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Factors Affecting the Desolventization of Canola Meal

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ABSTRACT

Factors affecting the level of residual solvent in hexane-extracted canola meal included the moisture content of the crushed seed and the temperature of the hexane at the time of extraction, the duration of the extraction process and the severity of the cooking procedure prior to extraction. Low moisture, low temperature extraction, short exposure to excess hexane and mild cooking procedures all contribute to minimizing the levels of sorbed hexane after desolventization was complete. Dry heat could drive off only part of the residual hexane. Moist heat, as steam, was more effective.

INTRODUCTION

Oil recovery from canola seed, as performed by the oilseed crushing industry, almost invariably involves solvent extraction with commercial hexane. Inevitably, a small residue of solvent is retained by the meal after the desolventization process. It is desirable for several reasons to minimize the amount of residual solvent in the meal. Toxicological effects must be considered, especially if canola meal is to be utilized as a source of protein for human food (1-4). There has been insufficient testing to establish whether any health hazard is associated with the levels of residual hexane that occur typically in canola meal, but the possibility of such a hazard cannot be ignored. For a crushing plant to operate on a continuous basis, hexane must be added to make up for the amount which is not recovered from the meal. High make-up volumes contribute significantly to operating costs and escalating prices for hexane have magnified this problem. In some circumstances, high levels of residual hexane may create a potential fire and explosion hazard.

A laboratory study has been performed to investigate a number of factors which conceivably could affect the amount of residual hexane sorbed on canola meal. The factors chosen for testing have been related to controllable parameters in the operation of a crushing plant. These include moisture content of the seed, cooking time, cooking temperature, solvent temperature and both heat and moisture input in the operation of the desolventizer. The results of the study have suggested modifications in processing conditions which the industry could explore in order to minimize residual hexane in canola meal, without adversely affecting either product quality or operating efficiency.

EXPERIMENTAL PROCEDURE

Starting Materials

Starting materials included canola seed, reroll meal (material removed from the processing stream of a commercial plant

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after cooking but prior to extraction), spent cake (material removed after oil extraction but prior to desolventization) and regular canola meal. These materials were obtained from a local canola crushing plant that was designed for direct oil extraction (no prepress). Additional starting materials were canola meats and hulls isolated from seed of the variety Tower and a prepress meal from the POS Pilot Plant, Saskatoon. Commercial hexane was obtained from the same local sources. Other chemicals were reagent grade or better.

Analytical Methods

The hexane content of the meal was determined by a modification of the procedure of Wan et al. (5). A 2.0-g sample of meal, two filter paper discs and 0.2 mL of water were added to a 160-mL hypovial. After sealing, a known volume of heptane (usually 3 μL) was injected through the septum as an internal standard. The vials were heated in an oven at 130 C for 1 hr. On removal, a 1.00-mL sample of headspace gas was withdrawn with a gas syringe and analyzed on an F & M model 700 gas chromatograph at room temperature, using a 180 cm x 3 mm id stainless steel column packed with 10% SE 30 on Gas Chrom Q, 80-100 mesh (Chromatographic Specialties, Brockville, Ontario) and a flame ionization detector. The ppm of hexane were calculated from recorder peak areas by comparison to a standard curve prepared from meal samples spiked with known volumes of hexane.

The effects of several modifications in the analytical procedure for hexane were examined, including variations in heating temperature, amount of added water, and the time interval between removal of hypovials from the oven and sampling of the headspace gas. The pressure within the hypovials was also measured as a function of time after removal from the oven, by connecting a calibrated pressure gauge to the vials.

Moisture contents were determined by the AACC air oven method (6). Oil contents were determined by AACC procedure (7) using hexane as the extractant. Nitrogen contents were determined by the Kjeldahl method (8).

Laboratory Processing Methods

Canola seed (or isolated meats) were flaked with an Allis Chalmers laboratory roller mill using settings that gave flakes which closely resembled the commercial product. Moisture contents were adjusted upward by exposure to a humid atmosphere for the required time interval. Samples were placed in open petri dishes in a desiccator containing water in the bottom compartment. The procedure was usually performed at room temperature, but in one series of experiments the desiccator was placed in a controlled temperature cabinet at various higher temperatures. If samples were to be processed further, they were stored for at least 24 hr in a sealed container to permit moisture equilibration. Moisture contents were adjusted downward in a vacuum oven at room temperature or in an air oven at various temperatures for time periods as required. In some cases, the flaked samples were cooked in sealed hypovials in a hot air oven. Preliminary experiments in which a thermometer was inserted in the filled vial were performed at various oven temperatures to establish time/temperature profiles for the cooked material. Further moisture adjustment was frequently performed prior to solvent extraction.

Most oil extractions were done with commercial hexane. However, in one set of experiments, pure solvents representing the major components that were identified in commercial hexane, were combined to give binary mixtures of known composition. Each mixture was subsequently used as an extractant for canola seed.

Two different oil extraction procedures were used. Extraction at the boiling point of the solvent was done with a large Soxhlet apparatus for various periods of time up to 24 hr. Extraction at room temperature was done by shaking one part of the sample with 5 vol of hexane for 30 min in a suitable flask, recovering the meal by filtration through a fluted filter and repeating the extraction four more times on the residue.

Two methods of desolventization were examined. In most instances, the meal was air-dried at room temperature for 30 min or more. Following that, 2.0-g samples were placed in open aluminum moisture dishes and heated in a vented air oven. Various temperatures and heating times were investigated but 55 C and 24 hr were adopted as the standard conditions. The hexane content of any sample where the final treatment before hexane analysis was 24 hr heating at 55C, has been defined as the residual hexane content (RH_{55}). Experiments which included the above sequence of steps (moisture adjustment, cooking, extraction and desolventization) were performed on samples of a high-protein canola fraction and a low-protein fraction as well as on flaked canola seed.

The other desolventization method utilized an apparatus consisting of a 3-cm diameter glass chromatographic column fitted with a fritted glass disk at the bottom and connected at the top by ground glass fittings to a water condenser, a liquid N_2 trap and a water aspirator, arranged in series. The column was placed vertically in a 100 C oven with the upper end emerging through a small hole on the top side. In most instances, meal samples were wet with hexane (1 mL of hexane per 3.0 g of meal) and equilibrated for at least 15 min prior to loading into the column. Loading was accomplished with the aid of a large stem funnel using 60 g of meal which gave a bed depth of 16 cm. The bottom of the column was connected to a steam generator at atmospheric pressure and steam was drawn through the sample by the aspirator using a slight vacuum (15-30 cm H_2O). Steam was passed through the column for varying periods of time. Following this, the sample was removed in sections and each section was analyzed for hexane content immediately after the steam treatment and for RH_{55}.

The meal samples that were tested in the apparatus described above had all been subjected to prior treatment which resulted in high RH_{55} values when desolventized in an air oven. A treatment that was frequently used for this purpose was to adjust the moisture content of normal meal to 10% or higher, expose to excess hexane at 60 C for 4-24 hr in a sealed container, and desolventize by a combination of 30 min air-drying at room temperature followed by heating in a shallow tray at 55 C for 24 hr.

Commercial canola meal is often somewhat lumpy. To investigate the effects of lumps on desolventization, a lumpy meal was prepared by sprinkling water on regular meal. Following this, the material was air-dried and screened to select lumps ranging from 6 to 12 mm in diameter. The lumps were exposed to excess hexane at 60 C and desolventized as described above.

Differential Sorption of Commercial Hexane Components

To determine whether or not there was preferential sorption of any of the components in commercial hexane, flaked canola seed was extracted under conditions which caused high RH_{55} levels (17 hr in a Soxhlet; moisture range 9.9-10.4%). The component ratios in the extracting solvent were determined by gas chromatography from recorder peak area ratios and compared to the component ratios in the residual solvent in the meal, which were

similarly determined from peak area ratios in the residual hexane analysis.

Preparation of High-Protein and Low-Protein Fractions from Canola Seed

A protein-rich fraction was prepared by a modification of the procedure of Sosulski and Bakal (9). Flaked canola seed was extracted with hexane at room temperature (four sequential 1-hr extractions with 10:1, v/w (mL/g) ratio of solvent to seed). The meal was air-dried for 72 hr and extracted at room temperature with 10 vol of H_2O adjusted to pH 11.0 with dilute NaOH solution. The supernatant was recovered by high speed centrifugation and adjusted to pH 4.0 with dilute H_2SO_4. After cooling for 72 hr at 5 C, the resulting precipitate was recovered by high speed centrifugation and freeze-dried to yield a high-protein fraction.

The residue from the aqueous extraction at pH 11 was extracted a second time under the same conditions and the insoluble material recovered by centrifugation. Two layers separated in the centrifuge. The lower more abundant layer was recovered and dried in a vacuum oven at room temperature to yield a low-protein fraction.

Experimental Design

Various laboratory processes as described above were performed under conditions where one processing parameter was held constant. Further details are included in the results sections. Several 2^n factorial block design screening experiments (10) were conducted. The variables that were tested included the moisture content of the samples at the time of solvent extraction, the cooking conditions and the temperature of the extracting solvent. The response variable was the RH_{55}.

Evaluation of the Analytical Method for Hexane

Heating of the hypovials for 60 min at 130 C with 0.2 g of added water per 2.0 g of sample was confirmed as the optimum condition (5) for driving sorbed hexane off the meal samples. Higher temperatures and greater amounts of added water contributed to the formation of degradation products in the meal which produced peaks that interfered with the hexane peaks in the gas chromatographic analysis.

For a series of analyses of identical samples, the areas of the residual hexane peaks became progressively smaller as the time interval was increased between removal of the hypovials from the oven and withdrawal of the 1.0-mL headspace gas sample. A similar observation was made regarding the peak areas of the internal standard, heptane, except that the heptane peak areas declined more rapidly. It was concluded that both hexane and heptane vapors had a tendency to resorb on the canola meal (or the wall of the vial) as cooling progressed, with heptane being sorbed more rapidly. Therefore, in the interest of analytical accuracy, it was desirable to maintain the cooling period as short as possible prior to sampling the headspace gas. A cooling period of 30 sec was routinely adopted.

During an early part of this work, difficulty was experienced in achieving consistently reproducible RH_{55} values. Some of the replicates gave excessively high results. It was discovered that this was due to inadequate cleaning procedures. Routine washing occasionally left adsorbed hexane on the walls of the hypovials. This problem was eliminated by autoclaving the vials for 90 min at 15 lb steam pressure as part of the cleaning procedure.

An attempt was made to determine how efficiently hexane was desorbed from a meal sample during the 130 C heating period of the analytical procedure. Recorder peak areas of the headspace gas from replicated series of meal samples spiked with analytical grade hexane, were determined at 30 sec after removal from the 130 C oven. These areas were compared to the areas obtained by direct injection of known volumes of hexane (in heptane solution) into the gas chromatograph. For 3×10^{-2} μL of liquid hexane, the recorder peak area was 34.93 ± 1.55 cm^2. At the same attenuation the calculated peak area for an equal volume of hexane spiked on a meal sample was 34.09 ± 1.98 cm^2, giving an average recovery of 97.6%. Within experimental error, the recovery was quantitative. Data cited are averages and standard deviations for 5 or more replicates. This calculation is complicated by two factors. There was some loss of headspace gas from the syringe when the needle was removed from the vial because the pressure inside the vial was above atmospheric pressure. Second, the fraction of the hexane vapor that was withdrawn in the syringe was greater than the ratio of syringe volume to total headspace volume because water vapor will condense and the gas volume will tend to contract on entering the relatively cool syringe. If the gas within the syringe cools to room temperature, it can be shown that the errors caused by these two factors compensate for each other.

RESULTS AND DISCUSSION

Composition of Commercial Hexane

The gas chromatographic analysis of commercial hexane showed it to be a mixture in which four components were resolved (Fig. 1).

By comparison with the retention times of known hydrocarbons, the second, third and fourth peaks, in order of emergence, correspond to 3-methylpentane, *n*-hexane and methylcyclopentane, respectively. The first peak corres-

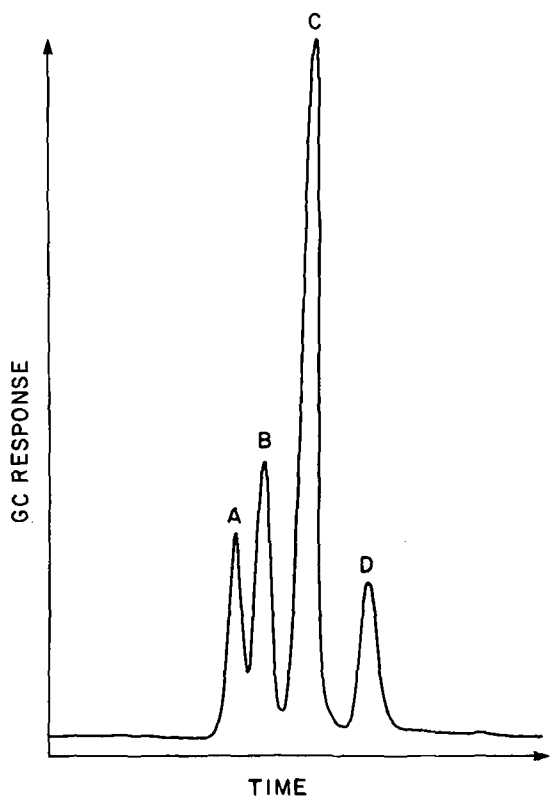

FIG. 1. Gas chromatographic separation on Gas Chrom Q of components in commercial hexane at 25 C; A = 2-methylpentane or 2,3-dimethylbutane; B = 3-methylpentane; C = *n*-hexane; D = methylcyclopentane.

ponds to 2-methylpentane and/or 2,3-dimethylbutane. Nine different samples of commercial hexane obtained over a 6-month interval were analyzed. The relative percentage abundance of these four components ranged from 8.7 ± 0.3 to 16.3 ± 0.4 for peak number one, 15.9 ± 0.4 to 22.3 ± 0.5 for 3-methylpentane, 46.3 ± 0.3 to 57.1 ± 1.3 for *n*-hexane and 12.3 ± 0.8 to 23.1 ± 0.3 for methylcyclopentane. Thus, considerable variation is to be expected in the composition of commercial hexane.

Effect of Dry Heat on Spent Cake

Dry heating of commercial spent cake for quite long periods of time, (up to 36 hr) drove off only part of the hexane. Figure 2 shows the decline in residual hexane with time of exposure at four different temperatures.

After the first 3 hr, further loss of hexane was very slow. Heating at 103 C was considerably more effective than at any lower temperature. In another series of experiments, meal samples were pretreated under various conditions so that the RH_{55} values varied over a wide range. Identical samples from each treatment were heated for 24 hr at 55 C or 103 C prior to hexane analysis. Results are in Table I.

The ratio of the hexane content after heating at 55 C to that after heating at 103 C shows a slight trend to smaller values for those meal samples which retained the greatest amount of hexane.

Effect of Time and Temperature of Exposure to Excess Hexane

A prepress meal was extracted with commercial hexane at room temperature to give a spent cake containing 1.3% residual oil. The meal (meal A) was adjusted to 10.0% moisture and samples were exposed to excess hexane at either 50 or 60 C for various periods of time before determining the RH_{55} values. Data are in Figure 3.

High solvent temperatures and long exposure times both contribute significantly to higher values for residual hexane.

TABLE I

Effect of Dry Heat at 55 and 103 C on Hexane Content of Canola Meals Subjected to Various Pretreatments

Sample	RH_{55}[a]	RH_{103}[a]	RH_{55}/RH_{103}
1	146 ± 54[b]	51 ± 17[b]	2.86
2	276 ± 61	85 ± 4	3.25
3	482 ± 28	180 ± 34	2.68
4	677 ± 52	298 ± 30	2.27
5	728 ± 26	236 ± 11	3.08
6	917 ± 33	368 ± 36	2.49
7	1104 ± 56	470 ± 54	2.35
8	1155 ± 61	489 ± 44	2.36
9	1391 ± 41	695 ± 31	2.00
10	1716 ± 42	906 ± 120	1.89

[a]ppm residual hexane after heating at 55 C (or 103 C) for 24 hr.
[b]Mean plus or minus standard deviation, 3 replicates.

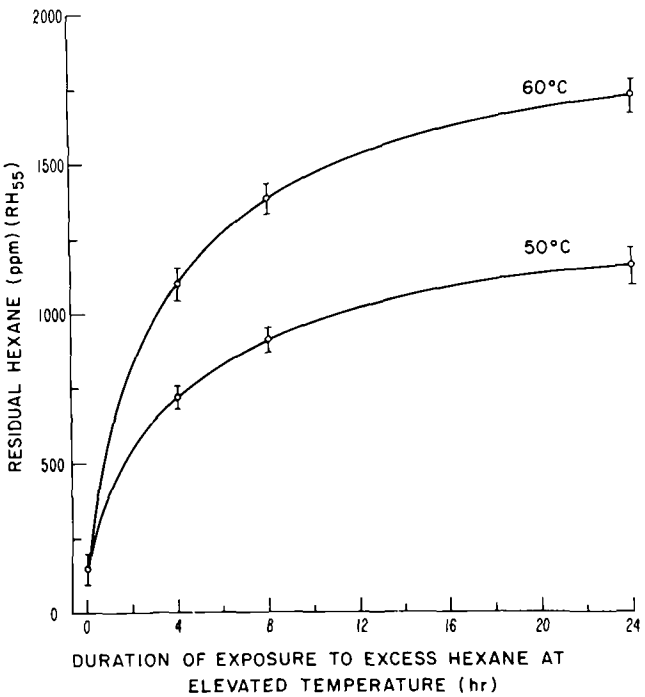

FIG. 3. Effect of time and temperature of exposure to hexane on residual hexane content of canola meal (meal moisture 10%). Error bars represent ± one standard deviation of 3 replicated hexane analyses.

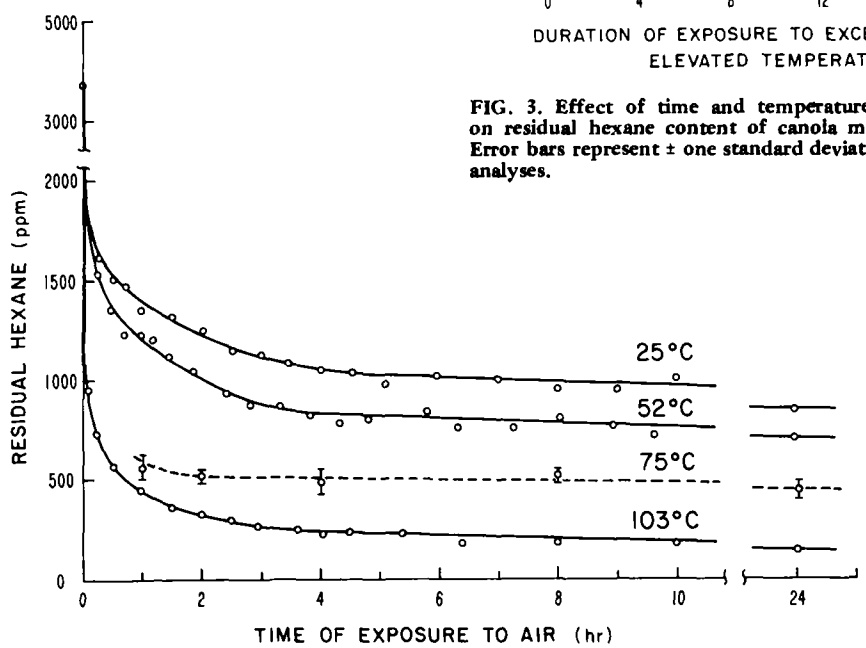

FIG. 2. Effect of dry heat on residual hexane content of canola meal. Solid lines are for identical samples of spent cake. The dashed line represents a comparable sample of meal for which the RH_{55} was 701 ± 53 ppm.

Effect of Moisture Content of Meal when Exposed to Excess Hexane at High Temperature

A further sample of meal A was partially dried in a vacuum oven to 4.8% moisture. Subsamples were further adjusted to higher moisture contents. All samples were subjected thereafter to excess hexane at 60 C for 4 hr and RH_{55} values were determined. Data are in Figure 4.

These data clearly indicate that the residual hexane content of canola meal increased with increasing moisture content at the time of exposure to excess hexane.

Effect of Cooking and Moisture Content

Whereas the experiments in the two previous sections were performed on meal samples after extraction of the oil at room temperature, the results presented below are from experiments on samples of isolated meats and isolated hulls in which the processing steps more closely resembled commercial practice. Prior to hexane analysis, samples were flaked (meats only), adjusted to the desired moisture content, cooked, partially dried, extracted with hexane in a Soxhlet apparatus for 5 hr and oven-dried at 55 C for 24 hr. (In some experiments, the cooking and/or partial drying steps prior to extraction were omitted.) Data are in Table II.

These data confirm that the residual hexane content was much higher in those samples where the moisture content at the time of hexane extraction, was relatively high. Samples of both meats and hulls had comparatively low residual hexane contents when they were partially dried prior to extraction. Partial drying in a vacuum oven at room temperature was compared to similar drying in a hot air oven. The data (not shown) indicated that the drying method had no significant effect on the results. The data in Table II further show that hulls extracted at 8.2% moisture had a much lower residual hexane content than meats extracted at 7.5% moisture. At moisture contents exceeding 16%, the residual hexane content in hulls was less than that in meals extracted in the 9-10% moisture range. This apparent difference may not be real because the initial oil content of the meats was 54.0%, whereas that of the hulls was only 5.0%. Assuming that most of the moisture was localized in the nonoil fraction, a moisture content of 8% in the meats was equivalent to a moisture content twice that high in the hulls.

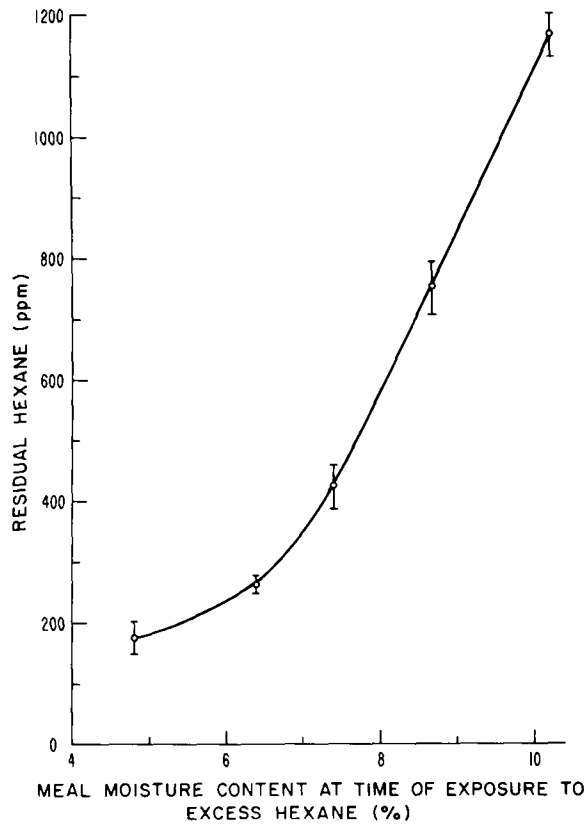

FIG. 4. Effect of moisture content at time of exposure to hexane on residual hexane content. Meal samples were exposed to hexane at 60 C for 4 hr deviation of 3 replicated hexane analyses.

With regard to cooking vs not cooking: for those samples that were extracted in the moisture range from 7.5 to 10%, the residual hexane contents in the cooked samples were approximately twice as high as in the corresponding un-

TABLE II

Effects of Cooking[a] and Moisture Content on Residual Hexane Content of Isolated Meats and Hulls

Sample	Cooking time (min)	Moisture content (%)			Residual oil content (%)	Residual hexane ppm
		Before cooking	After cooking	Before extraction		
Meats	30	7.7	7.5	1.5[b]		87 ± 5
	0	7.7		1.2[b]		61 ± 5
	30	10.2	9.6	2.7[b]	0.4	311 ± 32
	0	10.2		1.5[b]	1.8	86 ± 6
	30	7.7	7.5	7.5	0.8	2584 ± 11
	0	7.7		7.7	3.9	1334 ± 19
	30	10.2	9.6	9.6	0.8	5384 ± 269
	0	10.2		10.2	0.7	2778 ± 28
	25	8.0	7.7	7.7	0.9	3732 ± 633
	40	8.0	7.9	7.9	1.2	3108 ± 381
	25	10.1	9.6	9.6	0.9	5022 ± 418
	40	10.1	9.0	9.0	1.1	4987 ± 238
Hulls	30	6.5	6.6	6.6	2.1	128 ± 12
	30	8.2	8.2	8.2	2.7	119 ± 5
	30	17.3	16.7	5.3[b]	3.7	157 ± 13
	0	17.3		4.9[b]	3.0	113 ± 6
	30	17.3	16.7	16.7	3.2	2031 ± 15
	0	17.3		17.3	2.3	1970 ± 99

[a]Cooked in 130 C oven. Sample temperatures reached 100-105 C after 25 min cooking. For samples cooked 40 min, samples were transferred to a 100 C oven after 25 min.
[b]Samples in which the moisture content prior to extraction is much lower than that before cooking have been partially dried in a hot air oven at 100 C.
[c]Mean plus or minus standard deviation of 3 replicates.

cooked samples. In contrast, the effect of cooking does not appear to be significant in the hull fraction. With regard to the length of the cooking period, the residual hexane content of meat samples cooked for 40 min was not significantly different from that observed in corresponding samples that were cooked for only 25 min.

Desolventization with Steam

Passing steam through a column of canola meal at atmospheric pressure was an effective way to remove sorbed hexane, provided that the treatment was of sufficient duration. Data are in Table IIIA.

As soon as most of the solvent had been stripped from the meal, the temperature above the column rapidly rose to the temperature of the steam and drops of water began appearing in the condenser. Stopping the treatment at this time left all the meal samples with very high levels of hexane. However, extending the treatment time by 5 min reduced the level dramatically. For meals in runs 3-8, the extra 5 min reduced the average hexane content to 11% of the level prior to steam treatment. Extending the treatment yet another 5 min caused little additional reduction in hexane content.

As the bulk of the hexane was stripped off, the moisture content of the meal at the bottom of the column increased by 6-8 percentage points and 0-4 percentage points at the top (Table IIIB). After the column had reached steam temperature, further steam treatment resulted in a more uniform moisture distribution throughout the length of the column, but the average moisture content did not undergo any further significant increase. The final moisture content averaged 5-6 percentage points higher than it was prior to the steam treatment.

Not suprisingly, steam was less effective at stripping the residual hexane from lumpy meal (runs 9 and 10). Five min after the temperature of the column reached the steam temperature the immediate hexane content was reduced to an average 1400 ppm or ca. 35% of the original very high value. In this case, extending the treatment a further 5 min reduced the level to ca. 16% of the original value. However, the final RH_{55} after this treatment averaged only 6% of the original value, indicating that the steam treatment had affected the meal so that, on air exposure, the hexane continued to evaporate.

The hexane analyses were performed on the lumpy meal without crushing the lumps. There was some concern that the lumps might inhibit release of hexane during the heating step of the analytical procedure, giving erroneously low results. This was tested in a control experiment in which one part of a lumpy meal sample was analyzed after crushing the lumps with a mortar and pestle and another part of the same sample was analyzed directly. The measured hexane content of the crushed sample was 10% lower than that of the lumpy sample. Apparently, part of the sorbed hexane evaporated as the lumps were crushed. It was concluded that a better estimate of the true hexane content was obtained by direct analysis of the lumpy material.

Effect of Exposure to High Humidity

Since low pressure steam was effective in stripping sorbed hexane from canola meal, further experiments were carried

TABLE IIIA

Effect of Steam in Stripping Firmly Bound Hexane from Regular and Lumpy Canola Meal

Run no.[a]	Residual hexane before treatment (ppm)[b]	Time of exposure[c] to steam (min) past 98 C	Hexane content after steam treatment (ppm)[b]					
			Immediately after treatment			Residual hexane (RH_{55})		
			Top	Middle	Bottom[d]	Top	Middle	Bottom
1	267 ± 2	0	7349	6114 ± 1002	776 ± 105	603	654 ± 27	240 ± 27
2	267 ± 2	5	214 ± 13	183 ± 19	164 ± 1	147 ± 13	112	110 ± 9
3	2029 ± 58	0	685 ± 80	545 ± 47	415	159 ± 13	137 ± 16	116 ± 13
4	2029 ± 58	5	192 ± 15	187 ± 32	148 ± 16	106 ± 18	74 ± 12	74 ± 0
5	2029 ± 58	10	275 ± 28	203 ± 11	159 ± 34	92 ± 13	44 ± 10	53 ± 6
6	2029 ± 58	0	1683 ± 421	816 ± 17	661 ± 43	1392 ± 252	357 ± 8	270 ± 7
7	2029 ± 58	5	298 ± 30	262 ± 18	249 ± 13	132 ± 31	68 ± 10	72 ± 18
8	2029 ± 58	10	171 ± 34	137 ± 19	138 ± 9	78 ± 1	77 ± 5	56 ± 16
9	4064 ± 265	5	1477 ± 197	1413 ± 231	1268 ± 417	638 ± 228	504 ± 10	346 ± 74
10	4064 ± 265	10	722 ± 139	707 ± 180	540 ± 48	283 ± 35	247 ± 115	154 ± 0

TABLE IIIB

Effect of Steam Treatment on Moisture Content of Regular and Lumpy Canola Meal

Run no.	Initial moisture content (%)	Time of exposure to steam (min)		Water collected (mL)[e]	Moisture content after steam treatment		
		Total time	Time past 98 C[c]		Top[d]	Middle	Bottom
1	7.4	10	0	0	7.0	9.7	14.3
2	7.4	16	5	3	9.5	11.7	13.3
3	6.0	9	0	1	10.1	12.4	13.1
4	6.0	13	5	4	9.4	11.9	12.9
5	6.0	17	10	5	9.7	12.2	12.4
6	2.0	7	0	0	5.4	8.7	10.3
7	2.0	11	5	6	7.7	9.8	9.1
8	2.0	15	10	12	7.4	8.5	9.5
9	7.4	21	5	2	14.3	12.9	14.5
10	7.4	25	10	6	16.8	13.8	15.1

[a]Runs 1-8 were regular meal; runs 9 and 10 were lumpy meal; Tables IIIA and IIIB refer to the same set of experiments.
[b]Mean and standard deviation of two or more replicates.
[c]Run time after temperature above column reached steam temperature.
[d]Top, middle and bottom refer to positions within the column from which sample was recovered for analysis.
[e]mL of H_2O condensed and collected in receiver vessel.

out to determine the effect of high humidity at a series of lower temperatures. Meal samples, which had been pretreated to cause high RH_{55} values, were exposed to air saturated with water vapor over the temperature range from 30 to 50 C. Results are in Figure 5.

Increasing amounts of sorbed hexane were released as the moisture content of the meal increased. At 30 C, ca. 80% of the residual hexane was displaced by the time that the moisture content reached 15%. At 50 C, the equivalent amount of hexane was released as the moisture content approached 13%. As expected, the gain in moisture content was more rapid at higher temperature. To increase from 4 to 12% moisture required over 8 hr at 30 C but less than 3 hr at 50 C.

The history of the sample affected the nature of the response to high humidity. The data represented by solid lines in Figure 5 are for meal samples which had been extracted with hexane at room temperature and subsequently treated to cause a high residual hexane level. The dotted line represents a sample of canola seed which had been cooked and extracted with hexane under conditions that caused high RH_{55}. In the later case, the release of hexane was considerably slower.

Residual hexane contents as well as immediate hexane contents were determined on most of the samples which had been exposed to humid conditions. If the moisture content had not increased above 15%, heating at 55 C in a dry atmosphere for 24 hr caused very little further reduction in hexane content. If the moisture had increased above 15%, the additional heating resulted in the evaporation of approximately one half of the remaining solvent.

Preferred Sorption Among Components in Commercial Hexane

Preferential sorption among the major components in commercial hexane was investigated by comparing the composition of the residual solvent in the meal, as determined in the residual hexane analysis, to that of the solvent used to extract the meal in the first place. Data are in Table IV.

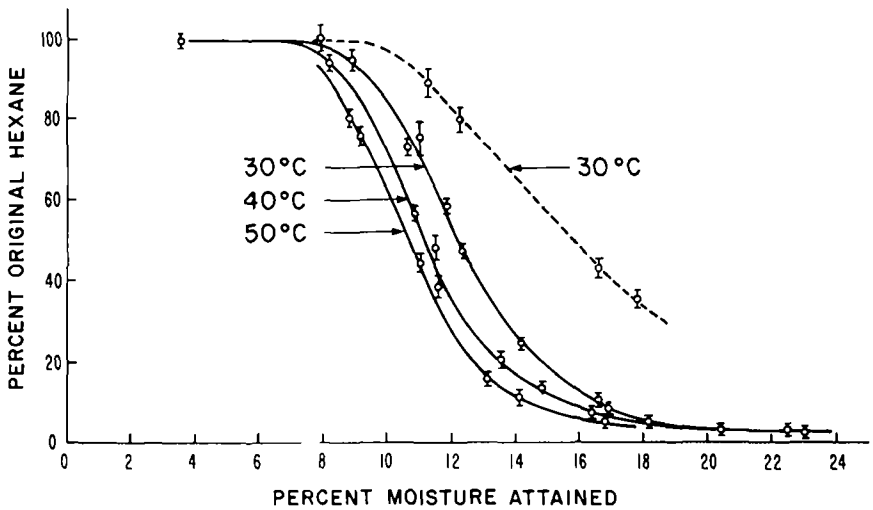

FIG. 5. Loss of sorbed hexane on exposure of canola meal to high humidity at different temperatures. Hexane analysis was performed immediately after exposure to high humidity. Solid lines were for meal samples treated to cause high residual hexane after recovery from the desolventizer. The dashed line was for a meal sample cooked and extracted under conditions that caused high residual hexane. RH_{55} values prior to exposure to humid conditions ranged from 1500 to 7000 ppm.

TABLE IV

Differential Adsorption of the Major Components in Commercial Hexane by Canola Meal

	Percent composition[a]			
	DMB	MP	H	MC
Extracting solvent[b]	9.0 ± 0.1	18.5 ± 0.2	50.9 ± 0.7	21.7 ± 0.6
Residual solvent[c]	10.0 ± 0.4	21.9 ± 1.2	45.7 ± 1.2	22.4 ± 0.6
Difference[d]	-1.0 ± 0.5[d]	-3.4 ± 1.4[d]	5.2 ± 1.9[d]	-0.7 ± 1.2[e]
Extracting solvent[f]	49.3 ± 0.6		50.7 ± 0.6	
Residual solvent	57.4 ± 1.0		42.6 ± 1.0	
Difference	8.1 ± 1.6[d]		8.1 ± 1.6[d]	
Extracting solvent[f]		50.7 ± 0.6	49.3 ± 0.6	
Residual solvent		53.1 ± 0.8	46.8 ± 0.8	
Difference		2.4 ± 1.4[d]	2.5 ± 1.4[d]	
Extracting solvent[f]			46.6 ± 1.0	53.4 ± 1.0
Residual solvent			44.8 ± 0.5	55.2 ± 0.5
Difference			1.8 ± 1.5[d]	1.8 ± 1.5[d]

[a]Mean±standard deviation for 5 replicates. Component identities: DMB=2,3-dimethylbutane; MP=3-methylpentane; H=*n*-hexane; MC=methylcyclopentane.
[b]Commercial hexane; 2-methylpentane may also be present; it overlaps DMB in the gas chromatographic analysis.
[c]Solvent retained by canola meal. The RH_{55} ranged from 2400-3600 ppm.
[d]Significant at the 99% confidence level. Means were compared by Student's t-test (10).
[e]Not significant at the 95% confidence level.
[f]Synthetic mixtures of pure solvents.

In all cases, the percentages of both 2,3-dimethylbutane and 3-methylpentane were significantly higher in the residual solvent than in the original mixture, whereas the percentage of hexane was lower. Thus, preferential sorption of the these two branched isomers was indicated. There was also a slight but significant preference for the meal to sorb methylcyclopentane rather than hexane in the binary mixture of these two components. The lower boiling components appeared to be more strongly sorbed, a somewhat surprising observation.

Although the sorptive tendencies of the major components in commercial hexane have been shown to differ significantly, the differences were samll. In comparison to the other factors which have been identified, the component ratio of the extracting solvent is not likely to have much influence on the amount of solvent retained by the meal.

Effect of Residual Oil Content in the Meal

Meal samples of varying residual oil content (0.3-30%) were prepared from reroll meal by varying the period of Soxhlet extraction but maintaining the total time of exposure to hot hexane constant. The residual hexane content in these samples ranged from 760 to 1200 ppm and showed a trend toward higher values in those meals with higher residual oil contents. For oil contents of 1.1% or lower, the highest observed RH_{55} was 935 ppm, 25% higher than the lowest observed value. It was concluded that within the limited range of residual oil contents that would be acceptable in a commercially operated plant (<1%), the effect of this parameter on residual hexane would be insignificant.

Results of Screening Design Experiments

Factors affecting the level of residual solvent in canola meal were further evaluated in series of 2^n factorial screening experiments (10). In one such experiment, using flaked canola seed as the starting material, four experimental variables were tested, namely cooking vs not cooking, cooking conditions, the moisture content at the time of exposure to hexane and the temperature of exposure to hexane. The design of the experiment and the resulting data are summarized in Table V.

Runs 13-16 were replicated "centerpoint" runs for the purpose of estimating response error and curvature effect. In confirmation of our earlier results, statistical analysis (10) of the data indicated that the two major factors were the moisture content at the time of exposure to solvent and the solvent temperature. High moisture and high temperature both resulted in high levels of residual hexane and both factors were significant at the 99% confidence level. There was also a highly significant interaction between these two factors. Cooked samples had higher residual hexane than uncooked samples but the effect was considerably smaller than the two main effects, although it was significant at the 99% level. The severity of the cooking procedure has the smallest effect, significant at the 95% confidence level but not at the 99% level. Analysis for a curvature effect revealed that these data could adequately be represented by an equation without any second-order terms. Further statistical analysis of the same data, but excluding those for uncooked samples, confirmed the two main effects and the interaction, but also indicated a significant curvature effect.

Additional screening design experiments were performed using the high-protein fraction and the low-protein fraction from canola meal as starting materials. The design of these experiments and the resulting data are summarized in Tables VI and VII.

Statistical analyses of these data again confirmed that moisture content at the time of exposure to hexane and the temperature of the hexane were the main factors. The highly significant interaction between these two factors was also confirmed. Cooking conditions, although significant, had a lesser effect. Curvature effects were not highly significant.

Comparison of the residual hexane data in Tables V-VII reveals that for samples which were processed under similar conditions, the highest RH_{55} values were observed in the high-protein fraction, and the lowest values were in the low-protein fraction. This was a strong indication that the main components responsible for hexane sorption in canola meal were the extractable proteins.

In general, the results show that moisture content was the most important single factor affecting the level of residual hexane. High moisture at the time of oil extraction apparently facilitated the intimate contact between hexane

TABLE V

Screening Design Experiment on Flaked Canola Seed

Run no.	Moisture content before cooking (%)	Cooking temperature[a] (C)	Moisture content at solvent extraction (%)	Solvent temperature (C)	Residual[b] hexane (ppm)
1		Not cooked	4.4	25	77 ± 12
2		Not cooked	10.3	25	746 ± 26
3	3.7	80	3.6	25	55 ± 3
4	10.0	80	9.7	25	1317 ± 77
5	3.8	120	3.8	25	79 ± 18
6	9.0	120	10.0	25	1876 ± 32
7		Not cooked	4.1	63	380 ± 18
8		Not cooked	10.2	63	3170 ± 291
9	3.8	80	3.8	63	268 ± 20
10	10.2	80	10.0	63	4682 ± 18
11	3.9	120	3.9	63	865 ± 16
12	10.2	120	10.3	63	5512 ± 797
13[c]	6.8	100	6.8	44	1224 ± 75
14[c]	6.7	100	7.2	44	1386 ± 15
15[c]	6.5	100	6.4	44	1196 ± 65
16[c]	7.1	100	7.5	44	1521 ± 72

[a]Temperature at the end of cooking period, cooking time was 30 min.
[b]Average ± standard deviation for 3 replicated hexane analyses.
[c]Centerpoint runs.

TABLE VI

Screening Design Experiment on Canola High Protein Fraction[a]

Run no.	Moisture content before cooking (%)	Cooking temperature[b] (C)	Moisture content at solvent extraction (%)	Solvent temperature (C)	Residual[c] hexane (ppm)
1	10.1	40	4.5	25	92 ± 8
2	10.5	40	9.6	25	1175 ± 58
3	10.1	40	4.2	63	1627 ± 56
4	10.5	40	10.3	63	4648 ± 230
5	10.1	120	3.8	25	68 ± 8
6	10.1	120	10.2	25	2519 ± 97
7	10.5	120	3.6	63	1460 ± 46
8	10.5	120	10.1	63	10402 ± 550
9[d]	10.1	80	6.9	44	1485 ± 46
10[d]	10.0	80	6.3	44	1127 ± 40
11[d]	10.1	80	7.2	44	1943 ± 75

[a]Protein content 83% (dry weight basis, N X 6.25).
[b]Temperature at end of cooking period, cooking time was 30 min.
[c]Average ± standard deviation for 3 replicated hexane analyses.
[d]Centerpoint runs.

TABLE VII

Screening Design Experiment on Canola Low-Protein Fraction[a]

Run no.	Moisture content at solvent extraction (%)	Solvent temperature (C)	Residual[b] hexane (ppm)
1	4.0	25	49± 6
2	10.3	25	74± 9
3	4.0	63	154±412
4	10.4	63	505± 24
5[c]	6.7	44	128± 31
6[c]	6.9	44	102± 17
7[c]	7.0	44	97± 8

[a]Protein content 22% dry weight basis (N X 6.25). All samples were cooked for 30 min to a final temperature of 100 C at moisture contents in the range from 10.1 to 10.4%.
[b]Average ± standard deviation for 3 replicated hexane analyses.
[c]Centerpoint runs (10).

and the relevant meal components (most probably proteins) which promoted high levels of residual hexane. However, high moisture (as low pressure steam) also provided the conditions which permitted desorption to occur when hexane vapor pressure was low. Dry heat drove off some of the sorbed hexane but apparently caused the remainder to be locked in.

The hexane temperature at the time of extraction was also an important factor, with high temperature associated with high residual hexane levels. Severe cooking conditions prior to oil extraction resulted in higher levels of residual hexane, but this factor was of lesser importance.

Recommendations for Commercial Processing to Minimize Solvent Sorption

(1) Prior to solvent extraction, reduce the moisture content of the crushed seed to the lowest practical level.

(2) Extract the meal under conditions which minimize both the temperature of the solvent and the duration of solvent contact (insofar as efficient oil extraction permits).

(3) During desolventization, steam injection should occur in the later stages of that process, in amounts to raise the meal moisture content to ca. 12%.

(4) Do not overcook.

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