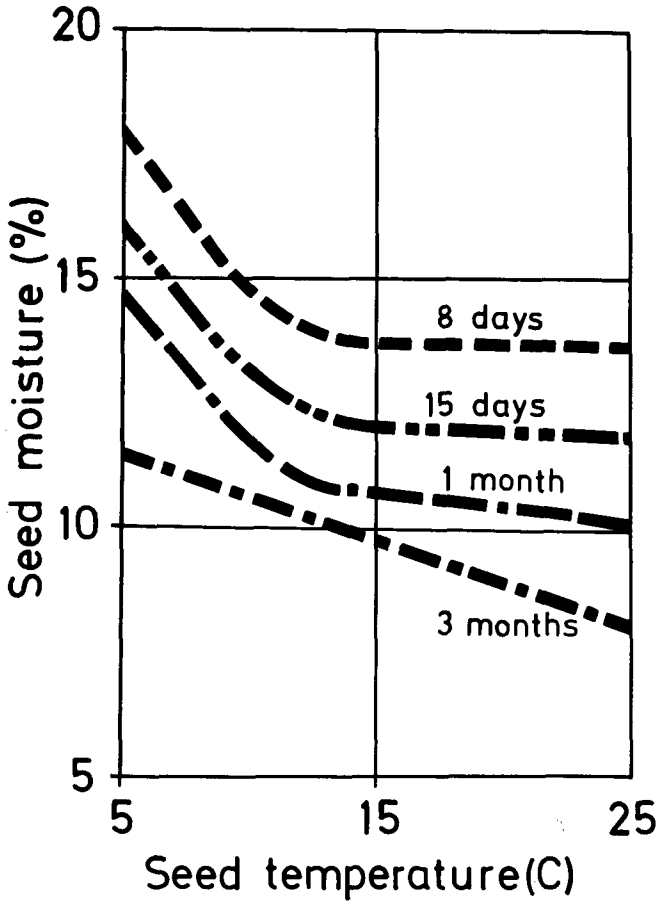

FIG. 4. Relationship between the moisture and temperature of the seed and maximal time of safe storage at continuous ventilation.

TABLE II

Content of Peroxides and Susceptibility to Oxidation of Oil from Undamaged and Heat-Damaged Seeds of Rape and White Mustard

	Peroxides (meq/kg oil)	
	With protection	Without protection
Rape, undamaged	0.00	5.9
Rape, heat-damaged	0.54	8.5
White mustard, undamaged	0.00	1.9
White mustard, heat-damaged	0.63	4.7

improved; it can only deteriorate more or less.

One of the most important considerations with regard to quality is to have a continuous and rapid flow of material from one piece of equipment to another. In crushed and flaked seeds, deterioration takes place rapidly, particularly so if the material has a high moisture content or is of poor quality. It is important to avoid oxygen contact with the oil, to keep the temperature low, to keep the hold-up times short, to eliminate sources of catalysis, and to carry out the treatments in the dark.

There are enzyme systems in all oilseeds (e.g., soybeans and rapeseed) that may influence oil quality, namely, lipase and lipoxygenase. These enzymes must therefore be inactivated at an early stage in the process. This is done by heat treatment in the cooker. The influence of the correct heat treatment on oxidation is shown in Table II (5).

The lipase activity may result in high FFA values in the oil. The hydrolysis of medium chain triglycerides will give a soapy flavor to the fat. The optimum temperature for lipase activity is 37-40 C. Lipase inactivation is highly dependent on moisture and temperature. Inactivation starts at 60-70 C and is rapid at 90-100 C in an aqueous medium, and even more rapid in an acidic medium. In the dry state, activity

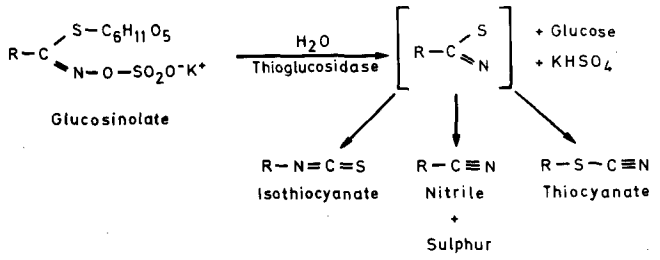

FIG. 5. The general structures of glucosinolates and products formed by enzymatic hydrolysis.

decreases only very slowly, and temperatures of 140-160 C are needed for rapid inactivation.

In rapeseed, there is also myrosinase that may influence the quality. The myrosinase catalyses hydrolysis of the glucosinolates to give glucose, sulphate, isothiocyanates, and (1)-5-vinyl-2-oxazolidinethione (Fig. 5). Some of these compounds act as a poison for hydrogenation catalysts. It is thus important to keep the glucosinolates intact by effectively inactivating myrosinase by proper cooking. Myrosinase and glucosinolates are brought together by the crushing of the seed (A. von Hofsten), but the hydrolysis can only take place if the moisture content is high enough (13%). The enzyme is most active at 40-70 C.

Inactivation of myrosinase starts at 70-80 C if the moisture content is 6-10% and is usually done at 80-90 C in the cooker. Eapen et al. (6) have made various laboratory heat treatments to evaluate their effect on myrosinase inactivation. Dry heat treatment (30 min, 105 C) proved unsatisfactory, but steam blanching (5 min), microwave heating (3 min), or immersion of the seed in boiling water (1.5 min) were effective. If the moisture content of the seed material is high and the temperature rise is not rapid enough, glucosinolates may be hydrolyzed before the myrosinase is inactivated.

Too extensive heat treatments during the process may also have a negative effect on oil and meal quality. If cooking temperatures above 110 C are employed, the extracted oil may be difficult to hydrogenate. This has been attributed to the chemical breakdown of the glucosinolates to give oil soluble sulphur-containing compounds. Microwave heating (1.5 min) and steam blanching (5 min) resulted in dark-colored oils, while dry cooking (30 min, 105 C) and immersion in boiling water (1.5 min) gave lighter-colored oils. Rapeseed stocks with green seeds often yield dark-colored oil, but an immersion of the seed in boiling 0.5% NaOH has been found to give lower color values (7).

Evans et al. (2) found a significant correlation between iron and FFA contents of hand-ground and laboratory-extracted oils. These data are shown in Figure 6.

A small reduction of oxidation stability of the oil may take place during the extraction process, together with a slight increase in the peroxide value and the benzidine value. Heat treatments of the seeds and exposure of the oil to light and heat result in higher peroxide values.

The fatty acid composition of the oil can also be affected by the extraction technique used. The fatty acid composition in the neutral oil is different from that in the phospholipids. These are most difficult to extract and are thus obtained only in the solvent-extracted oil. By using repeated extraction of white mustard seed with different solvents, Iverson (8) found that the last extracted oil was different from the first oil.

Storage of Crude Oil

How this is done is very important for the quality of the finished oil. To have a certain content of lecithin left in the oil often gives a better quality. Cooling and low temperatures are certainly an advantage, as has been already pointed out. Blanketing with nitrogen is another useful procedure, but even better is the bubbling of nitrogen through the oil.

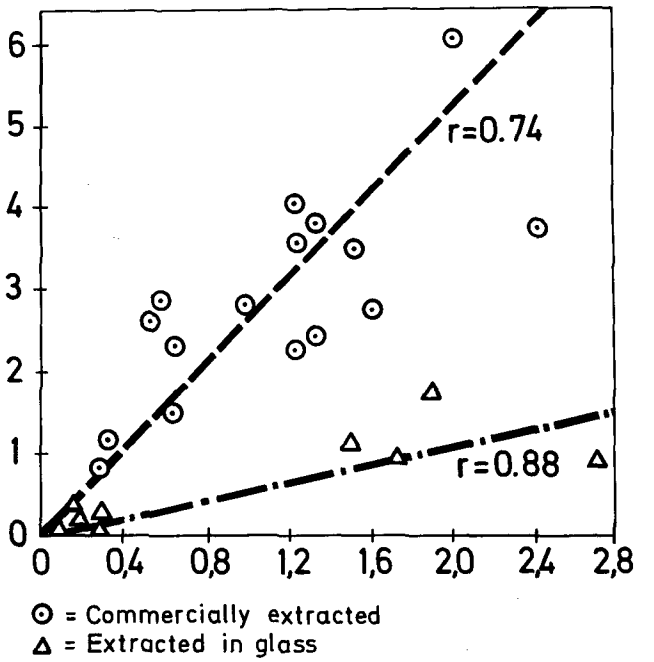

FIG. 6. Correlations of iron contents with the amount of free fatty acid in commercial crude oils and in oils extracted in laboratory under metal-free conditions.

ANALYTICAL METHODS

Oil quality must be determined by several analytical methods described below.

Moisture Content

Equipment for instantaneous determination of the moisture content of oilseeds is generally based on one of three principles: (a) the electric conductivity of the seed sample, (b) the dielectric constant of the seed sample, or (c) the nuclear magnetic resonance of water in the seed sample.

Instruments based on the first principle do not require a weighing operation. Small samples of a few grams are generally used. This means that considerable sampling errors may occur. Instruments based on differences in the dielectric constant of the sample are generally more reliable, and their use reduces sampling errors, since a considerably larger sample is used, generally ca. 200 g. A known weight of the sample must, however, be used in these instruments.

REFERENCES

1. Riiner, U., Lebensm.-Wiss. Technol. 4:76 (1971).
2. Evans, C.D., G.R. List, R.E. Beal, and L.T. Black, JAOCS 51:444 (1974).
3. Bek-Nielsen, "Technical and Economic Aspects of the Oil Palm Fruit Processing Industry."
4. Le Colza de sa Recolte a sa Commercialisation, CETIOM, 174 Avenue Victor-Hugo, Paris, France, 1963 (Duplic.).
5. Appelqvist, L.-Å, JAOCS 44:206 (1967).
6. Eapen, K.E., N.W. Tape, and R.P.A. Sims, JAOCS 45:194 (1968).
7. Anjou, K., in "Rapeseed," Edited by L.-Å. Appelqvist and R. Ohlson, Elsevier Publishing Co., Amsterdam, The Netherlands, 1972, p. 198.
8. Iverson, L.J., JAOCS 49:332 (1966).