A NEW APPROACH TO CANOLA PROCESSING

Levente L. Diosady and Leon J. Rubin

Department of Chemical Engineering and Applied Chemistry
University of Toronto, Toronto, Ontario, Canada, M5S 1A4

BACKGROUND AND OBJECTIVES

Rapeseed protein has a well-balanced amino acid composition thus it is a potential source of food protein. In the past the high glucosinolate content of the meal has severely limited its use in animal feed. Even today the meal is used mostly as a fertilizer by the largest rapeseed-producing country, China. Despite great advances in plant breeding canola still contains up to 30μM/g of glucosinolates, and high levels of fibre, phenolic compounds and phytate, which reduce its nutritive value, and prevent its use in food products.

Glucosinolates can be hydrolyzed to form toxic compounds that interfere with thyroid function. Phytates are strong chelating agents that affect the utilization of polyvalent metal ions, especially zinc and iron, by strongly binding these essential metals to make them unavailable for metabolism. Phenolic compounds lead to bitter flavour and a dark colour in the final products. Finally the hull, which makes up approximately 30% of the oil-free meal, is high in indigestible fibre.

These components and their toxic breakdown products must be removed as completely as possible before rapeseed protein can be used as a food ingredient. An economically feasible technological solution to the problem of their removal has not yet been reported.

In 1979 the authors set as one of the main goals of the Food Engineering Group at the University of Toronto the development of new technology specifically for the processing of canola and rapeseed.

GLUCOSINOLATE-FREE MEAL PRODUCTION

In the past there have been many attempts to remove glucosinolates from rapeseed by a variety of techniques. This work has been reviewed by Maheshwari et al. (1981). Attempts to remove the hull by conventional milling techniques and by air classification have not been commercially successful, since the hull contains significant amounts of oil that must be recovered if the process is to be economically viable. Perhaps the exception to this is in the French feed market, where the oil-containing hull can be readily sold as a high-energy feed for rabbits.

Schlingmann and Präve (1978) reported that ammonia dissolved in methanol can rupture the cell wall of yeast cells, and extract the lipids present. The solvent is highly polar, and it therefore seemed reasonable to try it for the extraction of compounds such as glucosinolates. We demonstrated that treatment of canola meal with this solvent lowered its glucosinolate content to less than 1.6μM/g. (Diosady et al.,1985a)

The methanol/ammonia solution cannot be used for the treatment of undefatted seeds since the solubility of oil in this solvent is low, quite insufficient to extract all of the oil from canola. Therefore, for the extraction of whole seed a two-phase solvent system was developed which uses methanol/ammonia in combination with hexane. Ground seed was contacted with methanol containing dissolved anhydrous ammonia and some water, and after a period of blending followed by a period of minimum or no stirring, hexane was added to the slurry and thoroughly mixed. On standing, the mixture separated into three well defined phases: a light non-polar phase, a denser polar phase, and a solid. Thus a very effective partition was obtained in which the oil was recovered from the non-polar hexane phase, while the polar phase contained dissolved waste materials consisting mainly of carbohydrates, but also containing glucosinolates and phosphatides.

The meal thus produced contained less than 2μM/g glucosinolates, it had a protein content of 50%, and its polyphenol content was substantially reduced resulting in a light-coloured, bland-tasting meal. (Rubin, et al.,1984).

Hexane is slightly soluble in methanol, but this solubility can be depressed with the addition of water to the alcohol phase. This effectively increases the partition coefficient, removing most of the oil from the polar phase, and also aids in the removal of glucosinolates. The presence of water in larger quantities increases the solubility of protein in the polar phase, resulting in some protein loss to the gum-phase. More importantly, an excessive water content results in the precipitation of some of the phospholipids by hydration on the meal, resulting in a less attractive, somewhat sticky product.

We have optimized the laboratory process in terms of solvent composition, solvent-to-seed ratio, contact time and temperature. (Rubin et al.,1986). A number of alcohols were tested, at various water and ammonia levels. Although several combinations produced acceptable products, the best composition was found to be methanol containing 10% (w/w) dissolved anhydrous ammonia and 5% (v/v) water. The results are shown in Table 1.

Table 1 Effect of solvent composition on glucosinolate removal

Water content	0%	5%	10%	15%
		Glucosinolate content in μmol/g		
Alkanol [1]				
Methanol	3.0±0.8	<1.6	<1.6	<1.6
Ethanol	10.4±0.8	10.4±0.8	4.3±0.8	<1.6
i-Propanol	15.1±0.4	16.0±1.6	13.0±0.9	9.28±1.1
t-Butanol	15.0±0.4	15.8±0.8	13.8±2.3	12.6±0.8

[1] Each solvent contained 10% by weight ammonia

A study of the functional properties of the meal has been completed. It is a good protein material, superior to soy protein in some of its properties although inferior in some others (Naczk et al.,1985; Diosady et al.,1985b). It binds fat very well, and therefore it may prove to be a useful binder in processed meat products such as wieners.

The process was also successfully tested on a Canadian high-glucosinolate rapeseed variety (Midas) and on mustard seed (Naczk et al.,1986). Tests on the Chinese rapeseed variety, Ninu 7, and on a commercial seed sample from Jiangsu Province indicate that the process is adaptable to high-glucosinolate, high-erucic-acid rapeseed varieties. The final protein content of the meal depended on the protein content of the seed used.

A program to develop appropriate technology for the application of this laboratory process on a large scale was initiated. Clearly the traditional percolating bed extractors are not suitable for contacting the finely ground seed with two solvents.

The Szegö mill, developed in our Department, (Trass 1980) can efficiently grind seeds as a slurry. The mill rapidly produces a finely-ground solid phase with a small average particle size and high surface area, thus allowing the extraction to reach equilibrium very rapidly (Diosady et al. 1983). Grinding of the seed in $CH_3OH/NH_3/H_2O$, followed by the contacting of the resulting meal slurry with hexane results in the effective extraction of glucosinolates and other polar constituents into the polar phase, and the dissolution of some 80% of the oil into the hexane. Thus the meal residue must be extracted further to remove all of the oil (Diosady et al., 1987).

Liquid-liquid extraction equipment also lends itself to leaching of solids. The solid particles fall through a rising column of solvent, which leaches the soluble components from it. It has been used in the extraction of minerals and its use has been proposed for oil extraction. Unfortunately the throughput of such a system depends on the terminal velocity of the solid particles, i.e. the upward flow of the solvent must be slower than the downward velocity of the solids. Otherwise no separation occurs, and the solids are swept out of the column by the solvent. Since the density differential between rapeseed and hexane is relatively low, the terminal velocity of finely ground solid particles becomes very small, and even minor turbulence in the column results in the wash-out of the solids.

We found that droplets of a slurry of finely ground seed particles suspended in $CH_3OH/NH_3/H_2O$ remained intact when passed through hexane in a Karr liquid-liquid extractor, as the surface-tension retained all of the finely divided solids inside the $CH_3OH/NH_3/H_2O$ droplets. Since the diameter of the droplets was typically some 10 to 200 times larger than that of the solid particles, their terminal velocity, and thus the throughput rate, was high. As the slurry droplet moves countercurrently through the hexane phase, oil is extracted from the seed simultaneously with the co-current extraction of the polar components. The results of typical extraction runs are presented in **Table 2**

Table 2 - Results of Karr-column extraction runs

Run number	Meal oil content %	Meal protein content %	Glucosinolate µmol/g	Extraction efficiency %
1	0.23	48.3	<1.2	99.7
2	0.36	47.7	<1.2	99.5
3	0.25	48.7	<1.2	99.7
4	1.70	50.5	1.2	95.7
5	0.14	50.3	1.5	99.3

In the best run the residual oil content of the meal was as low as 0.15%, while the glucosinolate content was reduced to 1.5µM/g. The meal contained low levels of polyphenols, resulting in a light-coloured, bland-tasting meal, with a protein content of some 50%. The meal still contained all of the fibre and phytate present in the seed (Diosady et al. 1989).

In order to reduce the energy usage, we have investigated the recycling of some of the methanol-ammonia after the extraction stage. Since the most efficient solvent-to-seed ratio (R) during grinding is lower (R=2-2.5) than during the glucosinolate extraction stage (R=6.7), the ground seed slurry must be diluted with methanol-ammonia. Some of the $CH_3OH/NH_3/H_2O$ could be recycled to either the grinding or the dilution steps after it is recovered from the meal slurry by filtration, thus reducing the amount of methanol-ammonia which needs to be distilled. We found that the extraction column effectively reduced the glucosinolate content of the meal to <2µM/g when the polar phase contained up to 75% of untreated, filtered $CH_3OH/NH_3/H_2O$ made up with 25% of fresh solvent. Since the recycled solvent is loaded with dissolved carbohydrates the quantity of solids dissolved in the $CH_3OH/NH_3/H_2O$ phase decreases, resulting in a higher mass yield but a lower protein concentration.

PROTEIN ISOLATE PRODUCTION

While the meal produced by the process is superior to commercial rapeseed meal, it still contains traces of glucosinolates, and retains all of the fibre and phytate originally present in the seed. Although high-quality soy-protein isolates are readily prepared by isoelectric precipitation of the proteins at an acidic pH, this procedure is not feasible with rapeseed or canola as the seed contains many proteins with a wide range of isoelectric points and molecular weights (Appleqvist and Ohlson, 1972).

Since glucosinolates, phytates, and phenolics have significantly lower molecular weights than rapeseed proteins, ultrafiltration could be used to remove these undesirable components, unless they become physically or chemically bound to proteins. Once the proteins are solubilized, hull, which is mostly insoluble, could be removed by filtration. In the first stage of our study we developed a simple process consisting of a single extraction step, followed by two stages of ultrafiltration. (Diosady et al., 1984). The process produced a

protein isolate of excellent quality; however its yield was low, and phytate levels were not reduced.

Serraino and Thompson (1984) reported that rapeseed protein interacted with phytic acid to form complexes that could not pass through dialysis membranes. Their results indicated that at pH≈3.5 phytate could be removed by dialysis in the presence of calcium chloride.

We have developed and tested five other processing schemes in an attempt to design a simple, effective process (Rubin et al. 1990). The best processes is perhaps the simplest. The extraction of rapeseed meal at an optimal pH dissolves most of the protein while leaving 80-90% of the phytate and all of the fibre undissolved. Isoelectric precipitation at pH 3.5 recovers approximately one-half of the dissolved protein as an isolate. This also helps to reduce the solids load in the later membrane-processing steps. Finally, ultrafiltration and diafiltration are used to concentrate and purify the acid-soluble proteins, which can be then recovered by conventional techniques. From lab-prepared canola meal the process produced an isoelectric isolate with a protein content of 87 to 101% (N x 6.25), and soluble protein isolates which contained 91 to 104% protein (Table 3). Both isolates were free of glucosinolates, low in phytate, light in colour, and almost bland in taste (Tzeng et al. 1990).

Table 3 Production of isolates from $CH_3OH/NH_3/H_2O$ extracted meal

Sample	Protein % (Nx6.25)	Glucosinolate µmol/g	Phytate %	Yield %
Starting meal	50.5	0.6	4.32	100.
Meal residue	33.1	<0.6	5.63	69.1
Isoelectric isolate	100.6	<0.6	1.54	12.0
Soluble isolate	103.1	<0.6	1.13	10.7

The isolates had lysinoalanine levels ranging from <10 to 220 ppm, which is similar to the lysinoalanine content of common foods and food ingredients (Deng et al. 1990).

The process is uniquely tailored to rapeseed. It permits the recovery of protein from the oil-free meal as two protein isolates. In the case of hexane-extracted meal, 75.4% of the protein in the starting meal was recovered as isolates. Some 60% of it was recovered as an isoelectric protein isolate and 40% as an acid-soluble protein isolate. Methanol-ammonia/hexane-extracted meal gave a lower isolate yield, but the residual meal contained 33.% protein, and may be used in animal feeds. It is important to note that some of the protein lost in the process is non-protein nitrogen, and some of the nitrogen in the meal residue is tied up in the insoluble hulls.

Most of the basic process development work that can be done at a university has been completed, and now further development must be done on a scale beyond the capability of the University. This must be followed by a nutritional and safety evaluation of the protein products.

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