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news feature

Experiences in refining rapeseed oil by the Zenith Process

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The Zenith Process, invented in Sweden in the early 1960's, is a unique method fo refining edible oils and fats. In refining rapeseed oil, excellent results in quality and economy are achieved. In this paper, after a short description of the process, quality figures on taste and color are shown and the necessity of a low oxidation value is stressed. Refining yields, based on some AOCS methods of analysis, and total refining costs are presented.

Rapeseed, and its varieties, is the only oilseed crop in Sweden today, mainly due to the climate. Although rapeseed has been grown for many years, it was not until WWII that the oil crop seeded area increased to appreciable quantities.

To make use of the increasing oil yield and to protect the higher domestic price level, the government made it mandatory to blend up to 35% of rapeseed oil into Swedish margarines. However the oil-consuming industry agreed to take care of the seed for export or domestic use, and thus remained free to make its own margarine compositions dictated by factors other than agriculture. This explains why Swedish refineries had to be skilled in rapeseed oil refining. The Swede today eats ca. 16 kg margarine and ca. 6 kg butter per year. This is not a matter of price levels, but the result of a determined quality drive, including oil refining.

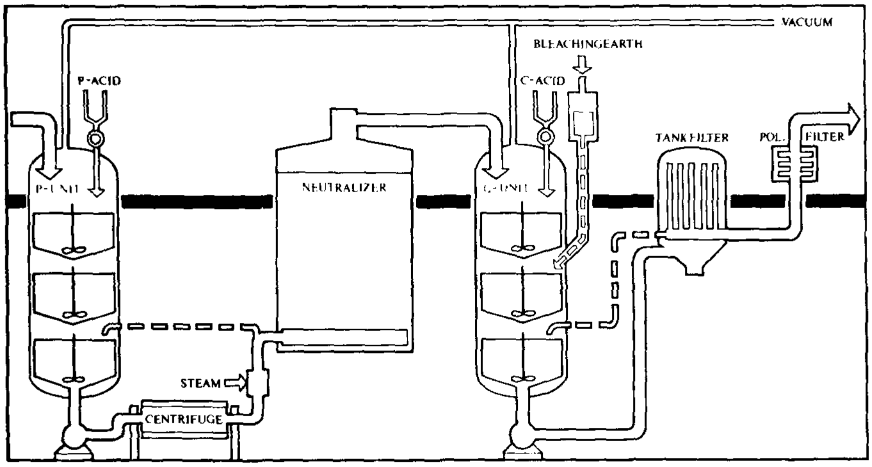

FIG. 1. Symbolic flow chart.

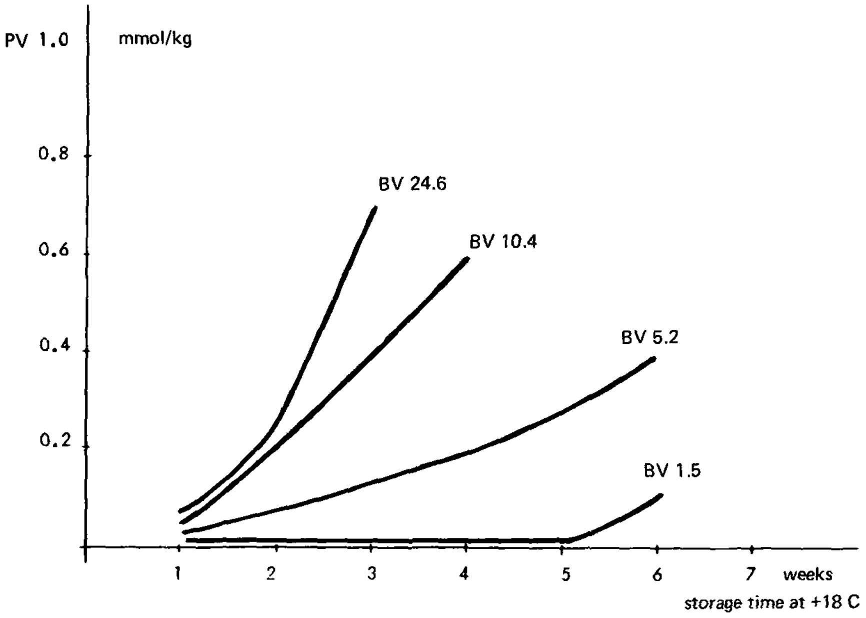

FIG. 2. Deodorized rapeseed oils on different oxidation levels (BV); stored at +18 C in presence of air.

Refining steps

The Zenith process was invented in 1960 to enable still better refining, especially of rapeseed oil. The following short description is based on a symbolic flow diagram (Fig. 1). The continuous process consists of three main refining steps, two being semicontinuous to maintain desired reaction times. The plant is made of stainless steel, and the operation is automatically directed and supervised.

The first step is treatment of the oil with concentrated phosphoric acid in order to remove some of the nonfatty substances, which have a great influence on forming emulsions. The green colorants in rapeseed oil are strongly affected by the phosphoric acid, and nonhydratable phosphatides are transformed into a hydratable form by removing the calcium and magnesium from the gums. The amount of phosphoric acid depends on the oil quality. It is normally ca. 0.2% by volume for rapeseed oil. The reaction takes 20 min and is performed under a vacuum. Phosphatide-containing oils such as rapeseed oil form appreciable amounts of acid sludge; this is removed in a sludge separator. Water is thereafter added in the form of live steam to allow the remaining phosphatides to form liquid crystals at the interphase between water and oil.

The second step is neutralization, based on the concept of using weak lyes with the formed soap completely dissolved in the alkaline solution. Neutralization is performed by introduction of the oil in the form of droplets at the bottom of a vessel almost filled with 0.35 N alkaline solution. The droplets, 1-2 mm in diameter, rise by difference in gravity and are collected in the upper conical part forming an oil layer with 0.05% free fatty acids (FFA), 0.2-0.3% water and 100 ppm soap. Due to the pretreatment of the oil and the uniform alkaline solution in the neutralizer, the formed soap solution is easy to split. The specially designed acidulation unit has no moving parts, and the acid oil contains up to 90% fatty acids.

The third step is bleaching, also performed under a vacuum. It starts splitting the soap traces by adding citric acid solution. After drying the oil, bleaching earth is added and left to react for 30 min.

Thereafter filtering can be performed with any type of filter. In order to offer a line as complete as possible, we manufacture a manually cleaned square filter of 10 m^2 filter area and a residue filter for final filtration when changing feedstock.

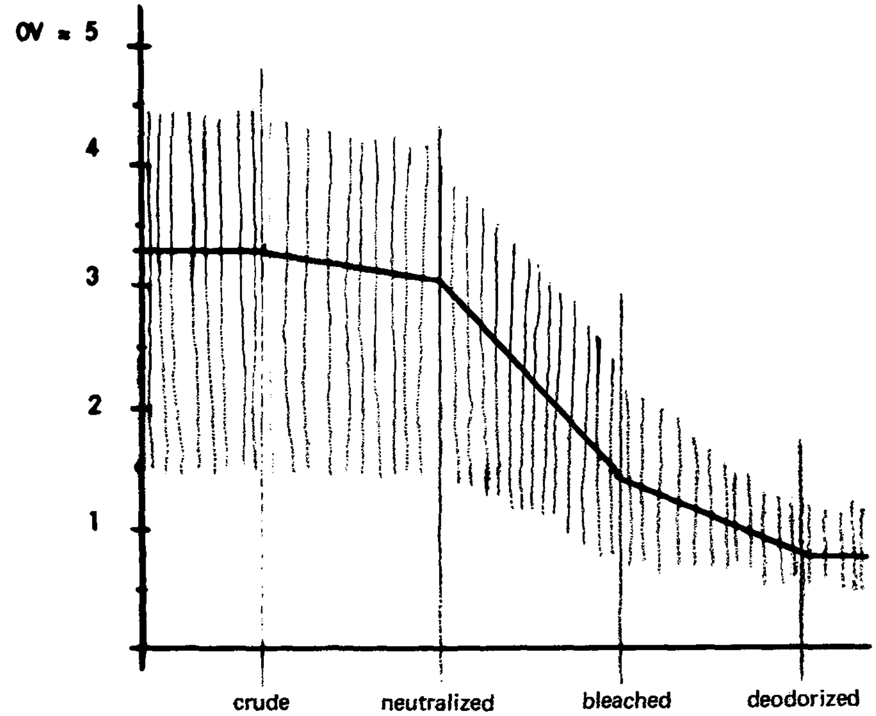

FIG. 3. Rapeseed oil refining: oxidation values. OV = 2 x PV + AV.

Refining quality

It is well known that the shelf-life of an oil is seriously reduced if the content of oxidation products after deodorization is high. Of course this is especially noticeable for oils containing linolenic acid as soybean and rapeseed oils. Holm (1) has published many convincing proofs of this. Figure 2 shows how destructive preoxidation (oxidation prior to deodorization) is to the oil's stability against oxidation. Samples of bleached rapeseed oil were oxidized to different levels and thereafter deodorized. The remaining nonvolatile aldehydes were measured as a benzidine value (BV) immediately after deodorization. The samples were left at +18 C in the presence of air for some weeks, and the peroxide value (PV) was controlled weekly. The figure demonstrates the catalyzing effect of the secondary oxidation products as a rapid increase in primary oxidation.

Since no method is known to remove the nonvolatile aldehydes, the only solution is not to produce them. This can be accomplished by delicate seed-handling and a suitable refining procedure. Figure 3 shows the decrease of the oxidation value during normal refining in the Zenith plant. This is performed by treatments under vacuum. Swedish crude rapeseed oil has an oxidation value (OV = 2 PV + BV) of ca. 3-4. After deodorization there is an OV of ca. 1, which results in a longer shelf-life of oils and margarines. Our standard household margarine contains ca. 15% liquid rapeseed oil.

The importance of a low BV and its correlation to taste can be illustrated by a test on mustard oil. Organoleptic triangle tests on 10 different oils at two BV levels resulted in the mean values listed in Table I. Starting with a low BV the oil is quite acceptable,

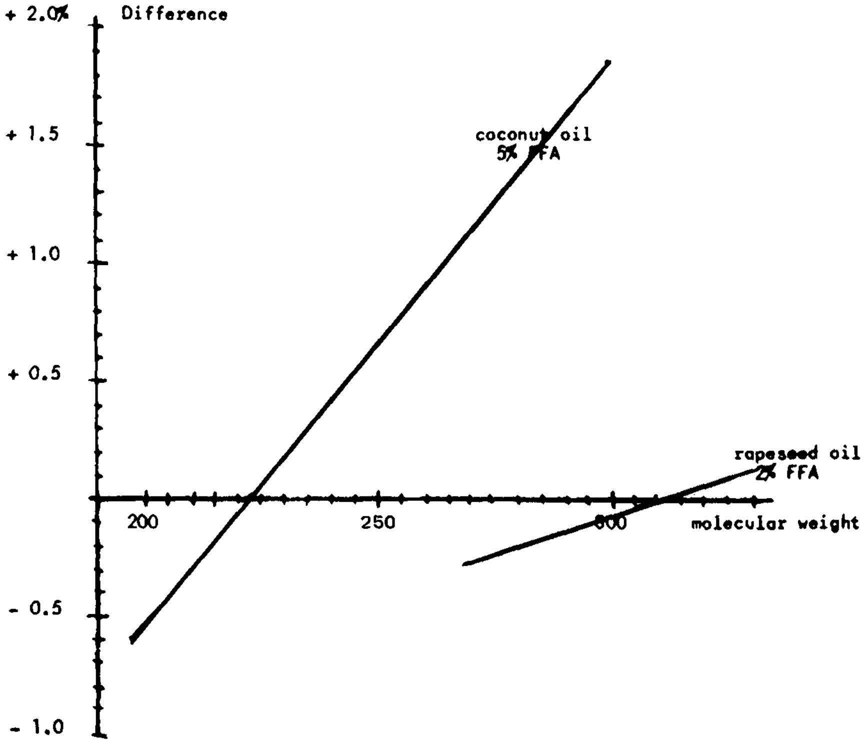

FIG. 4. Calculation of free fatty acids (FFA) using varying molecular weights.

TABLE I

Mustard Oil[a] Taste by Triangle Tests

Benzidine value on deodorized oil	Taste			Peroxide value
	1 week	3 weeks	7 weeks	7 weeks
0.6	4.0	3.9	3.7	
0.7	3.95	3.75	3.3	0.0
0.8	3.8	3.5	3.0	
1.6	3.7	3.6	2.8	
2.3	3.15	2.40	1.60	1.3
3.4	1.7	1.3	0.2	

[a]Ten samples each.

TABLE II

Rapeseed Oil Normal Color Values

Method	Crude	Neutralized	Bleached	Deodorized
Spectro				
460 mμ	14.3	11.7	0.21	0.031
550 mμ	0.30	0.28	0.016	0.005
670 mμ	1.32	0.70	0.004	0.000
Lovibond	1 in.	1 in.	5.25 in.	5.25 in.
R	4	5	1	0.8
Y	59	30	12	6

even after 7 weeks of storage.

Color values are also of great interest. We normally measure with a spectrophotometer at 460, 550 and 670 mμ, but Lovibond figures are also shown in Table II; 1% of activated bleaching earth and a deodorization temperature of 220 C are employed. Remaining in the bleached and deodorized oil are ca. 0.05% FFA and 0.5 ppm phosphor. Of course no soap is left.

Economic considerations

Refining yields are calculated according to Ca 9f-57, AOCS method for estimation of neutral oil. This chromatographic analysis is completed by estimation of FFA according to Method Ca 5a-40 and of phosphatides according to Method Ca 12-55. The difference, up to 100%, consists of water, impurities and analytical errors.

When calculating the FFA it is, of course, essential to use a proper molecular weight for each oil. An obvious way to show this is to estimate neutral oil and FFA titer on coconut oil. When calculating the FFA percentage using a different molecular weight, the line in Figure 4 is obtained.

The normally used molecular weight of oleic acid (282) gives a surplus of 1.42% and of lauric acid

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TABLE V

Summary of Refining Costs per Ton Input of Rapeseed Oil[a]

Classification	Neutralized	Bleaching included
Refining loss net	19:46	27:53
Cost of utilities	14:73	23:69
Labor costs (maximum)	6:00	6:00
Maintenance costs	1:60	1:60
Investment installment[b]	6:00	6:00
Total cost per ton	47:99	64:82

[a]100 tons per day x 250 days.

[b]Based on an investment of Sw. Crs. 1,000,000, paid in 10 years, 8% interest.

TABLE III

Estimated Refining Costs per Ton Rapeseed Oil[a]

Characteristic	Yield calculation		
	Analysis	Yield	
		Neutralized	Bleaching included
Neutral oil, AOCS Ca 9f-57	98.33	97.57	96.72
Free fatty acids (M 307), AOCS Ca 5a-40	0.97	1.45	1.45
Lecithin	0.51	---	---
Difference to 100%	0.19	0.98	1.83
Fatty acid factor		1.49	1.49
Refining efficiency		99.23	98.36

	Loss			
	Neutralized		Bleaching included	
	kg	cost	kg	cost
Refining loss gross	24.3	23:09	32.8	31:16
Restitution for acid oil	14.5	3:63	14.5	3:63
Refining loss net		19:46		27:53

[a]Refined by the Zenith process at 5 tons per hour capacity. Prices in Sw. Crs.

TABLE IV

Estimated Refining Costs per Ton Rapeseed Oil[a]

Utility		Utility consumption			
		Neutralized		Bleaching included	
		Quantity	Cost	Quantity	Cost
Phosphoric acid, 85%	kg	4.16	4:99	4.16	4:99
Caustic lye, 100%	kg	5.30	2:65	5.30	2:65
Softened hot water	m^3	0.38	1:52	0.38	1:52
Citric acid	kg	---	---	0.25	0:80
Bleaching earth activated	kg	---	---	8.50	6:80
Filter aid	kg	---	---	1.20	0:96
Steam, 3 atm	kg	75	1:88	85	2:13
Electric power	kwh	4	0:29	6	0:44
Pressure, air and vacuum			2:00		2:00
Sulphuric acid, 98%	kg	6.0	0:90	6.0	0:90
Steam for soap-splitting			0:50		0:50
Total cost of utilities			14:73		23:69

[a]See Table III.

Sept. 23–26, 1973–National Forum on "Growth with Environmental Quality?" Assembly Center, Tulsa, Okla. Contact: Bruce Carnett, manager, public relations, Metropolitan Tulsa Chamber of Commerce, 616 S. Boston Ave., Tulsa, Okla. 74119.

Sept. 24–26, 1973–Course on Noise Control in Manufacturing Plants, New York. Contact: Gloria Cianci, Bolt Beranek and Newman Inc., 50 Moulton, Cambridge, Mass. 02138.

Sept. 25–28, 1973–FILTECH 73 (International Filtration and Separation Exhibition), Olympia Hall, London, U.K. Contact: F. Wells, Shoemaker, Eaton-Dikeman, P.O. Box 126, Mount Holly Springs, Pa. 17065.

Sept. 27–29, 1973–Third International Symposium: Metal-Catalyzed Lipid Oxidation, Institut des Corps Gras, Association Francaise des Techniciens des Corps Gras and Ecole Superieure d'Application des Corps Gras, Paris, France. Contact: ITERG, 5 Boulevard de Labour-Maubourg, 75007 - Paris, France.

Oct. 9–12, 1973–Association of Official Analytical Chemists 87th Annual Meeting, Marriott Hotel, Twin Bridges, Washington, D.C. 20001. Contact: L.G. Ensminger, executive secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044.

Oct. 15–18, 1973–28th Instrument Society of America International Conference and Exhibit, Astrohall, Houston, Tex. Contact: Diane R. Schaffler, ISA, 400 Stanwix, Pittsburgh, Pa. 15222.

Oct. 16–19, 1973–10th (Jubilee) Symposium on Colouristics, Eger, Hungary. Contact: Hungarian Chemical Society, 1368 Budapest 5, P.O. Box 204, Hungary.

Oct. 23–25, 1973–Course on Noise Control in Manufacturing Plants, Memphis. Contact: Gloria Cianci, Bolt Beranek and Newman Inc., 50 Moulton, Cambridge, Mass. 02138.

Oct. 24–25, 1973–Symposium on Environmental Chemistry: Know-How and Chemicals in 1973-78, Brussels, Belgium. Contact: i.b./c.c. Administration, Nieuwelaan 65, B-1820 Strombeek, Belgium.

Oct. 25–28, 1973–Third International Symposium on Atherosclerosis, Kongresshalle, West Berlin, Germany. Contact: Kongressgesellschaft fur arztliche Fortbildung e.V., 1 Berlin 41, Wrangelstrasse 11-12, Germany.

Oct. 29–Nov. 2, 1973–Fourth International Conference on Atomic Spectroscopy, Toronto, Ont., Can.

Nov. 5–7, 1973–Course on Noise Control in Manufacturing Plants, Miami. Contact: Gloria Cianci, Bolt Beranek and Newman Inc., 50 Moulton, Cambridge, Mass. 02138.

Nov. 11–15, 1973–American Institute of Chemical Engineers 66th Annual Meeting, Bellevue Stratford Hotel, Philadelphia, Pa. Contact: F.J. Van Antwerpen, executive secretary, AIChE, 345 East 47th St., New York.

Nov. 12–14, 1973–World Soy Protein Conference, Munich, Germany. Contact: Jim Yancey, American Soybean Association, P.O. Box 158, Hudson, Iowa 50643.

Nov. 14–16, 1973–Joint Eastern Analytical Symposium and National Meeting of Society for Applied Spectroscopy, Statler-Hilton Hotel, New York. Contact: Michael W. Miller, NL Industries, P.O. Box 420, Hightstown, N.J. 08520.

Nov. 14–17, 1973–51st Annual Meeting and 38th Paint Industries' Show, Conrad Hilton Hotel, Chicago, Ill. Contact: Dennis A. Bergren, De Soto, Inc., 1700 South Mt. Prospect Rd., Des Plaines, Ill. 60018.

Nov. 19–21, 1973–Symposium on Water Quality Parameters–Selection, Measurement and Monitoring, Analytical Chemistry Div., Chemical Institute of Canada, Burlington, Ont., Can. Contact: S. Barabas, Analytical Methods Research Div., Canada Centre for Inland Waters, Burlington, Ont., Can.

Dec. 10–12, 1973–Second Joint Conference on Sensing of Environmental Pollutants, Sheraton-Park Hotel, Washington, D.C. Contact: Philip N. Meade, Instrument Society of America, 400 Stanwix St., Pittsburgh, Pa. 15222.

Apr. 1–5, 1974–International Conference on Animal Feeds of Tropical and Subtropical Origin, London. Contact: Public Relations C, Tropical Products Institute, 56-62 Gray's Inn Rd., London WC1X 8LU, U.K.

May 1–2, 1974–International Symposium on Flammability and Fire Retardants, Parkway Hotel, Cornwall, Ont., Can. Contact: Vijay Mohan Bhatnagar, editor, *Advances in Fire Retardants,* 209 Dover Rd., Cornwall, Ont., Can.

May 5–8, 1974–Sixth Annual Offshore Conference, Astrohall, Houston, Tex. Contact: Stan R. Houston, 6200 N. Central Expressway, Dallas, Tex. 75206.

Jul. 22–24, 1974–Sixth International Sunflower Conference, Bucharest, Romania. Contact: Ion Trifu, Academy of Agricultural and Forestry Sciences, Blvd. Marasti 61, Bucharest 1, Romania. ■

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(200), a deficit of 0.56%. An accurate calculation of refining yield is quite impossible if such differences are allowed. A molecular weight of ca. 220 for coconut oil seems most adequate. For rapeseed oil with FFA normally below 1%, differences in molecular weight are of less importance; but for an oil with 2% FFA there is a deficit of 0.18% when changing molecular weight from 310 to 282.

Table III shows a calculation of refining yield using the aforementioned simple system. It is a test refining of ca. 20 tons of oil with every kilogram weighed in and weighed out; even the soapstock is split and the acid oil weighed. The yield is presented in two ways. The first stops after the neutralization step, which is the normal presentation dealing with guarantees, etc. The second also includes the bleaching step, using a manually cleaned filter with ca. 50% oil retention in the spent filter cake. In both cases the loss in the soap-splitting unit is included. Based on these figures the cost for the refining loss is evaluated.

Table IV exhibits the quantity and cost for each utility used in refining, bleaching and soap-splitting, and Table V shows a summary of all costs involved in this refining. The labor costs are based on one man per shift. Normally less than 20% of his time will be needed, so one man operates two lines including the soap-splitting. Maintenance costs are actual figures from our own refinery and include both labor and spare parts. The total refining cost seems a reasonable price for high quality refining. Such a cost evaluation will give the most reliable economic comparison of different refining systems.

REFERENCE

1. Holm, U., Presented at the Third Scandinavian Symposium on Lipid Oxidation, Sandefjord, Norway, 1961.

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