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Food grade oilseed protein processing: sunflower and rapeseed

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Abstract. Industrial sunflower and rapeseed meals cannot be directly used as a food because of their high fiber content and because of the presence of some undesirable constituents (such as hulls, polyphenolic pigments, etc.) or precursors of toxic compounds (glucosinolates, etc.). Edible protein products (flours, concentrates, and isolates) from these two sources can be obtained by carrying out, to various degrees, and with different procedures, extraction operations of non-proteic and potentially toxic or antinutritional components. All the possible combinations of the single extraction operations (removal of fiber, lipids, polysaccharides, etc.) were studied by various authors in order to develop an optimum process both from the economic and the product quality points of view.

In this report the problems related to the individual extraction operations, rather than to individual processes, are reviewed for reasons of recapitulation and to provide a common basis for comparison. Although it is impossible to reach a definitive conclusion it appears that some of the processes reviewed are able to produce very attractive raw materials for food manufacturing industries. Nevertheless, no food grade sunflower or rapeseed proteins have appeared on the market to date. However, sunflower and rapeseed protein sources will have to be taken into account in the near future as an added promising means for attacking food shortage problems.

Introduction

Sunflower and rapeseed rank, with soybean, cottonseed and groundnut, as the most important annual crops in the world which are grown for oil production (Table 1) [45].

The reasons for the development of these crops are mainly agronomic, but the yield and the quality of the oil and the meal contribute to it. Chemical and aminoacid compositions of these seeds are reported in Tables 2 and 3 [46, 48]. At present, sunflower and rapeseed meals are regarded as potentially important foodstuff ingredients. Recently both of these products have been investigated with the objective of exploring their use for providing nutritional protein for human consumption.

Industrial meal cannot be used directly as a food because of its high fiber content and because of the presence of some undesirable constituents (such as hulls, polyphenolic pigments, etc.), or precursors of toxic compounds

Table 1. Major oilseed crops: world production (1000 Metric Tons)[a]

Period	Soybean	Cottonseed	Groundnut	Sunflower	Rapeseed	Total oilseeds
1971–72	45,890	23,515	11,780	9,980	7,270	109,599
1972–73	49,879	24,545	10,210	9,640	6,800	111,271
1973–74	61,330	24,750	10,850	12,150	6,810	125,952
1974–75	54,570	23,360	11,485	10,735	7,440	120,356
1975–76	66,040	21,285	12,485	9,930	7,925	129,285
1976–77	59,910	22,330	11,115	9,970	6,920	120,820
1977–78	72,770	24,800	11,135	12,935	7,940	141,500
1978–79	78,110	23,560	11,995	13,075	10,720	148,575
1979–80	93,750	25,465	11,455	15,660	10,100	168,080
1980–81	81,520	25,790	11,060	13,210	11,240	154,300
1981–82	86,600	26,630	12,120	14,450	11,450	163,250

[a]Data from: ISTA, Hamburg, West Germany [45].

Table 2. Composition of sunflower seed and rapeseed

	Sunflower			Rapeseed		
	Seed	Kernel	Hull	Seed	Kernel	Hull
Weight proportion (%)	–	70–79	30–21	–	81–84	19–16
H_2O	8–10	5–6	11–12	10–13	6–8	11–14
Oil[a]	38–19	49–55	2–3	40–42	45–50	16–16.5
Protein (N × 6.25)[a]	20–27	27–30	4–5	23–28	27–30	15–17
Ash[a]	3–4	3–4	3–4	3–5	3–5	3–5
Crude fiber[a]	15–20	2–3	60–62	6–8	1.5–2.5	25–28

[a]Moisture-free basis.

Table 3. Amino acid composition of sunflower and rapeseed meals [46, 48]

Amino acid	Sunflower (grams a.a. per 16 g N)	Rapeseed (grams a.a. per 16 g N)
Arginine	8.5	5.6
Histidine	2.4	2.6
Lysine	3.6	5.8
Tyrosine	2.9	2.6
Phenylalanine	4.6	3.5
Cystine	1.8	2.4
Methionine	2.6	1.8
Serine	4.2	3.7
Threonine	3.8	3.8
Leucine	6.2	6.3
Isoleucine	3.9	3.7
Valine	4.8	4.8
Glutamic acid	21.4	16.6
Aspartic acid	9.6	6.2
Glycine	5.4	4.3
Alanine	4.1	3.9
Proline	5.1	6.4

(glucosinolates, etc.). In order to obtain edible protein products from these sources, it is necessary to remove part or all the other non-proteic components and, especially, to remove or inactivate the undesirable factors.

In this area, several research initiatives have been undertaken in various parts of the world by government supported laboratories (such as universities), research foundations and industrial laboratories.

In the following discussion, the problems associated with the purification of protein from sunflower seed and rapeseed, and their potential usefulness, are examined separately.

Sunflower seed

Due to the absence of toxic or antinutritional factors, sunflower protein products are promising food ingredients. The only problems may be:

- polyphenolic pigments such as chlorogenic acid, responsible for discoloration of sunflower meal and reduced bioavailability of some essential amino acids under certain conditions [10, 12, 62],
- hulls, which contain an exceedingly high lignin content for food grade products, and pigments which give undesirable coloration [14, 80]

The main non-proteic components of sunflower seeds are:

- lipids, generally almost completely extracted due to the high value of the oil that is obtained. Nevertheless, technologies for producing partially defatted products have been proposed recently [36],
- polysaccharides, non-proteic nitrogen and mineral salts, produced as residue during protein isolation.

The protein products from sunflower (flour, concentrates and isolates) are obtained by carrying out extraction operations of non-proteic components to various degrees and with different procedures. Figure 1 gives a summary of the various processes proposed for obtaining edible sunflower protein products. All of the possible combinations of the four fundamental operations (removal of fibers, lipids, polysaccharides, polyphenols) were studied in order to discover the best processes, both on a basis of economics and product quality.

Although it is impossible to reach a definite conclusion on this point, it is nevertheless possible to underline the principal advantages and disadvantages relative to the different processes. For reasons of recapitulation and to have a common basis of comparison, we carried out this study by analysing separately the fundamental operations rather than the processes:

Elimination of fibrous components

Hulls which are the major source of fiber components (Table 2) may be removed by using as a raw material:

(a) *The defatted flour,* with physical processes (sieving [57, 61], hydrocyclones [69], etc.) or chemical processes (selective extraction of protein with production of an isolate; discussed later).

At present, from the meal obtained by conventional industries, it is possible to obtain products with a higher protein content and a lower fiber level by means of mechanical operations, such as milling and sieving. The resulting products possess a nutritional value and an organoleptic character suitable for applications as protein integrators for animal feedstuffs.

However, only by excluding drastic thermal and mechanical treatments (pressing, toasting, etc.) in the defatting process is it possible to obtain food grade products. The protein, yield and content of the products obtained with various separation procedures following this line, are reported in Table 4. The highest quality product (flour with a high level of protein (60%), chemical score of 80; PER of 2.19; creamy white color; no taste or smell), even though with a low yield, is obtained using the process developed within the framework of CNR's finalized project [10, 57].

(b) *The whole seed,* using a dehulling process in order to obtain kernels with a very low fiber content. Partial dehulling of the seeds, leaving up to about 10–12% residual hulls, is rather commonly carried out industrially by means of different technologies [9, 17, 23, 40, 52]. The resulting advantages are:

- decreased volume of product to defat, with the subsequent increase of plant capacity;
- decreased wear of the presses;
- better quality of the oil due to a lower wax content;

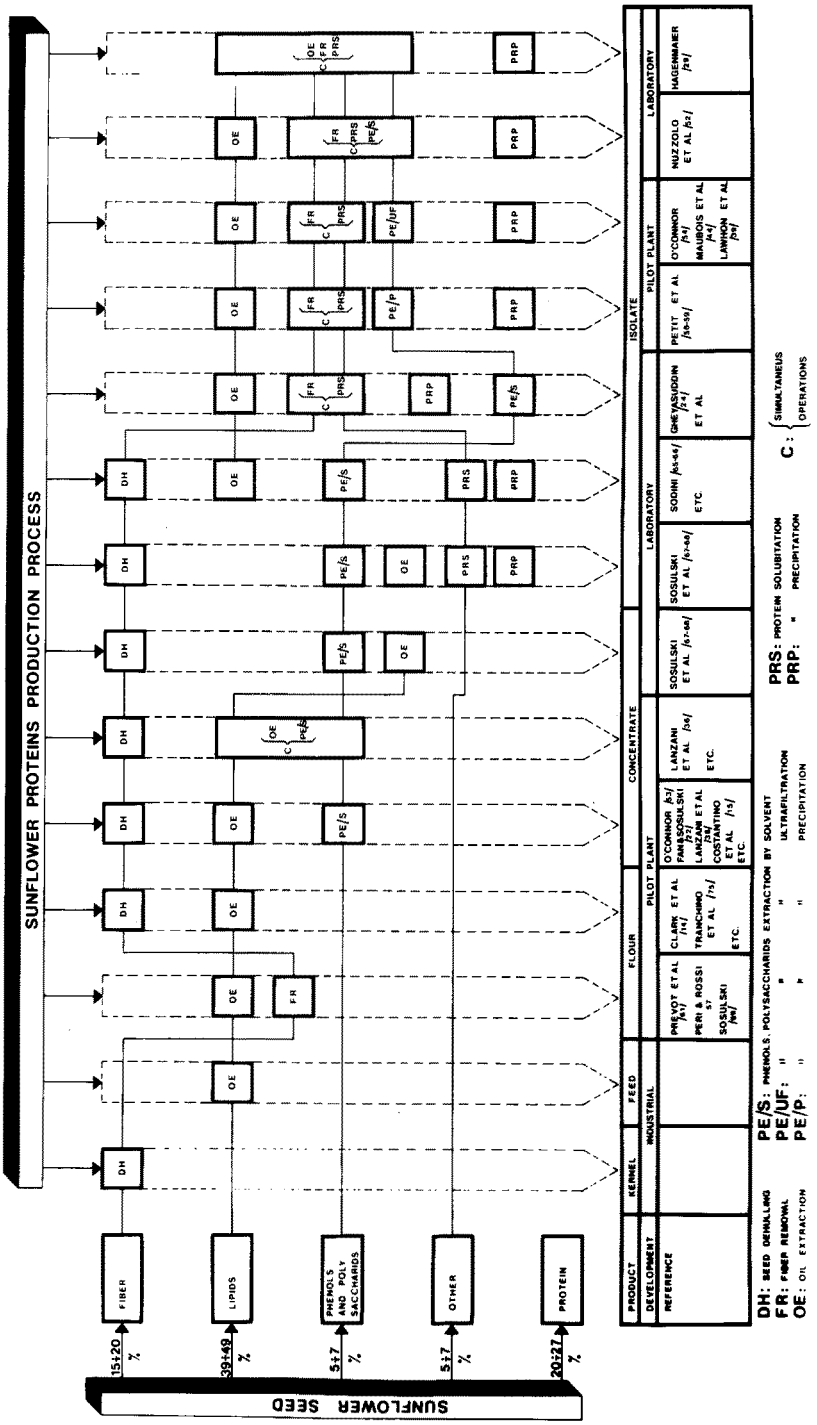
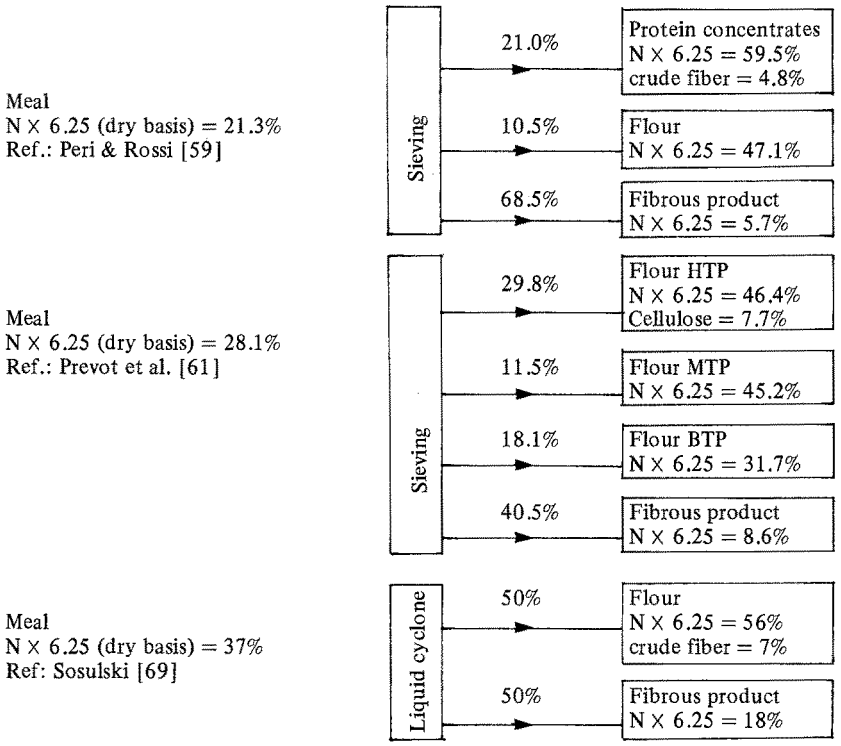

SUNFLOWER SEED
SUNFLOWER PROTEINS PRODUCTION PROCESS
FIBER
LIPIDS
PHENOLS AND POLY SACCHARIDS
OTHER
PROTEIN
15÷20 %
39÷49 %
5÷7 %
5÷7 %
20÷27 %
DH
OE
FR
PE/S
PE/UF
PE/P
PRS
PRP
C
PRODUCT
DEVELOPMENT
REFERENCE
KERNEL
INDUSTRIAL
FEED
FLOUR
PILOT PLANT
CONCENTRATE
LABORATORY
ISOLATE
PILOT PLANT
LABORATORY
PREVOT ET AL /67/
PERI & ROSSI /67/
SOSULSKI /68/
CLARK ET AL /74/
TRANCHINO ET AL /75/
O'CONNOR /67/
FAN & SOSULSKI /73/
LANZANI ET AL /76/
COSTANTINO ET AL /75/
ETC.
LANZANI ET AL /76/
ETC.
SOSULSKI ET AL /67-68/
SOSULSKI ET AL /67-68/
SODINI /65-66/
ETC
GHEYASUDDIN /72/
ET AL
PETIT ET AL /65-66/
O'CONNOR /67/
MAUBOIS ET AL /74/
LAWHON ET AL /76/
NUZZOLO ET AL /67/
HAGENMAIER /67/
DH: SEED DEHULLING
FR: FIBER REMOVAL
OE: OIL EXTRACTION
PE/S: PHENOLS, POLYSACCHARIDS EXTRACTION BY SOLVENT
PE/UF: " " ULTRAFILTRATION
PE/P: " " PRECIPITATION
PRS: PROTEIN SOLUBILIZATION
PRP: " PRECIPITATION
C: SIMULTANEUS OPERATIONS

Figure 1

Table 4. Fractionation of sunflower meals obtained by direct solvent extraction



– better quality of the extraction flour due to an increase of the protein content.

An almost complete dehulling (hull residues of about 1–3%) allows for limiting to a minimum the transfer of pigments from the hulls to the flour [14, 80] as well as reducing the fiber content of the finished product which can be then considered suitable for human use. Industrial applications regarding complete seed hull removal are unknown.

The Food Protein Research and Development Center, Texas University (FRDC), carried out detailed research regarding the feasibility of producing hull-free kernels by means of different industrial technologies [42]:

– rubber roll dehuller;
– single disc attrition mill;
– corrugated roll dehuller;
– bar dehuller.

The results of this study, and those of other researchers [37, 60, 63, 64] show the difficulties of dehulling high oil sunflower seeds, but do suggest,

however, the adoption of technologies based on impacting the seeds on to a target.

Research mainly devoted to the dehulling of high oil seeds with an air jet impact dehuller have been carried out by ASSORENI [74]. The effectiveness of dehulling has been measured as a function of the characteristics of the seed (variety, moisture, etc.) and of the operating parameters (impact velocity, etc.). The results obtained show the following effects:

– the variety of the seed strongly affects the degree of dehulling. It is well known that 'confectionary' seeds can be dehulled much more easily than 'high oil' seeds [37, 42, 60, 63, 64]. However, even within the high oil seeds, there is a perceptible variation in dehulling effectiveness in relation to variety (Figure 2). In any case it is interesting to note that the more

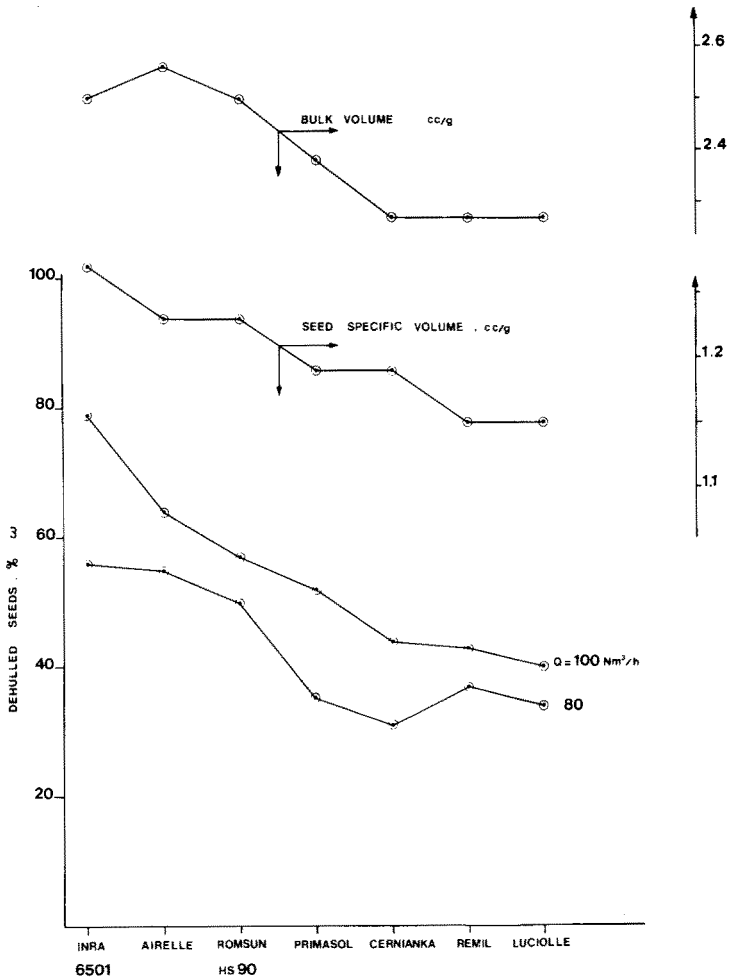


Figure 2. Influence of sunflower seed variety on the percentage of dehulling, and on bulk and seed specific volume.

easily dehulled varieties (Inra, Airelle, etc.) have a lower apparent and/or actual density (measured with the method described in [31]). This observation is understandable in terms of a greater air interspace between the hull and the kernel, and allows for roughly predicting the dehulling characteristics of commercial grade seeds.

- a decrease in the moisture of the seed increases the percentage of dehulled seed (100–(U); Figure 3), but also increases the quantity of product having a dimension less than 2 mm (fines, (F)). Preliminarily, a moisture of about 3% may be considered optimum as it allows reaching a minimum amount for the sum(U) + (F) (Figure 3). The proper optimum, however, is determined by considering the system performances of the integrated dehulling-separation operation and is found to be in the range of 3–5%, depending upon the characteristics of the seeds.
- increasing the impact velocity of the seed on the target, expressed as transport air flow rate in the acceleration tube, increases the quantities of dehulled seeds and fines, simultaneously, with a preliminary optimum at about 100 Nm^3/h for the acceleration tube tested (Figure 4). The performances of the integrated dehulling-separation system may be

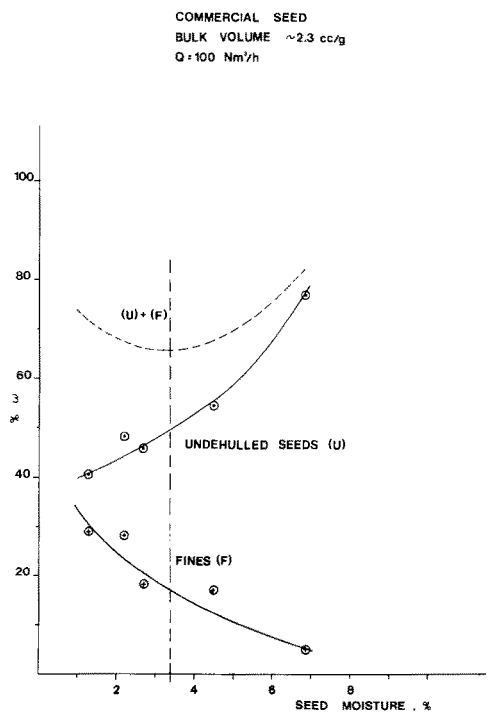


Figure 3. Percentage of undehulled seed and of fines (< 2 mm) as a function of seed moisture.

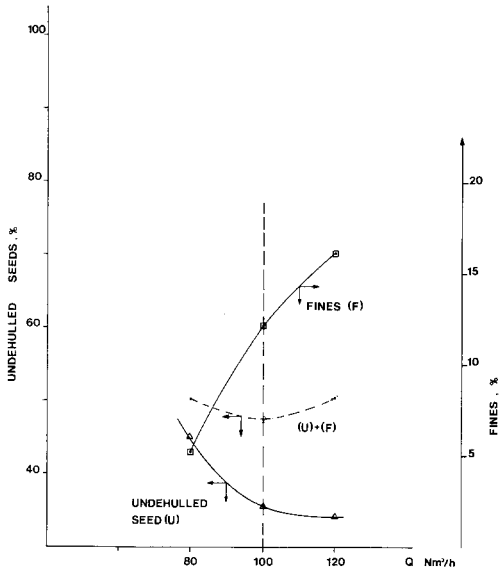


Figure 4. Percentage of undehulled seed and of fines (< 2 mm) as a function of the impact velocity, expressed vs. transport air flow rate.

characterized by curves, relating the kernel recovery vs the hull content in the final product for a given set of parameters related to seed characteristics and operative variables. Figure 5 shows an example of these curves obtained with a Hydromécanique et Frottements plant consisting of an air jet impact huller and a fluidized bed separator [5]. A negligible kernel loss (less than 0.5%) occurs if a high percentage of hulls (greater than 6%) is allowed within the air current of the dehulled product. On the other hand, the production of completely hull-free kernels requires a very high rate of product recycling back to the dehuller with greater fines formation and kernel losses (about 15%) in the hull stream.

In order to have an acceptable product at the completion of extraction, it is necessary to limit the hull content to about 2–3%; therefore in the example shown, there is a kernel yield of 95–97%.

Lipids extraction

The extraction of lipids may be carried out:

(a) directly on whole seeds: these are the conventional oil extraction technologies. The aim is maximum recovery of oil without any attention being given to the quality of the meal which is usually destined for animal feed;
(b) on partially, or nearly totally dehulled seeds: these are processes which

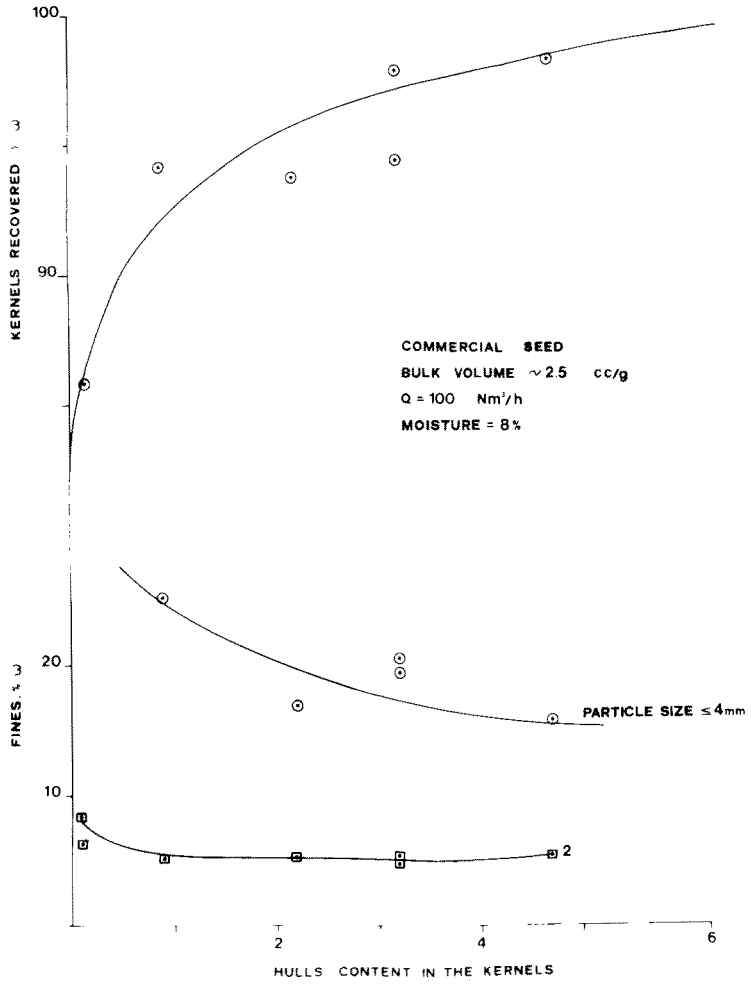


Figure 5. Kernel recovery and fines present in the final product as a function of the hull content.

emphasize, to a greater extent, producing flours (higher protein content and less fiber content) including 'food grade' flours;

(c) on dehulled and dephenolized seeds: these involve those processes which have been used on a laboratory scale by various authors as an alternative to dephenolization after defatting. Oil extraction from dephenolized kernels, however, does not seem to present specific problems [22, 67, 68].

(d) on dehulled seeds with simultaneous extraction of phenols: these processes are aimed at the production of partially defatted products, or concentrates.

Prepressing and solvent extraction processes are the most common procedures used to defat whole seeds and partially dehulled seeds. For economic reasons, prepressing is used to obtain all but some 15–25% of the oil in the kernel; subsequently, extraction with solvent (usually hexane) allows nearly total extraction of the oil (lipid residues between 1–1.5%).

Solvent extraction, either as a subsequent phase to prepressing or a direct operation, is carried out industrially with two types of processes [7, 10, 43]:

Immersion processes. These consist of a solid-liquid contact stage in which the continuous phase is the solvent, with a subsequent stage for separation of phases. This procedure is more suitable for removing the last fraction of oil contained in the seed, which is the most difficult to extract, and allows attainment of low amounts of residual oil in the flours.

Disadvantages of these types of extractors are the low concentrations of oil in the solvent (maximum 15% compared to 25% with percolation plants) and consequently the high costs of solvent recovery. The conventional plants of this type are very bulky and cannot reach high production rates. For these reasons, percolation extractors have been used lately to replace nearly all immersion extractors.

Percolation processes. These are systems which continuously pass a solution through the stationary bulk of seeds. An essential condition for the application of the process is the possibility of draining the solvent through the solid. The procedure is particularly suitable for obtaining the first fraction of oil (about 70%) which is most easily removable. The most serious disadvantages of the percolation extraction process are that it is difficult to obtain good recoveries of the remaining residual oil left in the flour after the first extraction, and above all, it cannot be used on materials which do not permit an easy drainage of the solvent, due to the size and/or physical characteristics of the product being extracted. For this reason, almost completely dehulled sunflower seeds are not easily treated with this type of extractor. Up to now, other types of industrial processes capable of extracting oil from completely dehulled seeds are not known.

Some data regarding oil extraction from dehulled seeds have been given [10, 14, 42]. These indicate the extractive and rheological difficulties in this material treatment.

To overcome these problems a research activity aimed at determining an appropriate extractive system, suitable for treatment of dehulled seeds, was carried out in the framework of the above mentioned ASSORENI research program [56, 75]. The rheological difficulties were bypassed in reconsidering an immersion process, and the extractive problems were solved by means of a proper selection of the operative variables. To realize the effect of these variables, the mechanism of the extraction and the characteristic parameters involved must be taken into account. From the results obtained, the oil

diffusion within the solid particles seems to be the rate-controlling step of the process; and the parameters affecting the extractive effectiveness appear to be:

- kinetic parameters: characterizing the oil diffusion rate within the solid particles;
- thermodynamic parameters: characterizing the distribution of lipids between the two phases under equilibrium conditions;
- technological parameters: characterizing the effects of homogenization and retromixing in the systems used. The most important of these is the coefficient of imbibition (i), which determines the quantity of solvent present in the solid after the solid-liquid separation;
- extraction parameters: characterizing the type of contact between solid and liquid (simple or multiple, cocurrent or countercurrent, etc.), the residence time (t), filling ratio (G), etc.

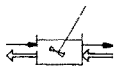
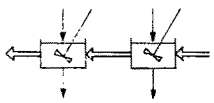
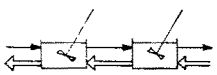
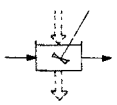
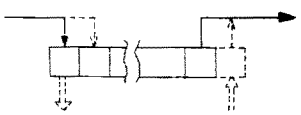
Each of these factors separately affects the extractive effectiveness, even though the main effect comes from their interaction. The equations characteristic of the elementary units of solid-liquid contact that constitute the different industrial extractive systems were derived in order to clarify this interaction. To reach simple explicit correlations, from which the effect of the parameters are made evident, the following simplified hypotheses were used:

- achievement of equilibrium conditions in every stage;
- linearity of the equilibrium relation: $C_L = \alpha C_S$;
- constancy of the imbibition coefficient i.

The correlations derived are shown in Table 5, and are graphically illustrated in Figure 6, in the case of an equilibrium coefficient $\alpha = 1.3$ kg flour/kg hexane, and imbibition coefficient $i = 0.35$ kg hexane/kg flour, corresponding to the system under discussion. The same figure shows the experimental results obtained with the two-stage mixer-settler countercurrent system, and with the five-stage semicontinuous system with a filling coefficient $G = 0.11$ kg flour/(kg flour + kg hexane) (curve 6), and $G = 0.31$ (curve 7). It appears to notably show effects of technological parameters (i) and of extraction parameters (G); the main effect, however is that of the equilibrium coefficient (α) during the initial phase of extraction, and the kinetic coefficient of the transfer of oil (K) in the final phase.

The possibility of simultaneous lipid and polyphenol extraction was studied within the framework of the above mentioned CNR finalized project [36]. The process involves a brief boiling water treatment of dehulled seeds kept in a homogeneous dispersion. Partially defatted meals (51% protein, 22% lipids) and oil have been obtained at both the laboratory and the pilot plant scales. The simultaneous extraction of lipids and polyphenols may be carried out with a hexane-ethyl alcohol-water ternary solvent. It is then

Table 5. Simplified correlation of elementary units of solid-liquid contact

EXTRACTION SYSTEMS	CORRELATION
1. Single stage mixed vessel	
	$\frac{(Cs)_i}{(Cso)} = \frac{1 + i\alpha}{1 + R\alpha}$ with $R = \frac{L}{S}$
2. Two stages cross flow	
	$\frac{(Cs)_i}{Cso} = \frac{(1 + i\alpha)^2}{\left(1+\alpha R/2\right)\left(1+i\alpha+\alpha R/2\right)}$
3. Two stages countercurrent	
	$\frac{(Cs)_i}{Cso} = \frac{(1 + i\alpha)^2}{\alpha^2 R^2 + \alpha R + (1 + i\alpha)}$
4. Single stage pseudo-batch (stationary solids)	
	$\frac{(Cs)_i}{Cso} = (1 + i\alpha)e^{-R^*\alpha}$ with $R^* = \frac{L \cdot t}{S}$, $G = 1$
5. Infinite stages pseudo-batch (plug flow liquid, stationary solid)	
	$\frac{(Cs)_i}{Cso} = 1 - \frac{\alpha R}{1+i\alpha}$

possible to obtain easily separable phases, good yields in oil, and limited denaturation of the protein.

Elimination of polyphenolic compounds

Polyphenolic compounds, and in particular chlorogenic acid, are responsible for giving undesirable colorations to sunflower protein products when used as foodstuff, as well as reducing the bioavailability of some essential amino acids. This phenomenon occurs at alkaline pH due to the chemical or enzymatic oxidation of polyphenols to quinones [10, 12, 62]. They react with some functional groups of the protein structures (amino groups of lysine, indole groups of tryptophan, sulfur bridges of methionine) with the formation of chromogenic groups in which the amino acid is bonded in a non-biodisposable form and is nutritionally unavailable.

Various attempts have been made for removing polyphenolic compounds, utilizing different raw materials according to different processes, in order to

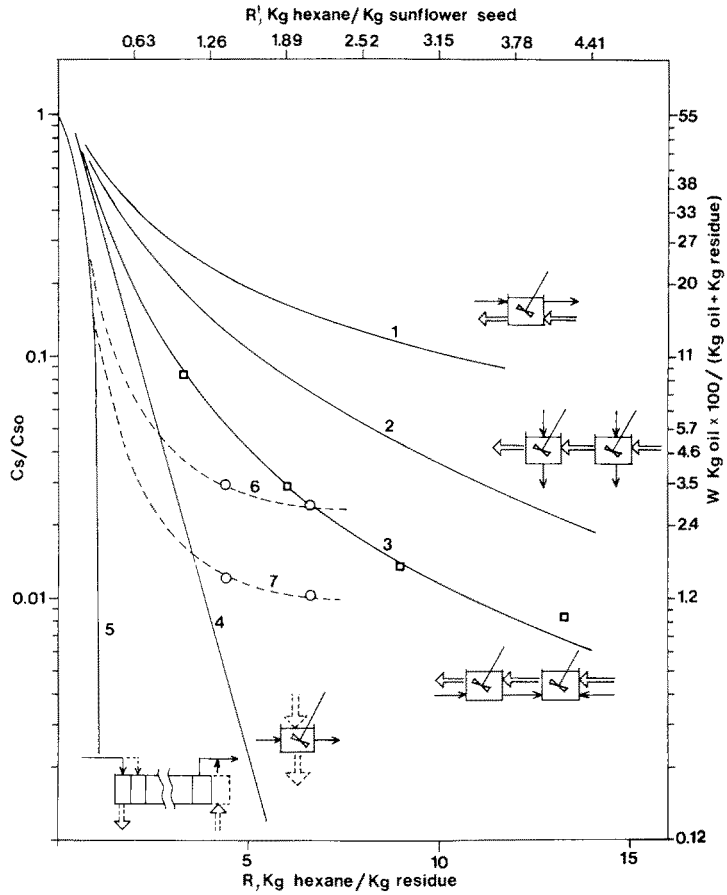


Figure 6. Residual oil concentration as a function of the extraction ratio for different extraction systems, with $\alpha = 1.3$ and $i = 0.35$ [29]: (1) Mixed extractor, single-stage. (2) Mixed extractors, two-stages (cross flow). (3) Mixed extractors, two-stages (countercurrent flow). (4) Semicontinuous mixed extractor, single-stage, $G = 1$. (5) Infinite semicontinuous extractors (countercurrent flow), $G = 1$. (6) and (7). Five semicontinuous extractors, $G = 0.11$ and $G = 0.31$ respectively, experimental results. □ Experimental results of system 3.

obtain protein products with good biological and functional qualities taking into account the technical-economic aspects of production:

(a) Dephenolization of dehulled seeds: the removal of phenols is carried out before or simultaneously with defatting. A very detailed work on the extraction of phenols from dehulled seeds with acidulated water at a pH of 4.5 was carried out by Sosulski et al. [22, 67, 68]. The fundamental advantages of this type of process, compared to those of dephenolization from flour, are basically rheological: easy mixing and separation of the liquid-solid system. From the extractive point of view, this process exhibits some

advantages compared to the extraction from flour with water. The seed membrane serves to contain or reduce the diffusion of protein, lipids, etc. (compared to extraction from flour with water, protein loss is reduced from 25–26% to 12–17%. However, it is undoubtedly less efficient than the extraction from flour with ethanol (protein loss ~ 3%; Table 6).

(b) Dephenolization of defatted flour with acidulated water or ethanol: dephenolization with acidulated water presents the above mentioned rheological difficulties as well as problems from the extractive point of view, with relatively low yields, about 60% (cases 3–8 in Table 6); or low protein content, about 66% (case 10 in Table 6); or very high denaturation (case 7 in Table 6) [22, 38, 53]. From the point of view of rheology and extractability, however, the system improves substantially if the dephenolization of the flour is carried out with a water-ethanol solvent. In this solvent, protein extraction losses decreased by about ten times due to the reduced solubility of the proteins. Therefore, the protein content in the final protein product (73–77%) and the yield (77–80%) increase simultaneously (cases 11–13 in Table 6). This line, which appears to be the most promising to obtain a sunflower proteic concentrate, was studied in detail by Assogna et al [4] and Costantino et al [15].

The scaling up of this laboratory and bench-scale data was verified during the operation of the pilot plant. The predicted values of extractive efficiency (cases 12 and 13 of Table 6) were confirmed with a certain scattering which reflected differences in the characteristics of the starting seeds.

Isolation of Proteins (Isolates)

All of the non-proteic components of sunflower seeds or derived products (flour, concentrate) may be removed with a protein solubilization operation at alkaline pH, elimination of the solid residue, and reprecipitation of the proteins when the solution is brought to an acid pH.

This procedure, when applied to seeds or flour that have not been dephenolized, gives rise to the undesirable oxidation of polyphenols (mentioned above in point 4), with the subsequent formation of undesirable coloration and reduction of the bioavailability of some amino acids. For this reason, the isolation of protein is preceded by or combined with dephenolizing operations. In any case, it must be remembered that the characteristics of the raw material are of fundamental importance in determining the efficiency of the dephenolization, the yield in protein, and the characteristics of color, solubility and purity of the isolate.

In particular, according to Sodini et al. [65], the pressing, but above all, the toasting stages in the production of the meal, strongly reduce the solubility of the proteins, hindering the removal of polyphenols and carbohydrates bonded irreversibly to the proteins (Table 7).

The processes to obtain protein isolate may be divided into the following principal classes:

Table 6. Influence of extraction conditions on the yield and characteristics of sunflower

N	Extraction conditions							
	Procedure	Raw material	solvent	pH	T (C°)	Number of extraction (N)	Total solvent to flour ratio (l/kg)	Total extraction time (min)
1.	Countercurrent Diffusion	Seed	Dilute HCl	4.5	80	5	6	150
2.	Idem	Seed	Dilute HCl	4.5	65	6	6	180
3.	Countercurrent Extraction	Flour	Dilute HCl	4.5	80	5	6	150
4.	Idem	Flour	Dilute HCl	4.5	24	5	6	150
5.	Idem	Flour	Dilute HCl	4.5	24	6	6	180
6.	Cross flow Extraction	Flour	Dilute HCl	4.5	24	5	25	150
7.	Idem	Flour	Dilute HCl	4.5	80	5	25	150
8.	Idem	Flour	Dilute HCl	4.5	60	6	90	108
9.	Idem	Flour	Dilute HCl	5	100	1	25	0.17
10.	Idem	Flour	Dilute HCl	5	100	3	75	0.50
11.	Countercurrent	Flour	Ethanol 70% Vol.		24	5	6	150
12.	Idem	Flour	Ethanol 75% Vol.	4.5	30	2	16	120
13.	Semicontinuous Countercurrent	Flour	Ethanol 75% Vol.	4.5	25	6	7.5	180

Table 7. Influence of technological processes on the extractability of phenols and on isolate protein yield obtained from sunflower meal

Processing		Concentrate		Isolate	
Defatting	Drying	Chlorogenic acid (%)	Total carbohydrates (%)	Protein	Color
Pressing	Toasting	0.9	1.5	46	Dark green
Direct-solvent extraction	Toasting	0.6	1.3	53	Brown
Direct-solvent extraction	Low temperature 30°C	0.3	0.5	80	Creamy

concentrate

Yield		Protein concentrate						
Extract protein loss (%)	Dry weight yield (%)	N × 6.25 (%)	Nitrogen solubility index (%) pH 5	7	9	9.5	Chlorogenic acid (%)	Ref.
12.1	73.8	70.5		9	41		0.4	[22]
17.0	69.6	70.6		13	69		0.8	
26.5	60.0	72.5					0.8	
24.9	60.6	73.4		43	90		1.2	[22]
26.1	57.2	76.5		57	94		0.5	
25.2	58.5	75.7		53	89		0.5	[22]
30.0	60.1	69.0		27	44		0.3	
	53.0							[53, 54]
			15			85	0.4	[38]
20.0	70.0	66.0	23			75	0.1	
2.8	78.0	73.8		18	76		0.4	[22]
3.0	80.0	70.0	9	25	64	66	0.3	[75]
3.0	78.0	73.9				72	0.3	[15]

(a) preliminary removal of polyphenols with the above-mentioned processes (leaching of the seeds or flours with water and/or ethanol) and subsequent isolation of the protein.

These kinds of processes certainly give a good quality product. The sole difficulty is the cost of preliminary double extraction (defatting and dephenolization). Total yields of isolate of 24% and 45%, respectively from flour or concentrate, can be deduced from the data reported by O'Connor [53] on dehulling/defatting/leaching with the acidulated water/protein isolation process. Substantially higher total yields were obtained with regards to dehulling/defatting/leaching using the ethanol/protein isolation process. The protein yields are 70% and 72% from flour and concentrate, respectively. In this case, the isolates have a creamy white color and a protein content (N × 6.25) of about 95% [65, 66].

(b) solubilization of the proteins in a nondephenolized product at an alkaline pH in the presence of an antioxidant and subsequent elimination of polyphenols through precipitation [58, 59] or ultrafiltration [16, 39, 44, 54].

The research work carried out by INRA along both of these lines have contributed to extremely interesting pilot plant results.

In order to avoid the oxidation of polyphenols into quinones (which are more reactive towards proteins), the preliminary phase of solubilization of the proteins is almost always carried out in the presence of an antioxidant (sodium sulfite [16, 24, 44], an inert gas [54], a chelating agent [52], or a surface active agent (sodium dodecil sulfate [39]) which allows solubilization of the proteins at an acid pH, thus hindering the oxidation of the polyphenols.

Nevertheless, these precautions are not generally sufficient to prevent the reaction of the proteins with the formation of chromogenic groups in the subsequent phase of precipitation of the isolate. Therefore, to obtain an isolate with good characteristics it is necessary to carry out subsequent dephenolization after the antioxidant treatment:

(1) Gheyasuddin [24] operates an extraction with isopropanol on the isolate.

(2) O'Connor [54], Culioli and Maubois [16, 44] and Lawhon [39] suggest an ultrafiltration treatment on the protein solution. Commercial microporous membranes with an approximate pore diameter of between 15 and 70 A and usable, and they make a separation at the molecular weight level of around 10,000–100,000. The low molecular weight polyphenol components are thus separated from the proteins. The isolate is obtained by direct atomization or dispersion or spinning of the protein solution, or, alternatively, by precipitaion at acid pH, washing and drying. The protein content of the isolate is in the range 87–97% and the protein yield is 40–60%, depending on the procedure used. The technical-economic feasibility of this technique will be dependent upon obtaining high permeation rates and membranes with a long technical life.

Another approach for eliminating polyphenolic constituents was suggested by Petit [58, 59]. The procedure consists of the precipitation of colloids and the pigments of the hulls with calcium acetate, and that of phenols with magnesium acetate, during the solubilization of the proteins in an alkaline medium. The protein isolates, obtained after the isoelectric precipitation (pH 4.5–5.5), or atomization or spinning of the protein dispersion, have a nitrogen content of 16–16.5% and are completely soluble in an alkaline medium.

The use of chelating agents, such as the aluminate ion reported by Nuzzolo [52], allows for the formation of stable complexes at alkaline pH between polyphenols and AlO_2^- or $Al(OH)_4^-$; the oxidation of the polyphenols is thus then avoided during the course of the solubilization of the proteins. The subsequent acidification of the solution by means of citric acid allows

obtaining a protein precipitate at the isoelectric point; simultaneously citric acid, acting as a complexing agent, maintains the aluminium in solution. A creamy white isolate with 95% protein content and 0.4% polyphenol is obtained with a yield of about 60%.

Finally, a completely different technique was suggested by Hagenmaier [29] which permits treating the whole seed directly with an alkaline solution for the solubilization of proteins in the presence of Na_2SO_3 and for the simultaneous extraction of oil. The proteins are then reprecipitated from the aqueous solution. However, rather serious difficulties are encountered in the solid-liquid separation and in the breaking of the water/oil emulsion. Further, the yield of oil is low and the isolate is of a dark color.

Solvent stripping

The problem of removing solvent from vegetable protein products is extremely important from the point of view of health, and with respect to the flavor of the products themselves.

Only few data on the levels of residual solvents in sunflower products are present in the literature: 300–900 ppm of hexane in edible flour prepared by the FPRDC [14], and about 200 ppm of hexane in the toasted flakes from the food oil industry [40]. On the other hand, much data are available for soybeans, although they are rather conflicting: the makers of desolventizer guarantee only a negative POP TEST; in a recent review Chessin [13] reported data showing 55 to 225 ppm of hexane in commercial soybean edible flours; Honig et al. [30] reported data indicating 90 to 410 ppm of hexane in commercial soy protein products; they also show a large variation in the effectiveness of various drying procedures for removing solvents from hexane-ethanol azeotropic extracted soy flours (Table 8).

All of these data are presented without an interpretation of the phenomenon, and therefore generalizations or extrapolations are not possible. But if the phenomenon is carefully studied, the following main effects appear:

- during the drying of protein products, an approximately linear reduction of the water content and an asymptotic reduction of the solvent content occurs as a function of the time (Figure 7);
- the value of the asymptote changes with varied drying conditions; more precisely, the faster the heating of the flour, the higher the asymptote.

These facts allow for interpreting the process in terms of the simultaneous transfer of heat and matter in which:

(a) the rate of water removal is controlled by the transfer of heat of the saturated evaporating surface;
(b) the rate of solvent removal is controlled by the rate of diffusion of the solvent within the flour particle.

On this basis, it is possible to formulate a mathematical model of the

Table 8. Levels of volatiles (μg/g) in azeotrope-extracted soy flours after various desolventizing procedures (Honig et al. [30])

Desolventizing procedures	Volatile component					
	Methanol	Ethanal	Ethanol	Acetone	Hexane	Hexanal
1. Air dried	3	3	3,600	11	2,200	4
2. Freeze dried, twice at 0.7 mm Hg after wetting to 35% moisture (w35%)	34		124		350	
3. Vacuum strip, no steam, on rotary evaporator at 50°C, w 35%	5		32		130	2
4. Vacuum strip, steam, on rotary evaporator whithe blending in steam	7	0.1	23	4	470	5
5. Toasted, steam heated at 100°C for 10 min	5		19	16	12	3

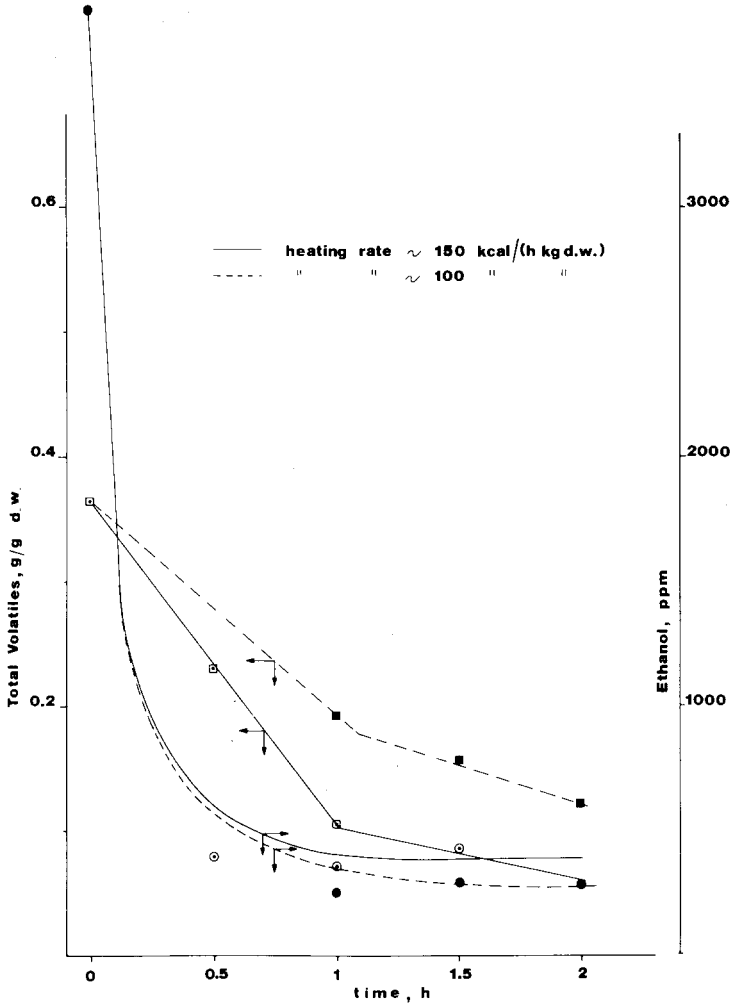


Figure 7. Water and Ethanol content of sunflower concentrate as a function of the time for the two heating rate values.

process which allows understanding the above-mentioned effects (theoretical curves in Figure 7). The same analytical approach appears satisfactory for interpreting both the removal of hexane from flour and of ethanol from protein concentrate, except for the different expression of the diffusion coefficients. Sufficiently low amounts of residual solvent in the proteic products are achievable if low heating-rate, wetting, and grinding of the products are adopted.

Microbiological control

Great emphasis is given in the literature to the necessity of microbiological

control in the plants used for production of food grade soybean proteins [47, 50]. However, for soybean, the seed thermal conditioning and the toasting or steam treatment of the meal allows for having low aerobic total counts (about 10^4 germs/g dry weight) with no problem.

For sunflower there are less data, but increases from 10^3 to 10^5 in the total count with the presence of coli have been reported during the finishing of food grade sunflower seed flour [14].

A statistical study concerning the microbiological content of commercial sunflower seeds showed that the most probable total count is around 10^6 with the presence of entero bacteria and E. coli (Figure 8 [18]).

The effect of processing on the microbiological content of sunflower products, as measured in the continuous pilot plant, is indicated in Figure 9, for the case of an oil extraction with hexane at 40°C, and of a phenol extraction with a 70% ethanolic solution at ambient temperature without thermal conditioning of the seeds or final toasting of the products. A notable reduction in the total microbiological count is observed only in the treatment with the water-alcohol solution. In any case, successive increases have been noted in the count during the finishing of the product. However, the protein concentrate obtained, contained a total count of about 10^5, without E. coli and pathogens; results which are better than observed in good commercial practice.

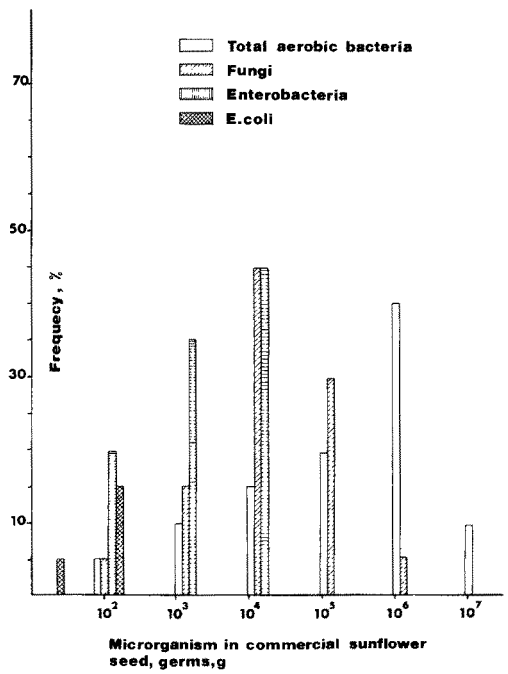


Figure 8. Statistical distribution of microrganisms in commercial sunflower seed.

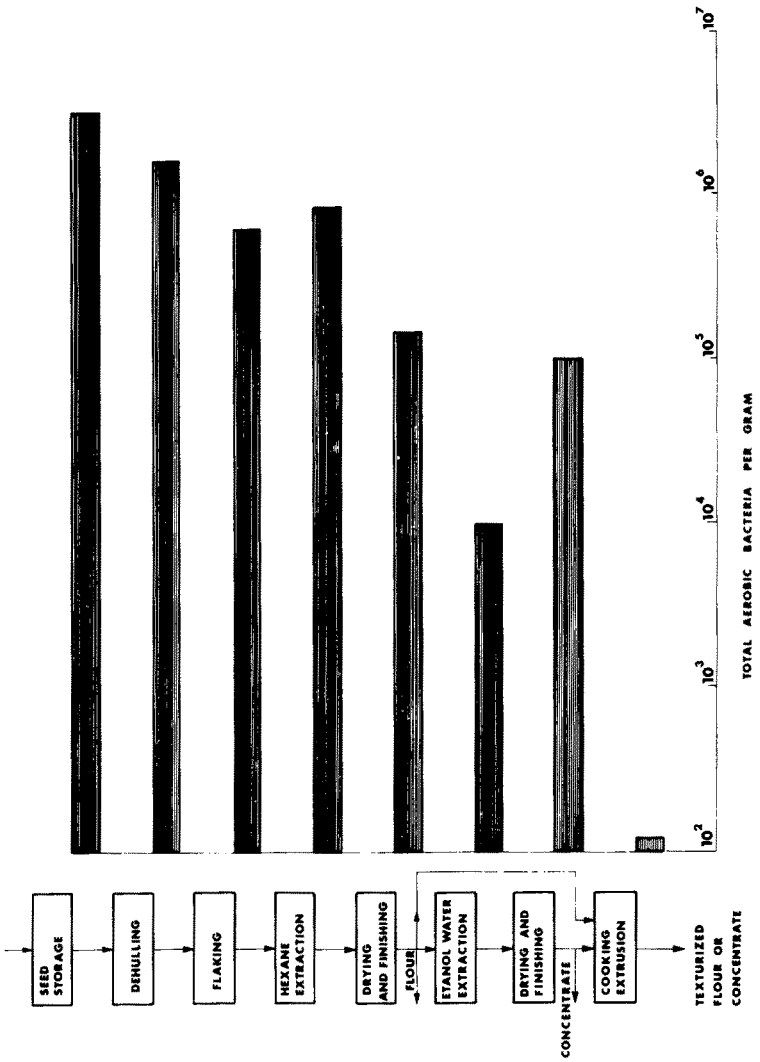


Figure 9. Effect of processing on microorganisms in sunflower products.

In the case of flour production, to obtain the same result, it is necessary to include a sanitizing phase in the process which avoids the transfer of a possible contaminant of the seed to the product. This phase may be a thermal conditioning of the seed or a final toasting of the flour.

The production of texturized protein by cooking-extrusion appears to be very efficient in reducing the total aerobic count to very low values (Figure 9).

Rapeseed

As with many oil seeds, rapeseed contains some undesirable factors. With rapeseed, erucic acid is present in the lipid fraction and glucosinolates are detectable in the flour. Both of these factors have hindered the diffusion of rapeseed and the utilization of its products for food. Considerable research was devoted to overcoming these problems, working in two main directions:

Genetic improvement: attempting to select varieties with low contents of low erucic acid and thioglucosides ('double zero' types). This research has shown good results with respect to the reduction of erucic acid (from about 50% of the total content of the lipids to about 2% in the new selected varieties). Meanwhile, further work is required for the reduction of the thioglucosides content which is present in the range 3–7% in the most common varieties.

Detoxication of the flour by removal of thioglucosides. Really, these substances, biologically inactive by themselves, are hydrolyzed by the enzyme myrosinase, contained in the seed as well, to produce toxins and bitter substances (nitriles, isothiocyanates etc.), which negatively affect the thyroid, the kidneys, the liver and other organs more or less seriously [3, 49, 81].

Actually, industrial rapeseed extraction meal is used as ruminant feed because the hydrolysis products of the thioglucosides are destroyed in the rumen, the only negative factor being in the nasty flavour. The use of rapeseed proteic products for monogastric animals, or human consumption, however, requires the removal of thioglucosides and/or the inactivation of the myrosinase enzyme.

The problems inherent to the preparation of raw material, the eventual dehulling, the oil extraction, and the proteic enrichment of the rapeseed meal, are similar to those already examined for sunflower [3, 5]. So only the problems specific to rapeseed processing will be discussed, i.e., myrosinase inactivation, thioglucosides extraction and protein isolation.

Myrosinase inactivation and glucosinolates removal

A preliminary thermal conditioning of the seeds (80–90°C for about 15 minutes) for myrosinase inactivation is always included in current rapeseed processing to improve both meal and oil quality. Afterwards, the extracted

meal is toasted to eliminate the volatile compounds formed by hydrolysis of thioglucosides. The thermal treatment of the seeds is not sufficient to detoxify rapeseed meal because even though myrosinase is completely inactivated, it is not possible to exclude possible hydrolysis of the thioglucosides through other nonenzymatic methods and, in any case, the possibility exists that myrosinase can be absorbed with other foods. So meal detoxication is effected only by removing, almost completely, the thioglucosides. For this the following processes can be adopted:

The extraction processes seem to be the most promising ones to prepare proteins for human consumption. These processes are characterized by the solvent (water, ethanolic solution or water-acetone mixture), the product to be extracted (whole or ground seed or meal), and by the processing system used. According to Belzile and Bell [6] and Solsulski et al. [8], the detoxication of rapeseed proteic products is more effective if the hydrolysis of the more water soluble thioglucosides is avoided.

The processes suggested by these authors therefore, include inactivation of myrosinase (heating at 100°C for 3 min [2, 6, 8], or treatment with an 80%(vol.) ethanol solution [3]) and then extraction of the thioglucosides with water, ethanolic solutions or water-acetone.

On the contrary, other authors [73, 76, 77, 78, 79] suggest the hydrolysis of the thioglucosides (enzymatic and/or thermic) before extraction with water or water acetone.

The processes pursuing the first idea are the most numerous. Of those we mention the Karlshamns patented process [1, 55] for the production of food grade rapeseed protein concentrate by water extraction of dehulled and ground seeds; the combination of the production line of food grade products with that of conventional oil production (pressing) allows building up an integrated system in which the by-products of the first line (fines, hulls, extract) find a valuable use, while also avoiding pollution problems.

Eapen et al. [18] suggest a similar process starting with enzyme inactivation (by cooking the seed in water for 2 min) and then removal of glucosinolates by acqueous extraction.

A detailed analysis of the acqueous extraction of thioglucosides from ground seed as a function of pH has been carried out by Staron and Guillaumin [70]. This analysis resulted in the determination that pH 8 was the pH value at which the yield of dry matter (68%), protein (70%) and oil (95.6%) were maximum. So a patented process for the production of an edible, high quality oil and of a food grade protein concentrate with high yields was developed [71].

Bhatty and Sosulski [8] suggest, on the contrary, a treatment of the whole rapeseed with a 50% (by vol.) ethanol solution (pH 12 with NaOH). An efficient diffusion of glucosinolates with minimum losses of other seed constituents (proteins and lipids) occurs. The ethanol both inhibits myrosinase and makes thioglucoside dissolution easier. The treated seed may be suitable, after partial dehulling and air classification, for protein concentrate preparation.

Also, Eklund et al. [20] suggest the use of an ethanolic solution (about 30% vol.) with NaCl to extract the thioglucosides from dehulled seeds. The direct use of the defatted product (48% protein, 31% lipid, 0.4 mg/g thioglucosides) was also proposed.

Protein isolate (isolates)

Rapeseed protein isolate can be prepared with about the same processing as for sunflower isolate. But the presence in rapeseed of proteins with widely different characteristics (molecular weights from 10,000 to 300,000 [3]; isoelectrical points from pH 3.6 to 11), would require, for obtaining good proteic yields, multistage solubilization and precipitation. Kodagoda et al. [33] obtain three distinct isolates with yields respectively of 11; 13 and 42%, with isoelectrical precipitation of proteic extracts obtained with water, with HCl at pH 2, and with NaOH at pH 10. The presence of precipitation coadjutants can nevertheless allow obtaining better yields of isolates and/or limiting the number of solubilization and precipitation stages.

In fact, as shown in [25], it is possible to increase the yields in dry matter (from 16 to 33%) and in nitrogen (from 35 to 75%) by adding sodium phytate to the rapeseed proteic extracts. Unfortunately the phytic acid is likely to exert an adverse effect on the nutritional value of the isolate so that other types of precipitation coadjutants have been studied: hexametaphosphate (HMP), carboxymethyl cellulose (CMC), electrolytes etc. [26]. An almost quantitative recovery of the extracted proteins was achieved with each one of the following schemes [41]:

- precipitation at pH 6.6 (Isolates A) followed by precipitations at pH 5 in presence of CMC (Isolate B). The isolate A is rich in high molecular weight proteins with isoelectrical points from 4 to 7; the isolate B is rich in middle-low molecular weight proteins with isoelectric points from 6 to 8.
- precipitation at pH 4.9 in the presence HMP (Isolate C), formed by proteins of various molecular weights with isoelectrical points from 4.5 to 10.

The presence of HMP, in the protein extraction phase also appears to increase the yield of protein isolated. An increase in nitrogen extraction from 61 to 81% was obtained when the HMP concentration was brought from 0 to 2% [72].

Greater protein yields (about 90%) are reported by Nockrashy et al. [21] following a counter-current protein extraction with acqueous solution of Na OH (0.02 N) and double precipitation at pH 6 and pH 3.6.

Yield, however, depends very much on the characteristics of the raw material (denaturation during myrosinase inactivation, etc.) and on the protein losses in the solid-liquid separation and in the isolate washings. The yield of solubilized nitrogen in NaOH (0.1 N) decreases from 89% to 62% if the rapeseed meal prepared under mild conditions is replaced by a rapeseed meal coming from oil industries [27].

The glucosinolate content in the isolate is usually much lower than in the starting meal. Thompson [72] reports that more than 98% of the glucosinolate initially present in the meal (12.11 mg/g) was removed during protein extraction, isolate precipitation, and washing. Therefore, the total glucosinolate level obtained in the isolate (0.14 mg/g) was not considered to involve any negative nutritional effect. However, the total exclusion of the thioglucosides and other chromogen impurities from the isolate is possible by means of ultrafiltration of the protein extract as suggested for sunflower isolate production [44].

Conclusions

In the present discussion, the problems related to the various processes suggested by different authors for producing edible sunflower and rapeseed protein products, have been briefly examined.

Some of these processes are in an advanced stage of development and can be used to produce economically feasible yields of good quality products for food manufacturing industries. Nevertheless, to date, no food grade sunflower or rapeseed protein is found on the market. However, sunflower and rapeseed protein sources will have to be taken into consideration in the very near future as a promising and potentially useful means for attacking food shortage problems.

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