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THE USE OF SOLVENT EXTRACTED OILSEED MEALS AND FISH FLOUR FOR HUMAN CONSUMPTION

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1. Introduction

The method of separating oil from oleaginous materials by the use of volatile solvents has found its greatest industrial application in the processing of soya bean and cottonseed.[1,2] Several types of solvents which have been used on commercial scale include (1) hydrocarbon solvents eg., n-hexane and n-heptane, (2) alcohol and (3) chlorinated hydrocarbons eg., trichloroethylene and ethylene dichloride. The chief advantage of the solvent extraction process is almost complete recovery of oil from the raw materials resulting in a high yield of oil and also in a meal of good keeping quality. During recent years increasing interest has been evinced in the use of solvent extraction processes in the preparation of edible oilseed meals and fish flour for use in the prevention and treatment of protein malnutrition in children. The problems involved are (i) the use of good quality raw materials, (ii) the use of non-toxic solvents conforming to approved specifications and (iii) complete removal of solvent residues from the meal with due precautions to reduce to the minimum the damage by heat to the quality of the proteins. In the present review, a brief account of available information on the effects of solvent extraction procedure on the nutritive value of oilseed meals and fish flour is presented.

2. Solvents in Common Use for Extraction of Fat

An ideal solvent should meet the following requirements:[3,4] (i) it should readily dissolve oils and fats but not other constituents such as sugars and water soluble vitamins present in the material, (ii) it should be volatile and stable thus enabling the complete removal of the last traces of solvent from oil and meal, (iii) it must not chemically react with the oilseed meal or corrode the solvent extraction equipment, (iv) it should be recoverable without undue losses so that the same solvent can be used repeatedly without increasing the cost of production, (v) it must be available in large quantities and at low cost and (vi) it should be non-toxic when present in small quantities as solvent residues in the meal or the oil.

In commercial solvent extraction plants the following solvents are commonly employed : (i) petroleum solvents, (ii) ethyl alcohol (to a limited extent) and (iii) chlorohydrocarbons e.g., trichloroethylene and ethylene dichloride.

2.1 *Petroleum solvents :* Perhaps, the most important factor which has contributed to the success of the solvent extraction industry is the availability at low cost of abundant hydrocarbon solvents such as n-hexane and n-heptane.[1] Mixtures of heptane and hexane have also been used to some extent. Traces of pure n-hexane or n-heptane present in foods appear to be non-toxic but the associated impurities present in them such as olefins, aromatic hydrocarbons, sulphur compounds and non-volatile residues appear to be harmful. The main disadvantage in the use of hexane and other petroleum solvents appears to be their high inflammability, but with the development of 'outdoor' units and with the proper safety devices and careful operation control, the chances for the fire-hazards involved in the process are no more than in other chemical plants.

2.2 *Ethyl alcohol* : Alcohol has been used only to a limited extent for the extraction of oil. The use of alcohol for the extraction of oil from soya bean was first reported from Japan.[5] Beckel and co-

workers[6,7] have reported extensive development work on an ethanol extraction system for soya bean Alcohol besides removing fat also removes pigments, simple sugars, bitter and flavouring principles and water soluble vitamins present in the raw material. Data on the alcohol extraction of oil from other oilseeds such as cottonseed, groundnut and sesame and fish flour have been recently reported.[8,8a] The most important limitations in the use of alcohol are (i) excise regulations on the production and use of ethyl alcohol which will require surveillance of every phase of the process, (ii) non-selectivity of alcohol as a solvent for fat and its inferiority to hexane in this respect, (iii) relatively high cost and unfavourable thermal characteristics as compared with hexane and (iv) difficulty involved in the production of industrial alcohol free from impurities at low cost.

2.3 *Chlorohydrocarbons*: In view of its non-inflammability, trichloroethylene was used to a limited extent in Europe and U.S.A for the extraction of oil from soya bean. The resulting meal was, however, found to be toxic to cattle and other animals; this aspect has been discussed in a later section. More recently ethylene dichloride has been used for the production of fish flour In view of the possible toxicity of meals produced by extraction with trichloroethylene or ethylene dichloride, these solvents are not suitable for the preparation of edible quality meals.

3. Specifications for Solvents

There is a need to have strict quality control of the solvents to be used for the extraction of edible oleaginous materials. The petroleum fractions, hexane and heptane have been used for many years particularly for preparing oilseed meals for use as animal feed In more recent years these solvents have been used for products intended for human consumption. In the light of present knowledge, food grade hexane among the different petroleum solvents can have the least non-volatile residue, the narrowest boiling range and the minimum content of olefin hydrocarbons. The tentative specifications for hexane suitable for use in defatting food materials suggested by the FAO/ WHO/ UNICEF Protein Advisory Group are given in Table I.

Table I. *Tentative specifications for 'food grade' extraction hexane for use in defatting oleaginous food material*+

Property	WHO/PAG Min.	WHO/PAG Max.
Paraffins + Naphthenes% Vol.	99·5	—
Olefines, % vol.	—	0·1
Benzene, % vol.	—	0·5
Other Aromatics, % vol.	—	0·5
Sp. Gr. at 15·5/15.5°C	—	0·682
Distillation°C		
Initial	65.5	—
Dry Point	—	70
Temp. Range of final 10%°C	—	1·57
Reaction of Dist. Residue	Neutral	—
Nonvolatile Residue, gm./100cc	—	0.0005
Colour	30	—
Doctor test	Neg	—
Corrosion	Neg	—
Sulfur, ppm.	—	50
Lead, ppm.	—	—*
Tricresylphosphate, ppm.	—	0

*In terms of lead (Pb), the minimum amount possible which should not be in excess of that normally present on food supplies

+From the FAO/WHO/UNICEF Programme for Protein Food Supplements by Hexane Extraction

3.1 *Possible toxicity of polycyclic aromatic hydrocarbons in petroleum solvents*: Considerable amount of literature has accumulated on the content and biological effects of polycyclic aromatic hydrocarbons in products such as petroleum waxes used for food packaging. Only recently the results of significant investigations appeared relating to commercial hexane solvents. Ryder and Sullivan[9] reported the complete absence of polynuclear aromatic carcinogens (eg 3,4 benzpyrine) in samples of hexane from a commercial U. S. vegetable oil plant. Lijinsky and Raha,[10] however, reported that 2 U.S. commercial samples of hexane contained traces of such compounds, one at a concentration of 0.00013 ppm (benzoperyline) and the other at 0.023 ppm (benzopyrene). The flourescence spectroscopy method adopted by these workers is much more sensitive than the

paper chromatographic technique used by Ryder and Sullivan.[9]

4. Solvent Extraction Process

Solvent extraction processes in vogue for defatting food materials have been exhaustively reviewed [11] The process consists of three steps: (i) flaking of the material for extraction, (ii) extraction of fat using solvents and (iii) removal of solvent left in the material using desolventizing equipment. The first two steps do not involve high heat treatment, but the third step involves varying degrees of heat treatment depending on the equipment used. Since moist heat brings about a lowering in the nutritive value of the proteins, desolventizing equipment involving indirect heating by steam will be preferable to equipment requiring direct steam for the production of edible quality meals.

5. Determination of Residual Solvent in Meal

It is essential to fix a minimum value for the solvent residues. left in the oilseed meals after desolventizing procedure. Varying amounts of residual solvents may be present in the meal because of the following factors: (i) changes in quality or changes in the composition of raw material, (ii) changes in the atmospheric humidity, (iii) fluctuating steam pressure and (iv) inefficient operation of desolventizing equipment.

There is a need to develop simple methods for the estimation of solvent residues in meals intended for edible purposes. There are a number of methods, both qualitative and quantitative, which are currently used by the industry for the estimation of residual solvent in the meal. They are briefly outlined below:

5.1 *Qualitative methods*: (i) A sample of the extracted meal is placed in a tightly covered can; size of cans, methods of mixing the contents and time and temperature of equilibrium vary appreciably. The lid is partially lifted and a small flame is inserted into the top of the can. If a pop or flash results, it is obvious that the residual solvent is too high. (ii) In the second method, a combustible gas detector such as the mine safety appliance is used for sampling the conveyor continuously or for sampling the atmosphere within a jar containing a sample. The alarm is generally set to sound when the concentration reaches 40% of the lower explosive limit. The main difficulty appears to be the clogging of the intake on account of the dusty and humid conditions in the atmosphere within the conveyor.

5.2 *Quantitative methods*: (i) In a quantitative method suggested for the estimation of residual solvent, moisture is first obtained by toluene distillation, then moisture and volatiles by the oven method. The difference is recorded as the percentage of solvent. The method is time consuming and the accuracy obtained has not been fully determined. (ii) In another method, nitrogen is passed through the sample at 150° F and the solvent hexane is absorbed on activated carbon. The activated carbon is weighed to determine the amount of hexane absorbed. (iii) A method using gas chromatography has been investigated but it does not appear to be feasible for routine use because of the cost of equipment and the need for a specially trained operator. (iv) A simple copper cup flash tester with concentric rings as heating surfaces for detecting solvent residues as low as 0·03% has been developed and has been tested in laboratory trials for its efficacy.[12] (v) A rapid method for the determination of residual solvent in meals, based on the vapour pressure of the solvent has also been developed.[13]

6. Nutritive Value of the Proteins of Solvent Extracted Oilseed Meals and Fish Flour

6.1 *Soya bean meal*: The nutritive value of solvent extracted soya bean meal has been the subject of investigation by a number of workers. The results are briefly summarized below:

6.1.1 *Hexane extracted soya bean meal*: Clandinin [14] reported that a meal of high nutritive value could be obtained by autoclaving hexane extracted soya bean meal at 105°C and 4 p.s.i. for 45 minutes. Miller and Morrison[15] prepared soya bean meal by solvent extraction at 52°C for 30 minutes, desolventizing the meal at 90°C for 20 minutes and toasting at 121°C for

70 minutes. The digestibility of the meal proteins determined in lamb was 8% higher than that of untoasted meals. Becker[16] investigated the nutritive value of hexane extracted soya bean meal that had been subjected to three different heat treatments. The meals were (A) desolventized at 99°C for 18–20 minutes (B) toasted at 105°C for 33-37 minutes and (C) toasted at 116°C for 48-55 minutes. The products were tested as the sole source of proteins for pigs fed synthetic diets. On the basis of average daily gain in weight, meal (C) was superior to meals (A) and (B) but the PER of meal (B) was higher than that of meals (A) and (C).

6.1.2 *Trichloroethylene extracted soya bean meal*: There have been a number of reports on the toxic effects of trichloroethylene (TCE) extracted soya bean meals in cattle, poultry and other animals. Pritchard[17] reported that acute aplastic anaemia developed in young heifers within four weeks of feeding TCE-extracted meal while hexane extracted meal was not toxic under similar conditions. Eveleth and Goldsby[18] fed 103 chicks with a mash containing TCE-extracted soya bean meal. Within 7 weeks, 27 chicks died. Pritchard[19] found that when chicken were fed a ration containing 73% TCE-extracted meal, signs of toxicity appeared by the tenth week. TCA-extracted soya meal was not toxic to pigs although it was inferior in its nutritive value to hexane extracted meal.[16] Hanson[20] reported that TCE-extracted meal known to be toxic to cattle did not depress the growth of young sows when incorporated at 10–20% levels in the ration. Pritchard[21] reported prolonged feeding of sheep on TCE-extracted soya bean meal resulted in the development of toxicity symptoms and death of the animals. It has been reported[22] that a toxic product is formed due to reaction of solvent with the protein.

6.2 *Groundnut meal*: Available data on the nutritive value of the proteins of groundnut meal extracted by different solvents are given below:

6.2.1 *Hexane extracted meal*: Cama and Morton[23] found that the PER of screw pressed (two stages) meal after extraction of oil with hexane and desolventization for 30–40 minutes at 100 lbs steam/hour was nearly the same as the screw pressed meal, while desolventization of the meal for 30-40 minutes at 2000 lbs steam/hour brought about a significant decrease in the PER. Carpenter and Ellinger[24] reported that the available lysine was not seriously affected by the commercial expeller process or during the conditions of commercial solvent extraction process using hexane. Feeding experiments on chicks showed that there was no significant difference between the hexane extracted and hydraulic pressed meals.[25]

6.2.2 *Chlorohydrocarbons extracted meal*: Meagre data is available in the literature regarding the nutritive value of TCE-extracted groundnut meal. Mitchell *et al*[26] found that the net protein utilization of ethylene dichloride extracted meal was of the same order as screw pressed meal in experiments with rats.

6.3 *Cottonseed meal*: A number of solvents have been used in commerce for the solvent extraction of cottonseed. If the residual meal is to be used for edible purposes the solvents besides extracting the fat have to be quite effective in removing the toxic principle, gossypol also. Eaves *et al*,[27] have compared the efficacy of five commercial solvents for extraction of cottonseed. Hexane though quite effective in extracting the fat from cottonseed was a poor extractant of gossypol. Acetone, butanol, ethyl alcohol and trichloroethylene are more effective than hexane in extracting gossypol. The studies of Mann *et al*,[28] have shown that a solvent system consisting of 53% acetone, 44% hexane and 3% water is effective in the removal of gossypol and oil from cottonseed.

6.3.1 *Hexane extracted cottonseed meal*: Both in experiments on rats and chicks, Eagle *et al*,[29] have shown that hexane extraction of cottonseed meal did not result in any lowering of the nutritive value of the proteins as compared with hydraulic press meal. The results of a co-ordinated study [30] on the nutritional value of prepress, hexane extracted cottonseed meals have shown that the meals were

about 80–90% as effective as a standard hydraulic press cottonseed meal.

6.3.2 *Alcohol extracted cottonseed meal*: Investigations carried out at the Central Food Technological Research Institute, Mysore [31] have shown that it is possible to prepare by alcohol extraction of cottonseed an edible quality cottonseed meal with a low gossypol content. The protein efficiency ratio of alcohol extracted cottonseed meal at 10% level of protein intake (1·80) during a 8 week period was comparable to that (1·61) of screw pressed cottonseed meal.

6 4 *Fish flour*: A number of solvents have been used for the extraction of lipids from fish. Hexane (or similar petroleum products) is a poor extractant of bound lipid fraction which comprises largely of phospholipids. Chlorinated solvents such as ethylene dichloride are somewhat better, but lipid extraction is far from complete. Acetone does not quite equal the lower aliphatic alcohols in their efficacy to extract lipids from fish. Ethyl alcohol is undoubtedly the most efficient solvent both in liberating and extracting bound lipids. No other solvent extracts the odoriferous components as thoroughly as alcohol.[32,33]

6.4.1 *Dichloroethylene extracted fish flour*: The use of dichloroethylene as solvent for extraction of fish has been found unsatisfactory. However, in a recent publication from Viobin Corporation it is stated that this defect has been overcome.[34] Morrison *et al*,[35] have reported that samples of fish flour obtained by extraction with dichloroethylene contained less lysine and methionine than those produced by extraction with isopropanol. The fish flour fed at 20% protein level, inhibited growth and food consumption of rats, indicating the presence of a toxic factor. The toxicity was directly related to the organic chloride content of the sample

6.4.2 *Alcohol extracted fish flour*: A sample of alcohol extracted fish flour from oil sardine has been exhaustively studied for its overall nutritive value at the Central Food Technological Research Institute; the results have shown that the nutritive value of the proteins of the fish flour is comparable to that of milk proteins.[36] Similar results have been reported by the Fishing Industry Research Institute.[32]

7. Conclusion

The object of this literature survey has been to assess the extent to which the solvents now in use in industry for the extraction of oilseeds can be considered safe in relation to the wholesomeness of the resulting oilseed meals for human consumption. The data may be summarised under the following heads.

7.1 *Hexane*: In recent years, commercial hexane of sufficient purity suitable for the solvent extraction of edible oilseeds and oilseed meals has been made available by the industry. A few short term feeding tests[23,37] have been conducted on the nutritive value of hexane extracted oilseed meals. The results have shown that these meals are quite wholesome. Large quantities of hexane extracted oilseed meals are being used as supplements in livestock, swine and poultry feed mixtures in Western countries with satisfactory results. There are strong indications in favour of commercial food grade hexane as a safe solvent for extraction of food and feed materials, and in view of the high standards of purity, stability and composition to which hexane is now being manufactured, there seems to be no logical reasons for assuming otherwise.

7.2 *Chlorohydrocarbons*: The chlorohydrocarbon solvents eg. dichloro and trichloroethylene, are still being used to a limited extent for the solvent extraction of certain oilseeds. From the available evidence, the oilseed meals obtained by the extraction of the oil with these solvents, cannot be considered safe for use in the feeding of animals or human beings.

7.3 *Ethyl alcohol:* Ethyl alcohol would appear to possess the advantage of not containing toxic substances and at the same time efficiently extracting bound lipids from fish flour; but it is less efficient and economical as a fat solvent as compared with hexane. Further its use as a commercial solvent would present difficult social and legal problems.

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