An Azeotropic Extraction Process for Complete Solvent Rendering Raw Tissues

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RENDERING, as it is generally known, is done by either one of two conventional processes, wet rendering or dry rendering, Both are used for producing edible fats from visceral or carcass fatty tissues, for obtaining industrial fats and protein meals from inedible packing house materials and dead stock, and for the reduction of whole fish and fish wastes into oils and meals.

Dry rendering is usually a batch operation, particularly suited in capacity for handling the by-product output of the average meat packing plant and the processing of dead stock and packing house materials from areas economically served by rendering plants.

Wet rendering, used in meat packing plants for batch treating of edible and inedible materials, lends itself readily to continuous operations. It is used extensively in the fish reduction industry, where capacities are large, as the fishing fleets, covering large water areas, funnel their catch into single coastal plants. The main operational problems of wet rendering center on the protein losses in press liquor fines and water solubles or on the elaborate procesing and equipment required for their recovery.

In either process, separation is incomplete as appreciable quantities of fat remain with the protein solids. Additional operations of pressing or solvent extraction or both are used to recover this residual fat and to lower the fat content of the solids for feeding purposes. In wet rendering, moisture must also be removed from the solids, generally by pressing and drying.

Pressing after dry rendering reduces the fat content of the solids to 8 to 15% by weight, depending on how completely and how well controlled the rendering is accomplished and on the type of press and how well it is maintained. In wet rendering, pressing also removes considerable quantities of water, which then must be separated, with its suspended solids, fines, and dissolved proteins, from the fat.

Solvent extraction is carried out on pressed and unpressed solid products from rendering plants to obtain additional fat yields and to produce low-fat protein meals. Batch operations, generally used, can reduce the fat content in the meals down to about 3% by use of three or four solvent washes. For continuous solvent extraction processes it is claimed that this fat content can be brought down to 1% if desired.

The equipment, operating, and other costs for use of solvent extraction to supplement dry rendering, with or without pressing, must be justified by the value of the additional fat yield and the increased value of the meal through lowered fat content. The outstanding difficulties encountered in solvent extraction of rendered tissues of animal and fish origin are the handling, separation, and disposal of solid fines that become suspended in the fat-bearing solvent or miscella. These fines, unsuited for filtering from the miscella, are usually separated in part by prolonged settling in the miscella through use of a battery of settling tanks.

The settled sludge or slurry must be disposed of or, if possible, recycled into the solids charge being extracted. The miscella from the settling tanks, still containing some suspended solids, is distilled to remove the solvent, and the remaining fat can then be filtered, centrifuged, or otherwise separated from the fines.

VioBin Process

The VioBin solvent rendering process is an adaptation of the process developed for the extraction of moisture and fat from animal tissue (1, 2) and accomplishes the processing equivalent to wet or dry rendering, pressing, and solvent extraction to obtain low-fat and low-moisture protein solids and high yields of fat directly from the raw animal tissues. The processing is completed in an appreciably shorter period of time than the conventional methods, and the operations can be readily controlled to give solid products of any desired fat or moisture contents from less than 1% by weight upward. There are no fines problems or losses of proteins. The solids can be separated with their total protein content from the fat-solvent solution by simple filtration to give a clear, fines-free miscella.

It is pertinent to mention that the low-moisture and low-fat contents obtainable in edible protein materials of fish and animal origin present a new method for food preservation. Desirable heat-labile factors are retained since the drying and defatting of the tissues are accomplished in short processing times and at low temperatures. As a source of non-perishable meat proteins of good nutritional values, the potentialities of this process should not be underestimated.

Using completely segregated raw animal organs, the VioBin Corporation has for several years been producing, on a commercial scale, defatted and desiccated animal tissues, valuable as pharmaceuticals because they retain hormone, vitamin, and enzyme activities (6). These special animal materials are dehydrated and defatted, using ethylene dichloride solvent, either under atmospheric pressure at 71.4°C.(160.5°F.) or under practical vacuums at 38°C.(100°F.) to produce stable tissue powders. The lower temperature products may be considered as raw tissue powders as they are dried and the fat is removed at temperatures below the denaturization temperatures of proteins. Thus various enzymes and other heat labile constituents are conserved.

It has also been presented as a possible new method for rendering lard (9), and recent tests indicate that high quality edible fats can be produced.

Description of the Process

Batch. For batch operations on, say, inedible packing house materials (3, 4), the raw soft tissue or the green bone, or a mixture of these by-products, is ground by standard size-reducing or disintegrating equipment; the soft tissue into particles one-fourth inch in size or less and the bone into one-inch or smaller fragments. As indicated on the flowsheet, Figure 1, the prepared raw material is loaded into

a vertical, steam jacketed vessel, or solvent cooker, containing one of the suitable, commercial, water-immiscible solvents.

The bulk of the water in the tissue is boiled off at an azeotropic temperature that is lower than either the boiling point of the solvent or water. For trichlorethylene, this azeotropic temperature is 73°C. (163°F.); for heptane 79°C.(174°F.). The residual available water may be removed, if desired, by continuing the heating until the boiling temperature of the solvent is reached.

The fat in the animal material that is being dehydrated dissolves into the hot solvent liquid, leaving in the cooker a dried animal tissue surrounded by a miscella of fat dissolved in solvent.

This remaining charge is pumped or discharged by gravity into a revolving shell-type, horizontal dryer, heated through a steam jacket and fitted with an internal filter frame supporting filter cloth. The miscella drains through this filter cloth and is pumped as a clear liquid to a steam-jacketed fat kettle, where the fat is recovered by distilling off the solvent.

The granular protein solids are retained on the filter cloth. They may be readily washed with one or two portions of solvent if a meal of low-fat content is desired. The wash liquors are used as solvent to treat fresh charges of raw animal tissue in the solvent cooker. Whether washed or not, the solids in the dryer, wet with solvent, are subjected to indirect jacket steam, to agitation by shell rotation, to vacuum, and to direct steam sparging to remove completely the solvent from the meat solids. Then the solids product can be further ground, if required, and bagged as a high protein meal component for animal feed.

Continuous. For continuous processing the reduction of raw fish materials into fish meal is used for illustration (5). The raw fish is first broken down into fine particles or a slurry by size reducing or disintegrating equipment, standard for the industry. The disintegrated raw fish moves into a continuous agitator vessel for pre-treating this material in the presence of heated solvent (Figure 1). By heating and agitation, the fish material forms small, discrete particles that will not stick together in large masses during later processing.

The fish material then moves into a continuous solvent cooker. An effective design consists of a screw conveyor in a long horizontal, vapor-tight, jacketed trough, with vapor collecting space above leading to condensers. Adequate heat is introduced to the cooker and applied to the solvent to boil off at reduced temperatures the water from the fish tissues together with definite quantities of solvent vapor. The miscella is drawn off from the cooker. The solids are discharged, drained free of excess solvent, and are fed into a continuous dryer for removal of solvent still entrained with the solids.

The continuous dryer, the units for evaporating and steam stripping solvent from the miscella to obtain fish oil, and the solvent recovery system may be any of the continuous types that are in established use in the vegetable oil industry for recovery of meal, fat, and solvent from solvent extracted oilseed, such as soybean and cottonseed.

The granular form of the protein solids with the absence of appreciable dust, even at low-fat contents, and the clear miscellas obtainable by this new process make such standard continuous equipment particularly applicable to the finishing operations after the solvent cooking of the raw animal materials.

Principles of Azeotropic Extraction

The removal of water from animal or vegetable tissues by the VioBin Process is based on the principles of azeotropic distillation of two immiscible liquids. It has been known that when two liquids, insoluble in each other, are heated together at a given temperature, the vapor pressure of the system is the sum of the individual vapor pressures of each liquid at that temperature. Since boiling of liquids occurs when the vapor pressure reaches the actual pressure imposed on the system, the combined immiscible liquids with their additive total vapor pressure will reach boiling at a lower temperature than the liquids would if heated separately. It is also known that the molar weights of the vapors azeotroped from each of the two liquids, that is the actual vapor weights divided by the molecular weights, are proportional to their vapor pressures. These principles can be expressed by the following formulae for any given temperature:

$$P_1 + P_2 = P_t, \text{ and } \frac{W_2}{W_1} = \frac{P_2}{P_1} \times \frac{M_2}{M_1}$$

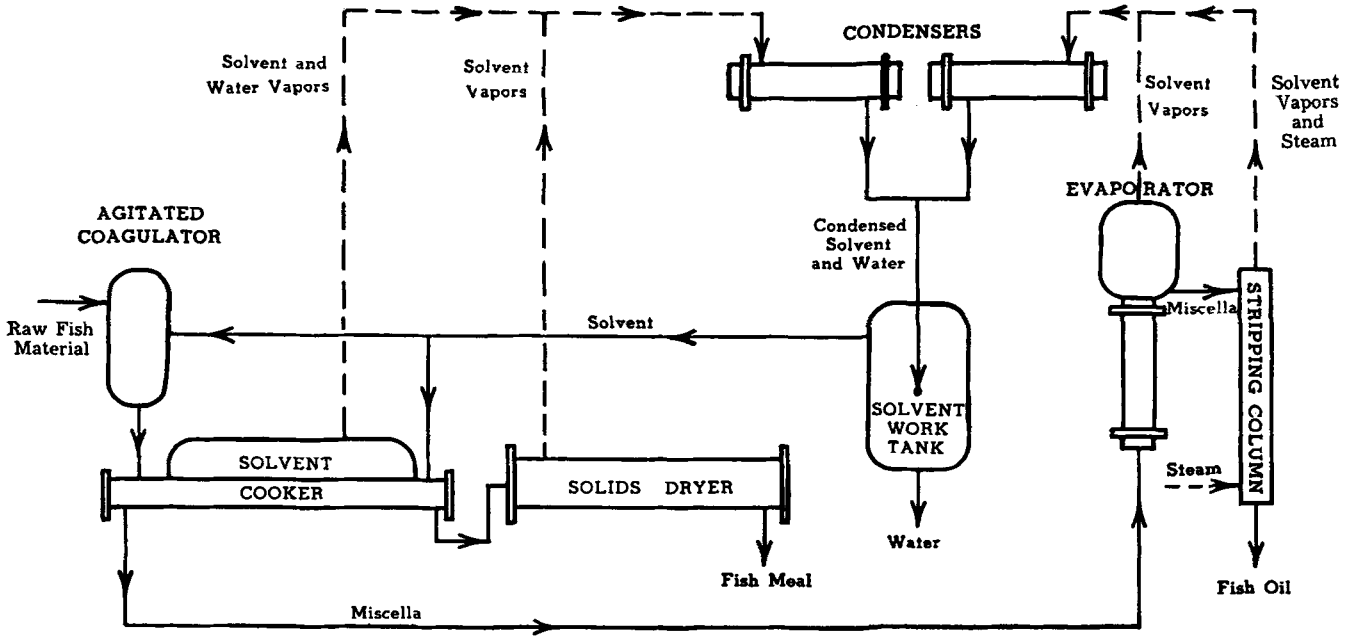
Where P_1 = vapor pressure of first liquid,
P_2 = vapor pressure of second liquid,
P_t = total vapor pressure of combined liquids, equal to pressure of system for boiling of the mixture,
W = vapor weights, and
M = molecular weights.

The significance of these principles is that the bulk of the moisture in animal and vegetable tissues, when heated in water-immiscible solvents, azeotropes as though the non-moisture portions of the tissue were not present. Also as the water content of the tissue is decreased, the hot unvaporized solvent dissolves rather thoroughly the fat from the tissue. Furthermore the low latent heats of the solvents as compared to water make it economically feasible to evaporate the larger relative quantities of solvent to remove the tissue moisture.

Advantages of the Process

Several advantages of the VioBin Process should be emphasized. By submerging the ground raw tissue in solvent and solvent dehydrating and defatting in a closed system, the obnoxious odors typical of conventional rendering are eliminated. The coagulation of ground, raw tissues to form granular solids reduces dust, even in low-fat solids, and makes possible the easy filtration of solid fines from the miscella. No proteins are lost as fines or dust, nor is there a loss through water-soluble proteins as the only water directly involved in this new process is that distilled at low temperatures from the tissue. This water, when condensed and separated from the solvent, can be disposed of without pollution to the surrounding water areas. In conventional methods, as in wet rendering, the proteins dissolved in water present a difficult pollution problem or require elaborate, expensive equipment for their recovery.

The power requirements and the maintenance costs are comparatively low. No pressing or centrifuging



CONTINUOUS OPERATION

FIG. 1.

or extensive solids conveying is required for this azeotropic extraction method.

Although the process may start with raw materials having appreciable moisture and fat contents, it can readily produce low-fat protein solids and give a full yield of fat as compared with conventional solvent extraction of pressed or unpressed rendered material of lower moisture and fat content.

The low-fat protein solids produced by azeotropic extraction from the usual edible and inedible soft animal tissues are granular in form, light grey in color, and of low bulk density. Although quality tests on products of the new process have been made mainly on beef and pork offals from a small meat packing plant, the results have been consistent in confirming that low temperatures and short-time processing in a solvent medium retain the desirable factors in the product.

A representative sample of protein solids so processed from beef offal was found by a Midwest renderer by comparative rat assays to be 91.7, representing the percentage of protein eaten that was digested. Another similar sample, containing 67% proteins and 0.95% fat, as analyzed by the technical men of a large packing house was also found by them to have a vitamin B_{12} value of 0.57 gamma per gram, judged by this group to be much higher than that normally expected in this type of material.

Independent analyses made on fat products from VioBin processed inedible animal offal from packing house sources gave the following results:

Sample	Crude Fat		Refined and Bleached Fat		Ref.
	FAC Color	Lovibond Color	FAC Color	Lovibond Color	
1	21	....	1	4 yellow, 0.2 red	(7)
2	27	....	1	7 yellow, 0.8 red	(7)
3	11	20	....	0.3 red	(8)
4	19GA	195 red (Too green for good reading)	....	0.3 red	(8)

Samples of the tallow produced were submitted to a large soap company, and its representative reported they showed unusually good bleachability (8).

Cost Data

Based on quotations on detailed specifications, the cost of equipment and accessories for batch plants for carrying out this complete solvent rendering has been estimated as varying from $20,000 to $50,000 as the capacity increases from 4 to 24 tons per 24 hours.

The cost of a continuous plant handling 50 tons per day of raw, inedible tissues has been estimated from equipment quotations to be $60,000. About $40,000 additional has been considered as adequate to cover installation and erection costs, not including the cost of the building. The equipment and costs for a continuous plant would be similar to those for standard, continuous oilseed extraction plants of equivalent capacities on the fat and solids content basis. The coagulating equipment and the continuous solvent cooker of the VioBin Process would replace the more expensive solvent extractor and the fines removal equipment of the oilseed plant.

Operating costs, as calculated for azeotropic processing in 15-ton per day batch plants as compared on the same basis with the average costs for 15-ton per day plants operated by a large Midwest renderer, are as follows:

	VioBin Process (per 100 pounds raw tissue)	Dry Rendering and Pressing (per 100 pounds raw tissue)
Labor	$ .280	$ .350
Power	.0075	.050
Fuel for steam	.0925	.085
	$ .3800	$ .485

To the azeotropic extraction process must be added the costs due to solvent loss which have been estimated as a maximum to be $.03 per 100 pounds of raw ma-

terial processed if heptane solvent is used. Higher maximum costs may be expected from the chlorinated solvents. However the actual solvent loss will vary appreciably with the solvent used, design of equipment and of solvent recovery unit, and care in maintenance and operation of the plant. In normal operations this solvent cost should be appreciably lower than the maximum costs indicated.

As a further adjustment in the evaluation of the two rendering methods, the additional fat yield of about 2 pounds per 100 pounds raw material should be credited to the azeotropic process in comparing with costs for dry rendering and pressing without subsequent solvent extraction.

For continuous plant operations, worthwhile savings can be obtained over batch operations. The total labor costs for a high capacity continuous plant will be no more than for a small batch plant, the steam and power will be more efficiently used, and the solvent loss will be less than one-third per unit of raw material processed.

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Reactions of Some Gossypol-Like Pigments With Aniline and p-Anisidine

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GOSSYPOL, the yellow pigment of cottonseed, reacts with aniline to give a stable, relatively insoluble product with a characteristic absorption spectrum (5, 8, 10). This product, known as dianilinogossypol, has been used as the basis of numerous methods for determining gossypol in cottonseed and cottonseed products (1).

Recently there was described (12) a new method for the determination of gossypol in cottonseed and cottonseed products in which *p*-anisidine was used in place of aniline. This method is simple and rapid and yields readily duplicable results. The authors (12) stated that pigments other than gossypol are simultaneously measured by the method but gave no further details concerning the nature or extent of the concomitant reactions. The following report deals with the reactions of other gossypol-like pigments with aniline and with *p*-anisidine.

In addition to gossypol, cottonseed contains a dark purple pigment which has been named gossypurpurin (2) and which has been assigned the empirical formula, $C_{30}H_{32}O_7N$, on the basis of some of its reactions and its elementary composition (11). Gossypurpurin has also been isolated from cottonseed pigment glands and has been prepared in the laboratory from diaminogossypol by a procedure involving the treatment of gossypol, $C_{30}H_{30}O_8$, with gaseous ammonia to form diaminogossypol, $C_{30}H_{34}O_7N_2$, which is then converted to gossypurpurin. It has been postulated that diaminogossypol also exists in cottonseed, particularly in seed which has been stored for long periods of time (7). It was found that the absorption spectra of non-alkali-extractable portions of chloroform extracts of stored cottonseed and that of diaminogossypol are quite similar. Their antimony trichloride reaction products also possess similar absorption spectra. On the basis of these similarities it was postulated that diaminogossypol occurs in cottonseed and is formed by the influence of metabolic changes on gossypol in the living seed.

These pigments, gossypurpurin and diaminogossypol, are known to be closely related to gossypol but are separate and distinct compounds. Gossypol, when treated with antimony trichloride in chloroform, has been shown to give a bright red reaction product with a characteristic absorption spectrum (3, 9). By contrast, the reaction product of diaminogossypol with antimony trichloride is yellow and that of gossypurpurin is blue-green (11). However both of these reaction products are unstable, and, if allowed to stand for prolonged periods of time, are converted to the characteristic red reaction product of gossypol and antimony trichloride.

The apparent close structural relationship of diaminogossypol and gossypurpurin to gossypol is sufficient evidence to justify application of the term "gossypol-like" pigments to these two pigments. The reactions of these two "gossypol-like" pigments with aniline and *p*-anisidine have been investigated with the results reported herein.

Experimental

Gossypol was isolated from cottonseed pigment glands by the method described by Castillon *et al.* (6). Its chemical and physical properties agreed with those previously reported for this product. The preparation of diaminogossypol from gossypol using gaseous ammonia and of gossypurpurin from diaminogossypol was carried out by the method of Pominski *et al.* (11). These reaction products agreed in melting point, absorption spectra in chloroform, antimony trichloride reaction product, and elementary composition with those previously reported for diaminogossypol and gossypurpurin.

Treatment with Aniline. A 0.3-g. sample of diaminogossypol was dissolved in 18 ml. diethyl ether, and

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