SYMPOSIUM

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♣ Desired Quality Attributes in Winter and Summer Rapeseed

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ABSTRACT

Quality assurance programs have played a significant role in rehabilitating and maintaining the importance of rapeseed and its products, in Europe, the processing of indigenous and Canadian rapeseed ensures uniform plant utilization throughout the year which in itself contributes to improving quality. Indigenous rapeseed is predominantly of the high-yielding winter type. The European oil mills have learned to adapt to differences in low erucic acid seed characteristics during processing. The influence of different conditioning and pre-expelling parameters on the characteristics of expeller and extraction oil is especially receiving attention. Sulfur compounds, phosphatide content, color and analytical oxidation values are important criteria for the required refining techniques, which can range from classical methods to physical refining, and the quality of the fully refined product, While low crucic acid rapeseed oil can generally be regarded as an alternative to soyabean oil, crystallization behavior of hardened products can differ significantly, which appears to be a function of fatty acid composition. Progress is also being made in upgrading meal quality, especially for application in poultry feed, by developing cultivars with glucosinolate levels below 1%. Such new varieties might also contribute to reducing the problem of fishy egg taint observed with some breeds of layers. Decreased numer degradability of rapeseed meal by treatment with formaldehyde may further improve flexibility of use. Various established and potential quality attributes for rapeseed, meal and oil are reviewed,

INTRODUCTION

Table I shows regional and total world production of rapeseed, expressed as oil. Rapeseed oil now amounts to ca. 15% of world production of vegetable oils and fars.

In Western Europe and Canada, virtually all the rapeseed oil produced is of the low erucic acid type. Indeed, it was this reduction of erucic acid a physiologically suspect fatty acid moiety which helped to restore the image of rapeseed.

FEC and Canadian regulations stipulate a maximal content of 5% erucic acid in oils intended to be used for edible purposes, and only rapeseed meeting this specification is eligible for EEC subsidy.

Traditionally, most European countries grow winter varieties. Canadian rapeseed is of the summer type (B. napus and B campestris to almost equal parts) because of the prevailing climatic conditions. Sweden and Denmark occupy an intermediate position, in that they grow both winter and summer varieties.

European oil mills now process both indigenous and Canadian rapeseed throughout the year. The resulting continuity in rapeseed handling and processing has, in itself, not only contributed to product improvement but also has increased know-how on dealing efficiently with variations in rapeseed characteristics.

Apart from smaller experimental parcels, double zero varieties are not yet on-stream in Europe and there is as yet little practical experience in Europe on the processing of Canadian double zero varieties such as Tower (B. napus), Regent (B. napus), Altex (B. napus) and Candle (B. campostris).

Typical compositional characteristics of rapeseed are shown in Table II. The yield per acre, shown in Table III, is significantly higher for winter than for summer varieties. Initial yield differences in favor of traditional, high erucic rapeseed varieties have been largely overcome.

The world market price of rapeseed oil closely follows that of soybean oil, the price difference in 1979 averaged on hfl 50 (Table IV).

PROCESSING OF RAPESEED (1)

Rapeseed is normally processed via the classical route of

The symposium contribution "Recent Advances in the Analysis of Glucosinolates," by O. Olsen and H. Sørenson, was published in the September 1981 issue of JAOCS.

TABLE I
Production of Rapeseed (in terms of oil; 1,000 t)

	1971/72	1972/73	1973/74	1975/76	1976/77	1977/78	1978/79
Ger. Fed. Rep.	91	100	90	80	89	107a	132a
Netherlands	13	18	16	15	14	12	9
France	266	288	260	210	224	168 ^a	249a
UK	4	. 5	12	24	44	56ª	57a
Denmark	20	20	29	52	32	28	44
Total EEC	<u> 394</u>	431	<u>407</u>	<u>384</u>	<u>405</u>	373	<u>491</u>
Sweden	88	114	11,7	114	98	84a	137a
Czechoslovakia	40	43	47	52	44	48	68
Hungary	28	21	30	24	24	26	44
Poland	238	270	216	290	392	280	280
Ger, Dem. Rep.	78	94	96	146	128	126	128
Total Europe	<u>892</u>	<u>902</u>	<u>951</u>	1.038	1.142	<u>991</u>	1.148
Canada	862	520	483	699	334	710b	1.390b
China	420	460	480	540	520	480	602
India	573	741	600	700	624	720	647
Pakistan				122	115	118	94
Total world	3.002	2.838	2.726	3.222	2.836	3.143	4.074

(Conversion factor: 1,000 t seed = 400 t oil.)

TABLE II

Average Rapeseed Characteristics

-	
Oil content	39-45%
Protein	~ 24%
Moisture	6-9 %
Harvest time	July-August
Yield	2.000-3.000 kg/ha
	(35.7-46.4 bushels/acre)a

^aAssuming 1 bushel rapeseed = 22,68 kg,

TABLE III

Average Rapesced Yields: Sweden, 1975-1977^a

•	Average yield (kg/ha)	Oil content in dry matter (%)	
B. napus			
Winter rape	2,850	45.2	
Summer rape	1.750	43.5	
B. campestris			
Winter turnip rape	2.240	44.8	
Summer turnip rape	1,610	41.6	

^aG. Olsson, 5th Int. Rapesced Conference, Malmö, Sweden, June 12-16, 1978.

cooking the flaked seed at ca. 90 C, followed by expelling about two-thirds of the oil and extracting the remainder from the expeller cake with hexane (Table V).

Direct extraction of comminuted rapeseed requires less capital investment but more energy, and tends to lead to higher residual fat levels in the meal with subsequent loss in yield of the higher priced oil.

A new general development is that of expelling without prior cooking or flaking; this process is claimed to lead to a better oil. It may be, however, that for rapeseed at temperatures between 30 and 50 C instead of 80-90 C, enzymatically induced oxidation, hydrolysis and glucosinolate decomposition will actually lead to an impaired oil extraction (2). The temperature and moisture profile during seed drying and cooking prior to expelling and extraction influ-

TABLE IV

Market Prices-1979 (hfl/t)

	Crude soybean oil	Crude rapeseed oil
Jan.	1.210	1,180
Feb.	1.220	1.160
March	1.330	1,270
April	1,350	1,300
May	1,310	1.270
June	1.300	1.260
July	1.350	1.290
Aug.	1,320	1.270
Sept.	1,330	1,290
Oct.	1.310	1.270
Nov.	1.270	1.230
Dec.	1,260	1.220
Average	1,300	1.250

TABLE V
Flow Diagram of Rapeseed Processing

Seed storage

Seed cleaning

Preconditioning

Flaking

Cooking

Expelling → Expeller Oil

Breaking and possibly also flaking of expeller cake

Hexane extraction → Extraction oil

Desolventizing / toasting

Drying / cooling → Meal

ences the quality of both expeller and extraction oil. Table VI demonstrates the effect of temperature in the range of 70-90 C on crude oil properties. On the whole, and looking at the combined expeller and extraction oil, flake conditioning at 90 C rather than 70 C tends to give a better oil.

Moisture content of the seed material has an influence on the concentration of the phospholipids in the oil (3). In

^aLow erucic acid varieties.

bLargely double-zero varieties.

TABLE VI

Influence of Conditioning Rapesecd Flakes (0.25-0.35 mm; ca. 7.5% moisutre) at Different Temperatures on the Characteristics of Expeller and Extraction Oils

	Expeller oil ²			Extraction oila		
Flake conditioning temp (C)	70	80	90	70	80	90
Free fatty acids (%)	0.72	0.76	0.77	2.8	3.1	2,0
E ₂₃₂ nm 1% 1 cm	•					
(characteristic of state of oxidation)	2,2	2.0	1.9	3.1	3.0	2.5
Pheophytin (ppm)	22	26	29	35	30	34
Lecithin in terms of phosphorus (ppm)	319	315	288	750	540	300
Nonhydratable phosphorus ^b	303	296	245	335	495	149
Lovibond color (1", red/blue)	3.1/1.2	3.1/1.2	3.2/1.4	4,2/2,3	4.6/2.3	4.8/2.8
Sulfur (ppm)	2.0	3.8	3.1	14.2	8.5	8.7

^aExpelling was done on production scale; the expeller cake was extracted in the laboratory with hexane at 60 C.

addition. Swedish work has provided some evidence that during seed heating in the presence of moisture, a considerable portion of phosphatidylcholine is hydrolyzed to phosphatidic acid (4) which is less easy to remove by degarming.

Seed from different origins can show deviations from this overall processing picture but, in general, these can be balanced out by, e.g., skillful variation of seed drying, temperature and moisture adjustment during processing. It is said that the new Canadian double-zero varieties such as Candle are relatively brittle and the corresponding seed disintegration gives rise to problems during rolling and extraction. Whether there would indeed be similar difficulties in European oil muls in adapting to these seed varieties remains to be seen.

Table VII shows some rapeseed specifications, the general validity of which we endorse. It is obviously very important to reduce the incidence of immature seed to a minimum because chlorophyl/pheophytin will migrate into the oil and eatalyze not only oxidative deterioration but also lead to oil losses during refining. Damaged seed and dockage lead to increased oxidation and free fatty and (FFA) content, and hence, also impair quality and yield.

CRUDE OIL SPECIFICATIONS

Crude oil characteristics can be conveniently divided into (a) fatty acid composition, (b) oxidation characteristics, and (c) refining yield criteria.

Fatty Acid Composition

Table VIII shows the average fatty acid compositions of soubean, sunflower seed and rapeseed oils. The average shelf-life of the fully refined oils decreases in the order sunflower, soy and rape, in which the difference between soy and rape is small.

There appears to be a basic correlation between linolenic acid content and shelf-life. In other words, the shelf-life of fully refined rapeseed oil should be improved if the linolenic acid content could be reduced. In analogy to selectively hardened rapeseed and soyhean oils, one would expect a significant improvement upon lowering linolenic acid content to 2-3%.

Breeding work in this direction apparently has little chance of success, although mutants with levels as low as 3.6% linolenic acid have been reported (5). The successful breeding of rapeseed with a high linoleic and a low linolenic

TABLE VII Various Rapeseed Specifications

Sweden	Grade I	Grade II	Unacceptable
Appearance/smell		Subjective assessme	nt
Purity (%)	90-100	90-100	< 90
Moisture (%)	max, 8	max, 8	. > 8
Chlorophyll (ppm)	max, 30	max. 70	> 70
FFA (%)	max. 1	max. 3	. > 3
•	(cf. JAOCS, Aug	g. 1973)	
Canada	Grade I	Grade II	Grade III
Damaged seeds (%)	max, 3	max. 10	max, 20
Heated damaged seeds	max. 0.1	max. 0.2	max. 0.5
Min, weight (lb/bushel)	52	50	48
Conspicuous seed (%)	max. 1.0	max. 1.5	max. 2.0
Moisture (%)	max, 10.5	max, 10,5	max, 10,5
Stones (%)	max. 0.05	max, 0.05	max, 0,05
	(Canada Grain A		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
Germany ("Sinola"-Standard)			
Oil content	EEC Standard		
Erucic acid (%)	max. 2.0		
Moisture (%)	max. 9.0		
Foreign matter (%)	max, 4,0		
(< 1.5 mm and > 3.0 mm)	•		
Seed-damaged	negative		

bHydration at \sim 70 C with \sim 2% water for \sim 5 min.

TABLE VIII

Average Fatty Acid Compositions

Fatty acid	High erucic acid rapeseed oil	Low erucic acid rapeseed oil	Soyabean oil	Sunflower oil
C ₁₆	3-4	3-4	7-10	4-9
C,,, [trace	trace	_	trace
C	1-2	1-2	3-5	3-6
Cr	11-24	ca, 60	22-31	14-35
C F	15-20	ca. 20	49-55	50-75
C, . F	8-10	9-13	6-10	trace
C,,,	trace	trace	trace	trace
C ₂₀ Γ	ca. 10	2-3	trace	trace
C,,	trace	trace	_	trace
C ₁₆ Γ C ₁₈ Γ C ₁₈ Γ C ₁₈ Γ C ₁₉ Γ C ₂₀ Γ C ₂₂ Γ C ₂₂ Γ C ₂₄	44-52	< 5	-	_
C.4	trace	_	trace	trace

acid level appears to depend on the existence of separate desaturase systems for the conversion of oleic to linoleic and linoleic to linoleic acid.

Occasionally, it has been claimed that the shelf-life or oxidative stability of oil from summer varieties is generally lower than that of oil from winter varieties, but we could not substantiate this. In particular, no relationship appears to be between oxidative stability and linolenic acid content in the 8-13% range. Whether differences in the sterol content of rapeseed oils could explain these variations in stability is being examined (6).

Oxidation Characteristics (7)

The state of oxidation of a crude oil determines the best shelf-life that can be achieved after refining. If the state of oxidation is above a certain limit, the probability of attaining satisfactory shelf-life drops significantly. For soybean and sunflower seed oils, the ultraviolet (UV) absorption at 232 nm, the anisidine value, the totox value (i.e., 2 x peroxide value + 1 x anisidine value), and the concentration of oxidized fatty acids are useful criteria for the state of oxidation.

These data are usually interrelated so that it normally suffices to determine just one of them. Little information exists on the practical application of these data to rapeseed oil, so that limits are as yet tentative.

The condition of the rapeseed itself largely determines the state of oxidation of the crude oil, provided crude oil processing and handling is done in such a way that access of oxygen at elevated temperatures is kept to a minimum.

Refining Yield Criteria

Refining yield is primarily governed by moisture, particulate impurities, FFA, phosphatide content, chlorophyll and sulfur content—all for a given process of refining.

Crude rapeseed oil normally is not deslimed and hence contains up to 500 ppm phosphorus. It is advisable to reduce (by desliming) the phosphatide content before lye neutralization in order to minimize neutral oil losses. The phosphatides "precipitate" about an equal proportion of neutral oil during neutralization. The bulk of these phosphatides is saponified and lost as effluent. Rapeseed oil that is to be physically refined should not contain more than ca. 30 ppm phosphorus. These low levels, however, cannot be obtained using the current desliming techniques.

The market for rapeseed lecithin is limited. This is in part due to the darker color and the somewhat inferior taste in comparison to soya lecithin. The limited work done in the direction of finding specific outlets has indicated no basic difference in attributes between lecithins obtained from high or low erucic acid and double-zero varieties.

The dark color originates mainly from chlorophyll and carotenoid pigments, most of which are concentrated in the seed coats; this does imply better legithin quality from varieties like Candle.

Chlorophyll is removed during the bleaching stage with corresponding losses of adsorbed oil. It is thus important, quite apart from the prooxidative effect, to aim for a minimal chlorophyll content; this is not a function of seed processing, but of excluding immature seed as much as possible.

The oil-soluble sulfur derivatives remaining in the filtered crude oil comprise at least 14 different compounds (8,9). Up to now, we have not been able to establish a simple relationship between glucosinolate content in the seed and concentration of sulfur compounds in the oil (9). These studies do not, however, include newer rapeseed varieties such as the Danish Line containing only ca. 0.3% total glucosinolate instead of the ca. 1% encountered in conventional double-zero varieties such as Tower and Candle.

Residual traces below ca. 5 ppm sulfur in the fully refined oil do not appear to be detrimental to oil quality. Sulfur compounds can, however, be detrimental during refining, in that they can impair the desired course of hydrogenation. Since oil-soluble sulfur compounds are not necessarily removed to a significant extent by desliming (10), neutralization and/or bleaching (9,11) (Table IX), their concentration in the crude oil preferably should not exceed 30-50 ppm, expressed as sulfur (12). We prefer to determine sulfur either by combustion or by reduction on nickel at 180 C; the Granatelli method tends to give lower values. Table X summarizes some quality criteria and limits that have been proposed.

Refined Oil Specifications

Rapeseed oil is, in principle, refined by the same methods as those used for soyhean oil. The higher FFA content permits the use of stronger lye. A higher incidence of pheophytin contamination means higher bleaching earth consumption.

Physical refining is theoretically possible, provided the crude oil is of good quality.

Table XI summarizes some premium raffinate specifications that have been proposed in Germany. Rapeseed oil is a real alternative to sovbean oil. Earlier fears that low entice acid rapeseed oil would be inferior to high erucic rapeseed oil in respect to shelf-life and frying performance proved insubstantial. Regarding turbidity at refrigerator or even ambient temperatures, an erucic acid content below 5% seems to be an adequate safeguard for complete liquidity at these temperatures.

TABLE IX Influence of Refining on the Characteristics of a Typical Rapeseed Oil $C_{22:1} \le 2.5\%$ (Unimills Thörl 1977, Production)

Product	Free fatty acids (%)	Lovibond color (yellow/red/blue)	Pheop (pp:		Sulfur	(ppm)	E232
Crude, deslimed oil Neutralized oil	2.4 0,09	30/5.0/4.0 (1") 30/4.0/2,3 (1")	22 18	(26) ^a (19)	12 9,4	(19) ² (16)	2,1 2.2
Neutralized and bleached oil Deodorized oil	0.09 0.07	30/6,2/0,7 (5 1/4") 11/1,1/- (5 1/4")	< 0.02	(0.02) (0.02)	7.7 1.8	(11) (1.9)	2.1 2.9

^aThe sulfur and pheophytin values in parentheses are for another batch of rapeseed oil.

TABLE X

Crude Oil Quality Attributes

	Unilever	Sweden	Canada ^a (crude/crude, degummed)
FFA (%)	max, 2 ^b	max, 1,3	max. 1.0
Moisture and impurities (%)	max, 0,5 ^b	- .	max. 0.5/0.3
Erucic acid (%)	max. 5 ^b	_	max, 5
Iodine value (Wijs)	110-126	_	_
Saponification value	180-195	– .	- .
Color (1" Lovibond cell)	max. 40y/4r/2b	_	_
Lecithin (expressed as phosphorus) (ppm)	ca. 500 (nondeslimed)	200-300 (deslimed)	-/max, 200
Flashpoint	min. 300 F (150 C)		min, 150 C
Sulfur (ppm)	max, 50	_	_ `
Anisidine value	<u>-</u>	max. 2.5	_
Peroxide value (meg/kg)	_	max. 1.4	_
Oxidation value (2 × POV + AV)	– .	max. 6.0	-
E ₂₃₂ nm 1%	max, 3.0	_	***
Fe/Cu (ppm)	_	max. 2.0/0.5	_
Chlorophyll (ppm)	max. 30	max. 20	_
Neutral oil yield (%)		_	min. 98.0/98.

aNational Standard of Canada/Canadian specifications board.

TABLE XI
Refined Rapeseed Oil: Quality Attributes

	"Sinola"/Germany (24)
Erucic acid content (%)	max. 5.0
Admixture with other oils (%)	max, 2.0
Material volatile at 105 C (%)	max. 0.2
Chlorophyll (ppm)	negative
Sulfur (ppm)	max, 5
Cloud test at 0 C	negative
Taste stability	min, 8 weeks

Hardened rapeseed oil can, however, pose problems. Presumably because of the high oleic acid content, hydrogenated rapesced oils with inciting points between ca. 30 and 45 C tend to crystallize relatively slowly. Subsequent post crystallization is accompanied by the formation of large, coarse crystals and by the danger of corresponding texture defects. The major changes in physical properties occur when the crucic acid content in the original oil drops below 10% (13). Most of these defects can be overcome by choosing suitable hydrogenation conditions (14) and by limiting the concentration of rapeseed hardstock components in margarine and shortening blends.

Rapeseed Meal Attributes

Full flexibility of rapeseed meal usage is primarily limited by the presence of glucosinolates in the seed. The so called Canola meals represent a major advance (Table XID, yet even these meals are not completely satisfactory (15).

Glucosinolate content plays a minor role in compounding feeds for ruminants. An interesting development here is the concept of "protected protein," i.e., protein which is used more efficiently in the intestinal tract in terms of milk production by having been made more resistant to rumen degradation by treatment with formaldehyde (16) or similar reagents. Products based on "protected" soybean and rapeseed meal are already being marketed in Europe. Since the degree of S-S cross linkage appears to influence degradation by rumen protease, changes in amino acid composition of rapeseed by breeding might be of interest in this area (17).

Glucosinolates and their decomposition products pose a far higger problem with poultry and pig feeds. Differences in acceptability by growing pigs could, for instance, be related to the consent of oxazolidinethione (18) (Scheme I). Furopean compounders tend to limit incorporation into pig and poultry feeds to ca. 5%. Even with Canola meals, chicken mortality rates can still cause concern. Obviously, certain undesirable factors, possibly tannins (19) primarily concentrated in the seed coat or specific glucosinolate degradation products such as alkyl nitriles (15) (Scheme I)

bE₂₃₂ = ultraviolet absorption at 232 nm of a 1% solution in a 1-cm cell.

bGuaranteed conditions,

TABLE XII

Recommended Usage Levels (%) for Canadian Rapeseed Meal (Canola)a

Turkeys Starter, grower Breeder Pigs Starter, grower, finisher	20 10
	20 10
	10
Cattle Calves Dairy cows Beef	20 10 10

^aThe name Canola signifies low erucic acid oil and rapeseed meal containing max. 2 mg or 18 µmol of glucosinolate, expressed as 3-butenylisothiocyanate/g dry, oil-free meal.

R"
$$CH - CH_2 - C$$
 $N - OSO_2O^*K$

Glucosinolates

Myrosinase, moisture, temperature

 $R'' - CH - CH_2 - NH_2 \leftarrow R - C$ $N - P$ $CH_2 - CH_2 - CH_2$

SCHEME Is Decomposition of glucosinolares in rapesced during processing (simplified scheme).

are still present. Apart from chemical treatment of rapeseed meal (1), newer cultivars such as the Danish spring variety Line (B. nupus) with only ca. 5 μ mol total glucosinolates/g seed in comparison to ca. 21 µmol in Tower, are of special interest. Conventional oxazolidinethione and isothiocyanate analyses are not necessarily reliable measures of total glucosinolate content. Conventional analysis, for instance, does not cover sinalbin (4 hydroxybenzylglucosinolate)presumably a precursor of free thioevanate ions, and this might explain relatively disappointing results of poultry feeding trials with, e.g., Tower and Erglu meals. Thus, improved methods of analysis of glucosmolate decomposition products (20,21) should be of further help in screening new rapeseed strains and novel meal products.

Sinapine, as a precursor of trimethylamine, has been associated with the development of a fishy taint in brown eggs. Recent work at Norwich, England, has indicated that the inhibition of normal hepatic trimethylamine-oxidase activity may be mediated via the thyroid (22). This implies that reduced progoittin in rapesced and meal will also help to reduce the incidence of brown egg tainting.

Another possibility to apprade rapeseed meal is to dehulf the seed (23), decreasing the crude fiber content from ca. 12% to ca. 6%. The composition of experimental hull fractions is very similar to that of grain, but unlikely to demand grain prices because of appearance alone, Moreover, separation of hulls from meats, e.g., with impact dehullers, under factory scale conditions is not yet sufficiently clean. For this reason, there must be a demand for novel rapeseed varieties with a large grain size and thin, light colored halls. which can, in addition, be cleanly separated from the meats. A further potential advantage of light-colored seed coats is that seed chlorophyll pigments can be readily perceived, thus reducing any tendency for producers to harvest too early

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