THE SOLVENT EXTRACTION OF OIL FROM ACORNS

by

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I. INTRODUCTION

The shortage of vegetable oils incident to the war has made the investigation of every possible source of supply desirable. The extraction of oil from acorns has never been conducted on a large scale, although the use of acorns as food and the possibility of using acorn oil has received some attention. This investigation is concerned with appropriate methods of solvent extracting oil from acorns.

Problems in Vegetable Oil Recovery. A number of problems are presented in the process of obtaining oil from an oleaginous seed. The most important of these from a commercial standpoint is the availability and probable price of the raw material and the value of the oil to be extracted. Such information as could be obtained, both as to the cost of acorns, and the value of the oil, is included in this dissertation. The second problem relates to proper storage of the nuts after harvesting. Such information as seems requisite to the solution of this problem has been obtained. The third problem, in the case of such seeds as acorns, is the removal of the shells. This was done satisfactorily using a machine built for shelling cocoa-beans.

Methods of Oil Recovery. There are two general methods for obtaining oil from oil bearing seeds expression and solvent extraction. Expression consists in retaining the oil bearing material in a container and forcing the oil out of it by exerting pressure on it. The container retains the solid material but is perforated, slotted or porous to permit the oil to flow out. Most cottonseed, flaxseed, olive and peanut oils are produced by expression. In solvent extraction the oil bearing material is mixed with an oil solvent for a period of time sufficient for this solvent to penetrate the material and dissolve the oil. Liquid and solid are then separated as completely as possible. The oil solvent mixture, miscella, is distilled to produce oil and recover solvent. The solid material, raffinate, containing solvent is dried in a drier equipped with a solvent condenser so that this solvent may also be recovered. The raffinate drier is often designated as a solvent evaporator. The extent of oil removal by solvent extraction is increased by the number of contacts between solvent and oil bearing material. All commercial oil solvent extractors are operated in a countercurrent manner to make the most effective use of solvent. Soya oil, corn oil, and cocoa-butter are produced by solvent extraction.

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Solvent extraction has the advantage of removing almost all of the oil from the seed and can be used on material of low oil content, which is not the case with expression.

Experimental Work. The experimental work of this research was largely the solvent extraction of oil from acorns. Cocoa butter was also extracted, and the extraction of these two oils is compared.

Definition of Acorn Oil. It is desirable at the start to define acorn oil, since it is a mixture of compounds. Acorn oil is the water insoluble liquid squeezed from acorns by pressing them. It is also the material extracted from acorn meat by almost any solvent, with the exception of water, and recovered from the solvent-extract mixture by evaporation of that solvent. The amount of this solvent soluble material varies widely with the solvent employed to extract it, and it might be more appropriate to refer to the ether soluble fraction, the n-butanol soluble fraction, etc., rather than to oil. It has been customary, however, to call this material oil, and since the other phrases are awkward, they will not be used.

There has not been much emphasis placed on the variation in quantity of oil extracted by different solvents by other investigators, although most reported analyses of oleaginous material do indicate which solvent was used for extraction. When it is required to compare an extraction with what would be expected in an ideal stage, it is necessary to use the same solvent for extraction and analysis.

Calculation of Extraction. A graphical method for the solution of leaching problems has been developed by J. C. Elgin and its utility extended by G. F. Kinney. This method has been used to compare the amount of extraction obtained in a particular experiment with that theoretically expected in an ideal extractor. Where the extraction is carried out in a number of separate stages, there is little difficulty in comparing the results with those required by the same number of ideal stages. In the case of a continuous extractor the number of ideal stages which will come closest to the actual performance of the extractor is calculated.

Purpose of Research. The purpose of this investigation is twofold:--(1) development of an appropriate continuous countercurrent extraction process for the recovery of acorn oil, and (2) comparison of experimental results with those calculated by Elgin's method.

The experimental part of the work involves processing about 700 pounds of acorns and the production of acorn oil. The theoretical part relates the extraction of acorn oil to solvent extraction theory, includes small scale experiments carried out for the purpose of clarifying this theory and relating it to actual extractions, and shows the utility and limitations of these graphical calculations.

II. REVIEW OF LITERATURE

Prehistorical Use of Acorns as Food. There is evidence that acorns were eaten as food well before written history.[64] The great respect in which oaks were held, the ceremony with which the high priest of the Druids every year cut away the parasitical plant which clings to it; the very name of the Druids, derived from a Celtic word signifying oak, indicate that in some remembered time oaks played an important part in the economy of these people.

Historical Use of Acorns as Food. Soyer[64] in his "Panthropheon," and Prentice[55] in "Hunger and History," record the following: The Spaniards and Arcadians regarded the acorn as a delicious article of food. Pluiry reports that in his time the Arcadians had the nuts roasted in wood ashes to soften them, and served them with dessert. According to Champier this custom still existed in Spain in the sixteenth century.

The regulation made by Chrodegand, Bishop of Metz, about the eighth century, for the canons, says expressly, that if, in an unfavorable year, the acorn or flour should fail, it will be the duty of the bishop to provide it.

When Du Bellay, Bishop of Mans, came to Francis I in 1546 to represent the frightful misery of the provinces to that monarch, he assured the king that in many places the people had nothing to eat but bread made of acorns.

According to Virgil, agriculture did not arise until the supply of acorns ran short.

In Greece the Valona oak forms considerable forests, especially on the lower slopes of Gaygetos and on the Island of Crete. Its acorns, which are large and variable in shape, are one of the commonest articles of trade in the bazaars and are eaten either raw or cooked as doubtless they were eaten in prehistoric times.

Edible Acorns. Acorns for food purposes may be divided into two classes, bitter and sweet. The acorns most palatable to man are those of the Illex ballota of the Iberian peninsula and North Africa, the Quercus aegilops of the Orient, the Quercus emoryi of the southwestern United States and northern Mexico, and Quercus michauxii of the southeastern United States.[64]

"In California the acorns of the Quercus lobata and Quercus arifolia are much used by the Indians. The acorns are long elliptical in outline, an inch and a half in length by a half inch or more in diameter.

The kernel is rather bitter but more palatable than any of our eastern oaks and quite nutritious."[47]

"Many of our oak trees bear edible fruits. The White oak (Quercus alba) sometimes has sweet acorns that are palatable when raw, but in most cases the nuts must be roasted or otherwise prepared to eliminate the bitter taste."[36]

Verill,[69] reports eating sweet acorns as a boy. He concludes that lack of care and cross pollination with bitter varieties have spoiled many trees, since he later tried acorns from the same trees and found them bitter.

Preparation of Acorns for Food. While acorns as such were eaten as described in the preceding section they have been and probably to a limited extent still are made into bread. Newberry,[47] describes the preparation of acorn bread by the American Indians.

"They (acorns) are prepared for eating by grinding the kernels to a kind of coarse flour, this is mixed with water to a thick paste; a circular depression with raised edges is made in the sand, into which the paste is poured. A fire is then built over it and it is half baked, half steamed, to the Indian taste. This treatment takes the bitterness from the acorn and the resulting cake, though according to our notion somewhat lacking in cleanliness, is well flavored and wholesome."

Webster,[71] in the American Encyclopedia, outlines a method very similar to the Indian's for making an acorn bread.

"Take ripe acorns, deprive them of their skins and beat them into a paste, steep them in water for a night and then press them dry which will take out their astringent quality. Then dry the mass and reduce it to powder to be kept as flour or meal when wanted. Form this into dough, knead it and mold it into thin cakes, which may be baked on an iron plate or in embers. This has been used, but we cannot recommend it."

Porcher[53] states, "From the acorn a kind of meal is produced which makes excellent bread, provided that a little barley meal be mingled with it to counteract its astringent qualities."

Acorns have apparently then been used as food and when appropriate varieties are selected and properly prepared the result is satisfactory.

Present Use of Acorns. The only present extensive use of acorns is as food for animals and this is rather more accidental than calculated. Pigs are encouraged to forage in woods in which acorns are available. Wild animals eat acorns and are reported particularly fond of certain varieties.[51] In this same reference, discussing the importance of the oaks of the Tennessee Valley, Perry[51] states, "The acorns are a great potential source of food for man and beast."

Figura[18] gives a method for preparing acorns as "a satisfactory and palatable food for man."

Muraoka[46] reported the results of an electric treatment of horse chestnuts and acorns.

Limonov and Kalugin[40] produced alcohol from acorns, as did Sugizaki.[65,66]

References to acorn coffee have appeared from time to time. Garrett[21] records, "it is stated that in Germany acorns are sometimes chopped up and roasted to be used medicinally by invalids as coffee; by this process of raosting much of their astringency is destroyed." Porcher[53] says of this coffee, "The acorn coffee, which is made from roasted and ground acorns, is sold in large quantities, and frequently with rather a medicinal than economical view, as it is thought to have a wholesome effect upon the blood. Acorn coffee is, however, made and used in many parts of

Germany for the sole purpose of adulterating genuine coffee."

Acorn Oil. Table I, Oil Content of Acorns, shows that oil is present in all the varieties of acorns investigated.[6,31,45,57,59,65,70,72] The amount present varies from 2.5 to 16.0 percent by weight. A number of analyses of acorn oils[25,31,37,45,56,74] give the results presented in Table II, Constants of Acorn Oils.

Hutchins[31] says of acorn oil, "This oil, if ever produced commercially in sufficient quantity, could be satisfactorily used for edible purposes."

Wittka[73] states that, "Since acorn oil is similar in properties and composition to peanut oil, soybean oil, etc., and since the residue left after producing acorn oil is of value for feeding animals, it is recommended that acorns be used in Germany as a source of oil for making margarine, soap, etc."

There are some possible uses of acorn oil which have not been published. It can be hydrogenated like cottonseed oil to produce a solid fat.[14] It can be treated with sulfur chloride to produce a factice, for use as art gum, in adhesives, etc., better than cottonseed oil, and as well as rape-seed oil.[26]

Vahlteich[68] reported on the progress made in "custombuilt fats," and while he does not mention acorn oil, its reported constants indicates that it could be used with other oils for this purpose.

TABLE I

Oil Content of Acorns.

Investigator	Variety of Acorn	Per cent Oil, by weight.
Baker[6]	Quercus robur	5.0
Baker[6]	Quercus robur	4.7
Cranfield[72]	-	4.57
Wainio[70]	Red Oak	12.87
Wainio[70]	Rock Chestnut Oak	2.52
Wainio[70]	Scrub Oak	11.61
Wainio[70]	Scrub Chestnut Oak	3.52
Wainio[70]	White Oak	3.33
Hutchins[31]	Q. palustris	13.40
Remlinger[59]	Q. ilex	2.5
Remlinger[59]	Q. suber	3.3
Puntambaker[57]	Q. incana	16.0
Monarca[45]	Q. rubra	11.03
Sugizaki[65]	Q. glanca Thumb	3.24

TABLE II

Variety of Acorn	Oil Constants				
	Specific Gravity at 25°C.	Refractive Index at 25°C.	Saponification No.	Iodine No.	Acid No.
_[25]	0.909	1.4696	199.3	100.7	-
Q. palustris[31]	-	-	192.9	99.4	7.0
Q. agrifolia[37]	0.909	-	199.3	100.0	-
Q. rubra[45]	0.9141	1.4725	195.3	100.1	4.5
Q. incana[56]	0.9081	1.4594	192.2	85.5	13.0
Q. dilatata[56]	0.9084	1.4606	188.4	90.3	22.2
Q. ilex[56]	0.9079	1.4594	189.9	83.0	8.5
_[74]	-	-	193.2	97.2	-

Note:

For the sake of uniformity the author has converted specific gravities and refractive indexes, reported at temperatures other than 25°C. to 25°C. Specific gravities have been converted by the formula given in "Methods of Analysis" of the A.O.A.C.[2] Indexes of refraction have been calculated to 25°C. by the formula given in Griffin.[28]

Availability of Acorns. Acorns are not a standard article of commerce and consequently there are no statistics on acorn production or acorn prices. The Sino-Java Company of New York was sufficiently interested in the possibility of producing oil from acorns to send a representative to Georgia to investigate a supply of acorns from that state. Mr. Perry[52] interviewed a number of the county agents who assured him that a large quantity of nuts would be available at about a cent a pound.

Some acorns for this research were purchased commercially from the Anderson Hardware Company of Anderson, South Carolina. Mr. Brown[12] of this company writes, "There is an abundance of acorns in and near Anderson, South Carolina. I have no way of estimating how many, but considering all varieties there is an abundance. I believe if it were possible to pay the pickers five cents a pound and the person that assembles and stores for shipment about two cents a pound, that you could be supplied with acorns enough to accomplish your needs."

Neither acorns nor acorn oil are listed in the United States Tariff Commission's report for 1941 on "Fats, Oils, and Oil-Bearing Materials in the United States."[67]

Thus, while it is certain that acorns are available, there is no reliable information on the quantity produced per year, nor on the value of this crop.

Solvent Extraction Practice. History of Solvent Extraction. Expressing oil-bearing seeds has the disadvantage of leaving around five to ten per cent of the oil in the cake. Schonfeld[63] reports that solvent extraction was recognized as early as 1843 as affording a means of more complete oil recovery and that in this year Jesse Fisher of Birmingham, attempted to extract oil with carbon bisulfide. Ferand and Millon[63] used a mixture of ether and carbon bisulfide in 1855. Deiss[1,63] in France operated the first real extraction system in 1856. He employed carbon bisulfide as solvent.

This system of Deiss's, Vohl's extractor and Seiffert's battery of extractors are described in Andes, "Vegetable Fats and Oils."[1] These early systems consisted of a cylinder (or cylinders) to contain the material undergoing extraction; a means of circulating solvent; a still to separate oil and solvent, returning solvent to the extractor; and a condenser to condense solvent vapor. Sieffert used a battery of four or more extraction cylinders so that charging, discharging, and extraction could be carried on at the same time. His system used compressed air to remove more solvent from the extracted material than would drain off.

Andes[1] also describes two more elaborate extraction systems; the Scott and the Garrigue. These included storage for raw material, solvents, and miscella, as well as mills for preparing the material for extraction. They were both batch systems; the Scott process employing vertical extractors; the Garrigue a horizontal, rotating, steam-jacketed extractor. They advanced the art of solvent extraction by the introduction of a continuous still to handle the miscella and by the inclusion of means of recovering solvent from the extracted material.

<u>The First Extractors in the United States</u>. Goss[23] gives an account of the progress of solvent extraction in this country. A Bollman type of extractor at Norfolk, Virginia, ran local soybeans in 1924-1925 and attempted to process imported flaxseed, but the project was unsuccessful. During the same period another Norfolk plant used Scott rotary extractors on a variety of oil-bearing seeds, including soybeans and copra.

The first successful large-scale operations were those of the Archer-Daniels-Midland Company and the

Glidden Company. They both installed Hildebrandt type extractors in Chicago during 1934 and 1935 for the extraction of soybeans. The Glidden plant was destroyed by an explosion in 1935 but was immediately rebuilt with a doubled capacity.

Modern Solvent Extraction. According to Goss,[23] there are five solvent systems used in large-scale soybean extraction in this country. Soybeans and corn germ are handled in a Hildebrandt extractor at Clinton, Iowa. This installation is similar to the two mills in Chicago. Soybeans are processed at Decatur, Indiana, and Decatur, Illinois, in Bollman type extractors. The French Oil Mill Machine Company's process, which is much like the Bollman system, is installed at Louisville, Kentucky for soybeans. There are Allis-Chalmers installations at Cedar Rapids, Iowa, for soybeans; and at Hiram Walker's plant in Peoria, Illinois, for recovering corn oil from dried distiller's grains.

In the Hildebrandt system extraction is carried out in a large U-tube through which flaked oilseeds are conveyed, by means of perforated screws, against a counterflow of solvent.[23,29,62]

The Bollman extractor uses a vertical series of sieve-bottomed baskets which are carried through the system on a pair of endless chains. Flaked soybeans or other oleaginous materials are charged into the baskets and are sprayed with solvent during their passage through the extractor.[23,29,62]

The Allis-Chalmers' extractor comprises a vertical, cylindrical column containing a central rotating shaft fitted with a series of horizontal slotted plates. Stationary scraper arms cause the solid material to fall from one slowly revolving plate to another, descending against an upward stream of solvent.[3,8,23]

The Kennedy extractor uses a number of four bladed paddle wheels to propel the solid material through a horizontal chamber against a counterflow of solvent. A Kennedy extractor is under construction at Hershey, Pennsylvania, for extraction of cocoa butter. A similar scheme is used in the solvent extraction system currently offered by the Vulcan Copper and Supply Company.[23,44]

Other Systems. A great many other extractors are described, particularly in patents. References are given to a good many of these, but since most of them are only variations of the apparatus already described, they can be summarized as follows:

A solvent extractor consists of a closed, solvent-tight system into which oleaginous material may be introduced and conveyed; by gravity, paddles, conveyer chain, perforated screw conveyer, perforated baskets, or link belt; against a flowing stream of solvent, (usually countercurrent, sometimes co-current in one part of the extractor, countercurrent in another), then drained of solvent and discharged from the extraction part of the system. Means of admitting solvent and removing miscella are provided.

The extracted material, after draining, is carried through some type of vapor-lock into a solvent evaporator where solvent is recovered and from which solvent-free extracted solids are discharged.

A solvent recovery still and solvent recovery system are included in the extraction system although they, as well as the solvent evaporator, are not part of the extractor proper.[13,28,30,39,42,48,49,50,60]

<u>Solvents</u>. The solvent used must first of all be a good solvent; that is, it should penetrate into the cell structure of the solid and dissolve out the desired soluble substances and only these. It must also be easily removable from both miscella and residue leaving both the extracted solids and the extracted oil in a marketable condition.[23]

Gasoline (benzine) is the most widely used solvent because of its cheapness and because it extracts less color and non-oil constituents.[33,41] The soybean Industry uses hydrocarbons to extract about 350,000 tons of beans per year.[3,8,23] Methylene chloride is used by Rockwood and Company to extract cocoa butter.[13] Table III, Solvents, gives the important physical constants of solvents which are most frequently employed in extraction.[63] Propane and butane have been proposed.[61]

Preparation of Feed. Successful extraction requires an appropriate feed. "Beans which are for solvent extraction are, after cracking and moderate heating, rolled into flakes to give the largest practical amount of surface for solvent contact. The moisture content of the beans should be 10-12 per cent for best results."[41] McKinney discusses preparation of tung meal for solvent extraction in his articles on solvent extraction of tung oil.[19,20,43,44]

Solvent extraction has been more successful with soybeans than with other oil seeds according to Goss[23] because they are easy to prepare for extraction. The soybeans can be rolled into thin, firm flakes which retain their structure even after the oil has been leached from them. Proper methods of preparation of cottonseed and flaxseed for solvent extraction have not yet been commercially perfected.

Solvent Extraction Theory. Evans[17] stated in his paper on "Countercurrent and Multiple Extraction," that, "It is desirable to have a simple and rapid means by which, knowing the feeds and equilibria involved, the effects of a definite number of stages can be calculated. In this way, relative results and efficiencies to be expected can be estimated and a decision made as to what will be preferable or feasible in practice."

Hawley[27] derived formulas for the number of extracting cells required for a particular process. These formulas were largely empirical and would not serve to calculate terminal conditions.

Baker[5] gives a method which is discussed in Badger and McCabe.[4] This method is not used if the ratio of solvent drained off to solvent retained is a function of concentration.

Ravenscroft[4,58] solved the case where the ratio of solvent drained off to solvent retained varies with concentration.

The most general and simplest method is that developed by Elgin.[15] The utility of Elgin's triangular plot has been greatly extended by Kinney's method of enlargement.[34]

A pseudo-countercurrent scheme has been developed which gives results comparable to those obtained in a countercurrent process.[16,32]

TABLE III

Solvents[63]

Solvent	Boiling Point, °C.	Sp. G. (temp. is °C.)	Sp. Heat, cal. per gram	Latent Heat, cal. per gram	Vapor Pressure, mm. ofHg, at 20°C.
Hexane	68	0.6630 at 17°	0.4	79	124
Heptane	98	0.7006 at 0°	0.4	74	64
Benzene	80	0.88 at 0°	0.41	93	76
Carbon disulfide	46.5	1.293 at 0°	0.25	90	298
Diethyl ether	35	0.730 at 15°	0.53	90	442
Acetone	56	0.814 at 0°	0.53	125	185
Ethanol	78	0.789 at 15°	0.60	125	44
Trichlor-ethylene	87	1.470 at 15°	0.23	57	56
Carbon tetra-chloride	77	1.594 at 15°	0.21	46	91
Methylene chloride	42	1.336 at 15°	0.25	60	350
Ethylene chloride	99	1.24 at 20°	0.31	85	61

III. EXPERIMENTAL

Purpose of Study

The purpose of the experimental work of this thesis is twofold; first to illustrate solvent extraction theory and to make clear its application to the extraction of oil from oil-bearing materials; second to produce acorn oil by solvent extraction on a pilot plant scale. These two objectives are related since the results of the pilot plant extractions are evaluated by the use of extraction theory and all experiments, as far as possible, were carried out in such a way as to test the use and limitations of this theory.

The two purposes for which the experimentation was planned require quite different scale experiments. The theoretical work could best be carried out working with grams of material; the practical extractions with pounds of acorns and gallons of solvent. The experimental section is therefore divided into two related parts.

A. Small Scale Experiments to Illustrate Solvent Extraction Theory.

B. Pilot Plant Study of the Solvent Extraction of Oil from Acorns.

A. SMALL SCALE EXPERIMENTS TO ILLUSTRATE SOLVENT EXTRACTION THEORY.

Plan of Investigation

Artificial Systems. Two artificial systems; sand, acetic acid, water and; sand, acetylene tetrabromide, acetone; were to be investigated. These systems fulfill all of the assumptions required by the derivation of the theoretical method for calculation of the results of solvent extractions. The sand to be used was prepared in such a way that there would neither be adsorption nor absorption of solvent or solute. This sand was truly an inert carrier solid being insoluble in solvent, solute, or in mixtures of solvent and solute. Equilibrium would be quickly and certainly established in these systems since there was no interstitial space within the sand grains to retain solute.

The experimentation with these artificial systems was planned as a test of the experimental extraction technique employed and of the correctness of the interpretation given to Elgin's method of calculation. There was no question of the validity of Elgin's derivation, so that, if the extraction experiments gave results in agreement with theory, the experimental procedure would be proven satisfactory and the interpretation of the experimental data would be shown to be precise.

Natural Systems. Artificial systems are of limited interest in the solvent extraction field and are not typical of such extractions as that of oil from acorns. The extractions in artificial systems were therefore to be followed by experiments with natural systems to show the agreement to be expected between theory and experiment in the solvent extraction of vegetable oil. The systems selected for study were: inert cocoa matter, cocoa butter, methylene chloride; and inert acorn matter, acorn oil, n-butanol. The investigation of the systems containing cocoa butter was planned because Rockwood and Company have made a commercial success of the extraction of this oil and, if it could be shown that the extraction of acorn oil was no more difficult than that of cocoa butter, acorn oil extraction would become a commercial possibility. Whether or not it would be an attractive possibility would then depend on other factors than extractability, such as the cost of acorns, the yield of oil and the value of the product.

Selection of Solvent. Skellysolve C was chosen for one solvent because it is typical of the hydrocarbons which are the most widely used industrial oil extraction solvents. Methylene chloride was to be employed since it is the solvent used by Rockwood and Company. n-Butanol was to be used in the acorn oil extraction to see whether or not it would be satisfactory. It would not be possible to test out any large number of solvents, nor would such testing be pertinent to this investigation. If these three solvents gave results compatible with theory, solvent extraction theory, (which should be valid irrespective of solvent), would be experimentally verified for a hydrocarbon, a chlorinated hydrocarbon and an alcohol as solvents.

Materials

Acetone, Technical, 99-100 per cent dimethyl ketone. Commercial Solvents Corp.

Acid, Acetic, C.P., Glacial, Baker's Analysed. J. T. Baker Chem. Co.

Acid, Hydrochloric, C.P., Baker's Analysed. J. T. Baker Chem. Co.

Acorn Meal, from White Oak, Red Oak and Spanish Oak Acorns. The Anderson Hardware Co., Anderson, South Carolina. The acorn hulls were removed by hand. The meats were gound in a hammer mill producing a meal of which 93.2 per cent passed a 35 mesh sieve and two per cent was retained by an 8 mesh sieve.

Butanol, n-Butyl Alcohol, distillation range 115°C. to 118°C. Commercial Solvents Corp.

Acetylene Tetrabromide, Eastman's s-Tetrabromoethane, P 240, Pract. This material as received contained a small amount of acetone as a stabilizer. It was washed with water to remove this acetone and after washing had a specific gravity of 2.91 at 25°C.

Acetylene Tetrabromide, reclaimed. This material was obtained by the distillation of mixtures of acetone and acetylene tetrabromide from a steam bath. The residue from this distillation was washed with water to remove traces of acetone and was used as reclaimed acetylene tetrabromide. It had a specific gravity of 2.91 at 25°C.

Cocoa Expeller Cake. This material is the residue from which oil has been removed by an Anderson Duo Expeller at Rockwood and Company's plant. It was crushed and then screened. The fraction passed by a one quarter inch mesh screen and retained by a one eighth inch mesh screen was used for extraction with Skellysolve C and methylene chloride. After the expelling operation there is still some cocoa butter in the expeller cake. This residual oil is removed by extraction with methylene chloride in Rockwood's large extractor. The amount of cocoa butter in the crushed, screened cake was determined by soxhlet extraction with both Skellysolve C and methylene chloride. Soxhlet extraction with Skellysolve C gave 8.19 per cent of cocoa butter, (Skellysolve C extractable material), in the expeller cake; extraction with methylene chloride gave 7.0 per cent cocoa butter, (methylene chloride extractable material). The crushed cake was screened to give a similar to the solid feed employed by Rockwood and Co.

Methylene Chloride, C.P., Eimer and Amend.

Methyl Orange, Indicator, Mallinckrodt Chem. Co.

Oxalic Acid + 2 H_2O, A.R., Mallinckrodt Chem. Co.

Phenolphthalein, Indicator, Mallinckrodt Chem. Co.

Sand. This was Ottawa Sand from Eimer and Amend of New York City. It had the following screen analysis:

Screen Test Number	1	2
Per cent between 0.046" diameter and 0.0328" diameter.	1.8	1.7
Per cent between 0.0328" diameter and 0.0232" diameter.	98.0	98.1
Per cent between 0.0232" diameter and 0.0164" diameter.	0.2	0.1

This screen analysis shows that there was no considerable amount of material in this sand in the colloidal range. "It is arbitrarily considered that particles with diameters between 0.001μ and 1μ, (10^{-7} and 10^{-4}cm.), are colloids, although there is no sharp distinction in these extremes. --- Particles larger than 1μ may be regarded as ordinary matter,"--[26] Since all of this sand was plus 0.0164" in diameter there was no colloidal material present, and hence the sand neither absorbed nor adsorbed solvent or solute.

Skellysolve C. Essentially n-heptane, boiling range 60 - 70°C. Residue on evaporation less than 0.003 per cent. Skelly Oil Company.

Sodium Hydroxide, A.R., Pellets, Mallinckrodt Chem. Co.

Apparatus

Hammer Mill. A Raymond Laboratory Mill, Serial Number 40127, made by the Raymond Pulverizer Division, Combustion Engineering Company, Inc. of Chicago, Ill. Fig. 1, is a photograph of this mill.

Ro-Tap Sieve Shaker and Tyler Std. 8" Testing Sieves. Ro-Tap No. 1663, the W. S. Tyler Co., Cleveland, Ohio. This equipment was used for screen analyses.

Laboratory Apparatus. Laboratory apparatus of standard specifications; soxhlet extractors, constant temperature baths, burettes, glassware, balances and weights. This equipment was used as required for experiments and analyses.

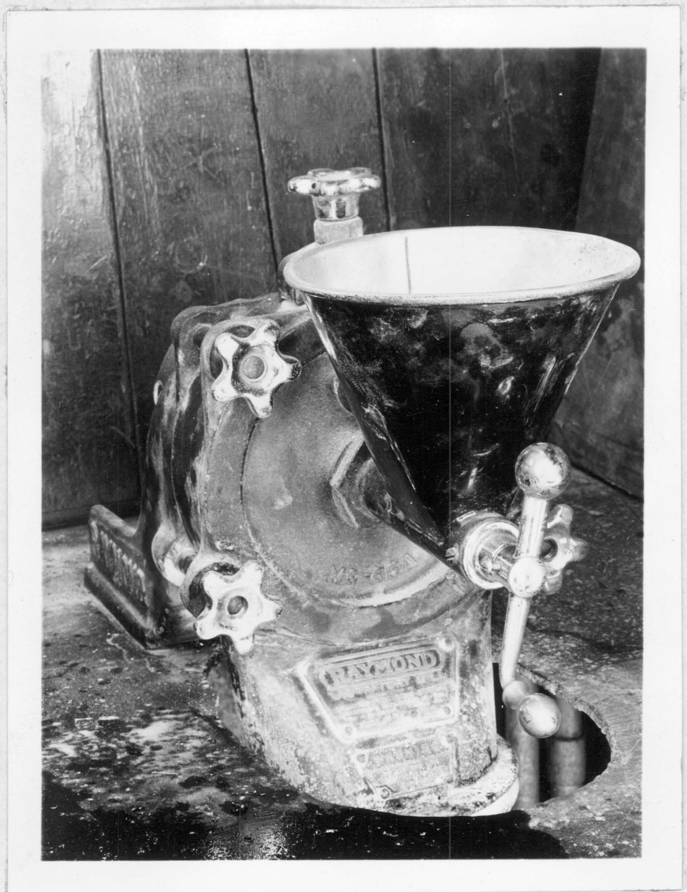


Figure 1

The Raymond Laboratory Hammer Mill.

Method of Procedure

General Procedure for Laboratory Extractions. The seven laboratory scale extraction experiments all used the pseudo-countercurrent extraction scheme described by Elgin.[20] This scheme is presented in Fig.2. Feeds corresponding to the number of extraction cycles and partial extraction cycles employed were weighed out. Solvent was measured, (and its weight calculated from its known specific gravity), and shaken with feed or partially extracted material in 250 ml. wide mouthed bottles until equilibrium had been established. The contents of the bottle (extraction stage) were settled until a reasonably clear overflow could be drawn off with a pipette. This was the overflow and was transferred to the next stage or taken out of the system as indicated by the extraction scheme being followed. The residue in the bottle was the underflow and its disposition also followed the extraction diagram. Each bottle was tared and was weighed before and after every transfer of overflow. Thus the weights of the two streams, overflow and underflow, were known at every point in the extraction scheme.

The first six of the laboratory extractions were carried out in the manner just described. The seventh experiment, the extraction of acorn oil from acorn meal

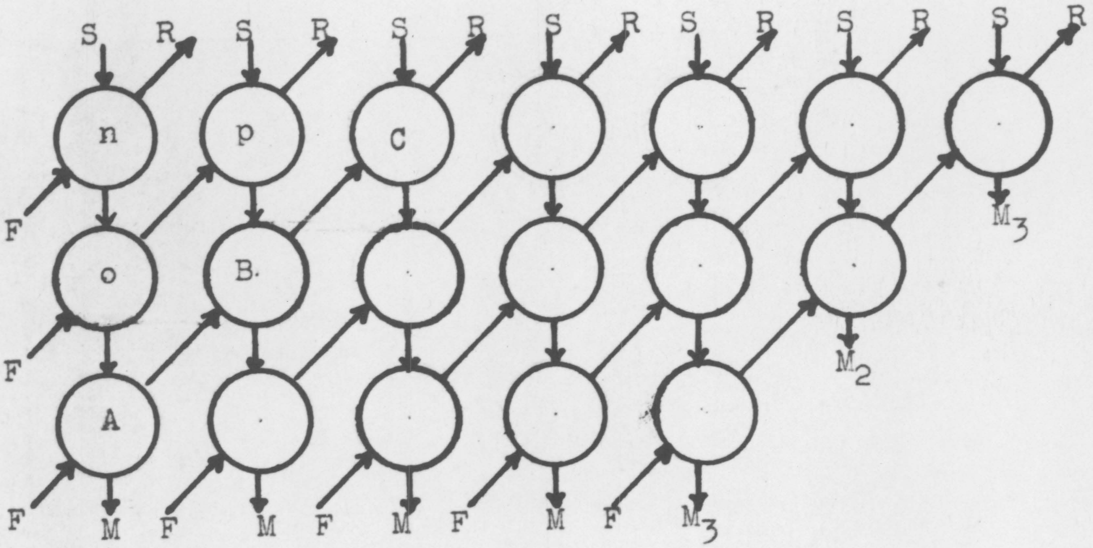


Figure 2.

Pseudo-Countercurrent Extraction Scheme

The number of horizontal rows, (in this diagram three), is the number of stages. The number of times that three circles, (as A, B, and C), are joined diagonally indicates the number of extraction cycles, (five in this case). n, and o, p are two incomplete cycles; required to start this kind of extraction scheme.

with n-butanol, differed from this procedure in that the overflow was not fixed. Solvent and feed were mixed as usual in this seventh experiment but then, instead of drawing off the overflow with a pipette, the contents of the stage were poured into a Buechner funnel and filtered. Underflow and overflow were weighed before passing them on to the next stages. This experiment is illustrated by Fig. 3, Quantitative Flow Diagram of the Extraction of Acorn Meal with n-Butanol.

The individual experiments are described in Table IV, Laboratory Extractions.

The experimental conditions for these small scale experiments are given in Table V, Experimental Conditions for Laboratory Extractions.

The results of the experiments are presented in Table VI, Results of Laboratory Extractions.

Calculation of Extraction. The per cent extraction is based on the quantity of solute removed. Thus 95 per cent extraction means that 95 per cent of the solute originally present in the feed has been extracted. The experimental per cent extraction is obtained by analysis as given in Table VI. Experimental extractions are tabulated in Table VII, Extraction in Laboratory Experiments, and are compared in that table with theoretical extractions calculated by the graphical method.

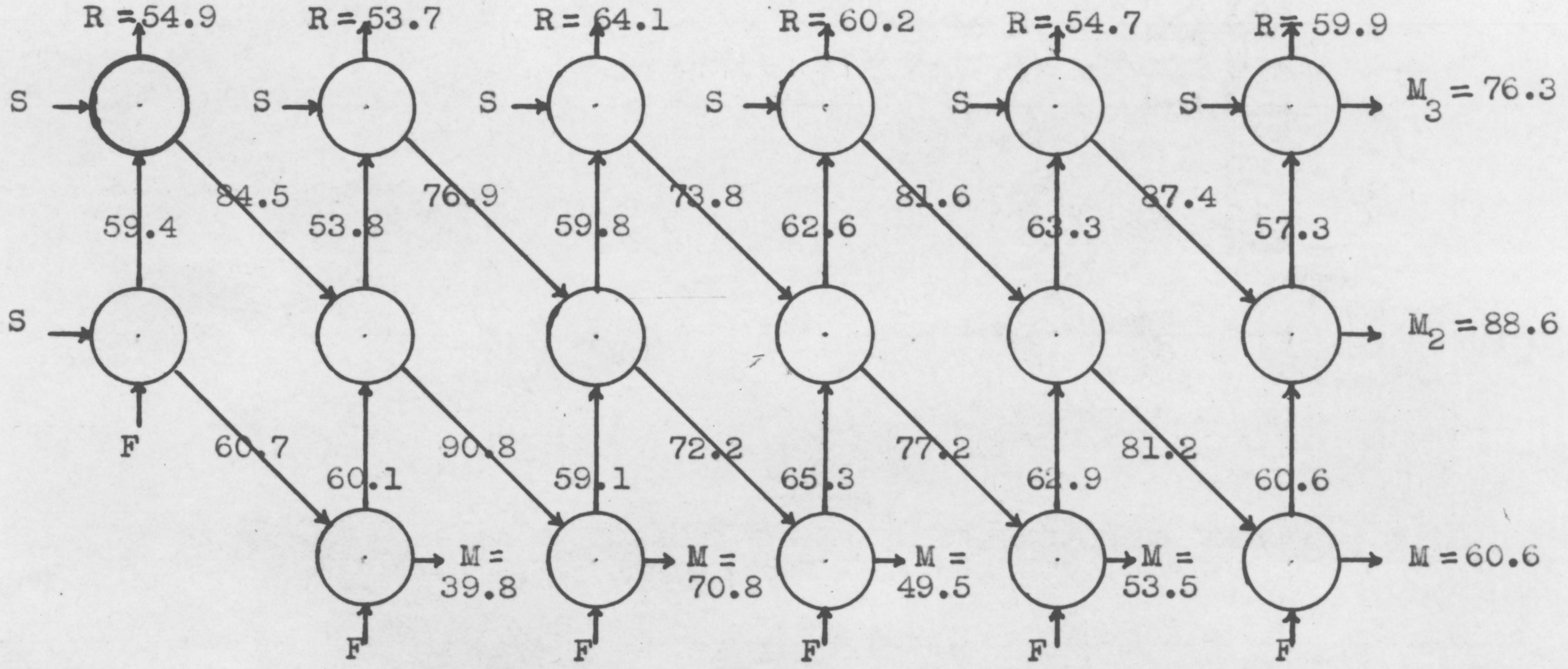


Figure 3

Quantitative Flow Diagram of Experiment 7, Extraction of Acorn Meal with n-Butanol.

S = 80 grams n-Butanol, F = 40 grams Acorn Meal. All figures are weights in grams.

TABLE IV.

Laboratory Extractions

Experiment	System	Extraction of:-	Solvent
1	Sand, acetic acid, water	Acetic acid	Water
2	Sand, acetic acid, water	Acetic acid	Dilute acetic acid
3	Sand, acetylene tetrabromide, acetone	Acetylene tetrabromide	Acetone
4	Sand, acetylene tetrabromide, acetone	Acetylene tetrabromide	Acetone
5	Inert, cocoa butter, Skellysolve C	Cocoa butter	Skellysolve C
6	Inert, cocoa butter, methylene chloride	Cocoa butter	Methylene chloride
7	Inert, acorn oil, n-butanol	Acorn oil	n-Butanol

TABLE V.

Experimental Conditions for Laboratory Extractions

Experiment	1	2	3	4	5	6	7
Number of stages	2	3	3	4	3	3	3
Number of cycles	5	5	3	5	5	5	5
Temperature, ^{o}C.	27	27	27	27	25	25	25
Extraction time, minutes	7	7	7	7	12	12	12
Feed:							
Weight, Grams	100	125	100	100	103.8	150.2	40.0
Solute, Per cent	25	40	50	50	3.9	2.3	36.0
Solvent, Per cent	25	20	25	25	51.8	66.7	0.0
Solvent, Grams	50	100	79.2	79.2	71.7	133.6	80,0
J, Mixture of feed and solvent:							
Solute, Per cent	16.7	23.4	37.9	27.9	2.35	1.2	12.0
Solvent, Per cent	50.0	54.4	58.2	58.2	71.50	82.4	66.7
Inert, Per cent	33.3	22.2	13.9	13.9	26.15	16.4	21.3
Miscella, Ml.	50.0	100.0	100.0	100.0	100.0	100.0	37.6

TABLE VI.

Results of Laboratory Extractions.

Experiment	Miscella, M, Grams	Raffinate, R, Grams	Solute in miscella, Per cent	Solute in raffinate, Per cent	Solute in solvent-free raffinate, Per cent
1	50.0	100.0	33.7	8.7	14.8
2	105.0	120.2	44.0	7.2	14.7
3	113.6	63.3	40.8	4.5	10.1
4	112.0	63.3	42.5	3.5	8.2
5	72.4	102.4	4.7	0.8	1.5
6	130.2	138.5	2.0	0.4	1.15
7	60.6	56.9	25.53	1.8	3.90

TABLE VII.

Extraction in Laboratory Experiments

Experiment	1	2	3	4	5	6	7
Solute in feed, Grams	25.0	50.0	50.0	50.0	4.1	3.5	14.4
Solute in miscella, Grams	16.8	46.2	46.4	47.6	3.4	2.6	14.3
Solute in raffinate, Grams	8.7	8.65	2.85	2.22	0.82	0.55	1.02
Solute extracted, (solute in feed - solute in raffinate), Grams	16.3	41.35	47.15	47.78	3.28	2.95	13.38
Extraction, Per cent, (based on raffinate)	65.2	82.6	94.3	95.5	80.0	84.3	92.8
Theoretical extraction, Per cent	67.2	82.6	92.8	96.0	83.0	86.5	94.0

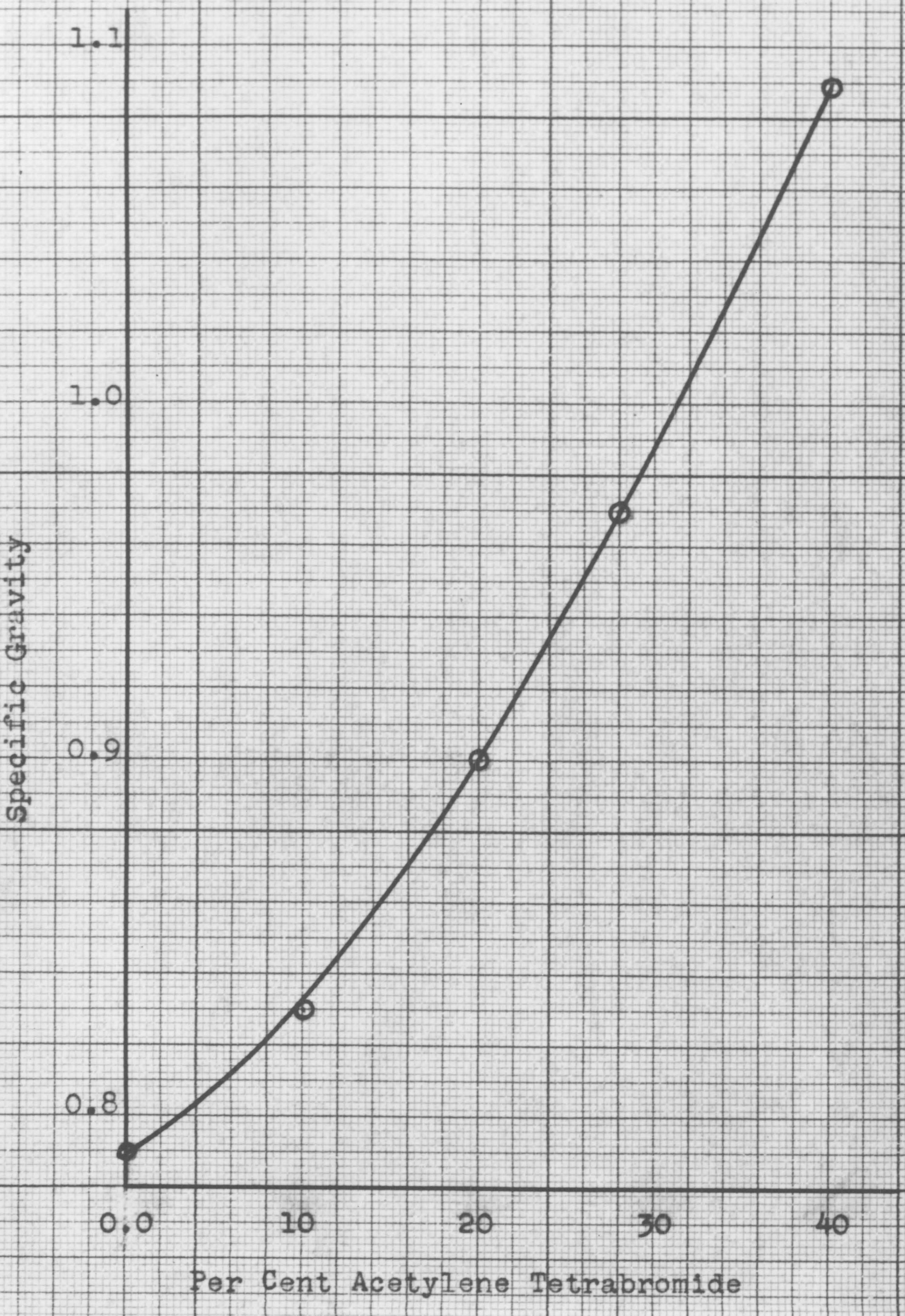
Analytical Methods. The miscellas, consisting in experiments 1 and 2 of mixtures of acetic acid and water, were analysed by titration with standard sodium hydroxide solution. The raffinates in these same experiments, mixtures of sand, acetic acid and water, were analysed similarly. The specific gravities of mixtures of acetone and acetylene tetrabromide were determined at room temperature, 27^{o}C., and Fig. 4, Specific Gravities of Mixtures of Acetone and Acetylene Tetrabromide, was constructed from these determinations. The miscellas of experiments 3 and 4, consisting of acetone and acetylene tetrabromide, were analysed by determination of their specific gravity and comparison with Fig.4. The compositions of the raffinates in experiments 3 and 4 were determined by analysis of the liquid in contact with the sand, (specific gravity determination as with the miscellas), and calculation based on the known weights of sand and liquid.

The compositions of the feeds in experiments 1,2,3 and 4 were known since the constituents of these feeds were weighed out. The compositions of the feeds in experiments 5,6 and 7 were determined by soxhlet analysis with the extraction solvent, Skellysolve C, methylene chloride and n-butanol respectively.

The miscellas in experiments 5, 6 and 7 were analysed by evaporating a weighed quantity of the stream to constant

Figure 4.

Specific Gravities of Solutions of Acetylene Tetrabromide in Acetone at 27°C.



weight at 105°C. in experiments 5 and 6 and at 135°C. in experiment 7.

The compositions of the raffinates in experiments 5 and 6 were determined by analysis of the liquid in contact with the inert material, (evaporation of a known quantity to constant weight as with the miscellas), and calculation based on the known weights of inert matter and liquid.

The raffinate in experiment 7 was analysed by evaporation of solvent from a sample of known weight at 135°C. followed by soxhlet analysis of the solvent free residue with n-butanol as solvent.

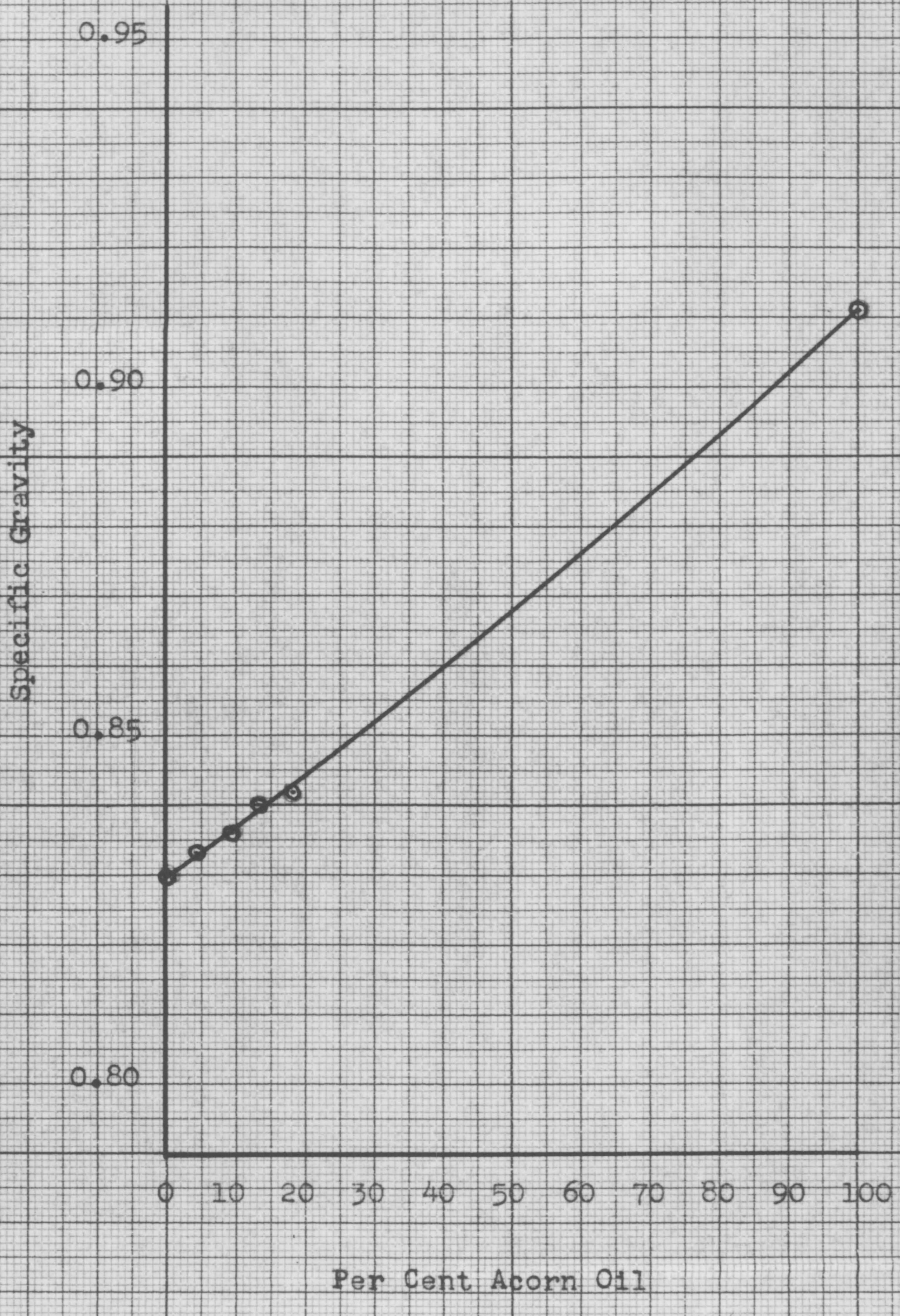
Theoretical Determination of the Underflow, xx line. The composition of the theoretical underflow depends on the amount of inert material present, (which does not change during an extraction, except as fine material is carried off with the overflow), and the composition and specific gravity of the liquid associated with this material.

In all these experiments except 7 the volume of liquid in the underflow was kept constant. Thus, knowing the variation in specific gravity of this liquid with solute concentration, Table VIII, Theoretical Composition of the Underflows, was constructed. Specific gravities of acetic acid-water solutions were taken from Lange.[42] Specific gravities of acetylene tetrabromide-acetone solutions from Fig. 4. Where the change in concentration during extraction was small, as in experiments 5 and 6, the composition of the underflow was taken as constant and the liquid in it given the same specific gravity as the solvent.

For experiment 7 the xx line was calculated by averaging the weights of the raffinates, Rs in Fig. 3. The amount of inert material was the same in each of these so that the average amount of liquid present could be calculated. This liquid had the composition of M_3. The specific gravities of acorn oil-butanol solutions at 25°C. are given as Fig. 5. Thus from Fig. 5, the amount of

Figure 5.

Specific Gravities of Butanol-Acorn Oil Solutions at 25°C.



inert material present, and the volume of solution in the average raffinate, the theoretical underflows were calculated as presented in Table VIII, Theoretical Compositions of the Underflows.

Calculation of the Theoretical Extraction. The information requisite to the prediction of the theoretical extraction to be expected with a number of stages equal to the number experimentally employed is available in Table V and in Table VIII. The method of calculation is that proposed by Elgin[17] as modified by Kinney.[38]

Specimen Calculation. A specimen calculation of experiment 7 is given to illustrate the calculations which were common to all of these extraction experiments and which lead to the results given in Table VII, Extraction in Laboratory Experiments.

Experiment 7 is a three stage extraction; the feed, (F), has the composition 40.0 per cent acorn oil, 60.0 per cent inert material; the solvent, (S), is pure butanol; 80 grams of solvent are fed to 40 grams of acorn meal; the mixture of solvent and feed, (J), had the composition:

14.4	grams	acorn oil	......	12.0%
25.6	"	inert	......	21.3%
80.0	"	butanol	......	66.7%
120.0	grams			100.0%

TABLE VIII.

Theoretical Compositions of Underflows, xx.

Experiment	Per cent inert at solute per cent of:-						
	0.0	2.0	5.0	10.0	15.0	20.0	25.0
1	50.0	50.0	49.8	49.6	49.5	49.4	29.2
2	41.6	41.6	41.5	41.3	41.4	41.0	40.8
3	39.2	39.1	39.0	38.2	37.2	36.2	35.2
4	39.2	39.1	39.0	38.2	37.2	36.2	35.2
5		constant at 44.3 per cent					
6		constant at 33.0 per cent					
7	45.1	45.1	45.0	44.9	44.9	44.8	44.7

The information is taken from Table VIII for the xx line. Fig. 6, The Graphical Calculation for Experiment 7, can now be constructed. The points F, S, J, and the xx line have the following coordinates in the two component system, solvent-solute, plotted in Fig. 6.

F is 40.0% acorn oil, 0.0% butanol
S is 0.0% acorn oil, 100% butanol
J is 12.0% acorn oil, 66.7% butanol
xx line:-

Acorn oil, Per cent.	Butanol, Per cent.
0.0	54.9
2.0	52.9
5.0	50.0
10.0	45.1
15.0	40.1
20.0	35.2
25.0	20.3

Assuming values of M set corresponding values of R, since MJR is a straight line, and values of M were tried until one was found which gave the exact number of stages, three. This theoretical value of M, 22.2% acorn oil, gave a solvent-free raffinate containing 3.0% acorn oil.

Analysis of the solvent-free raffinate showed that it contained 3.9 per cent acorn oil, Table VI. The amount of inert material in this raffinate was the same as that in the feed, 25.6 grams. Therefore, there were 25.6/0.961 = 26.7 grams of solvent-free raffinate.

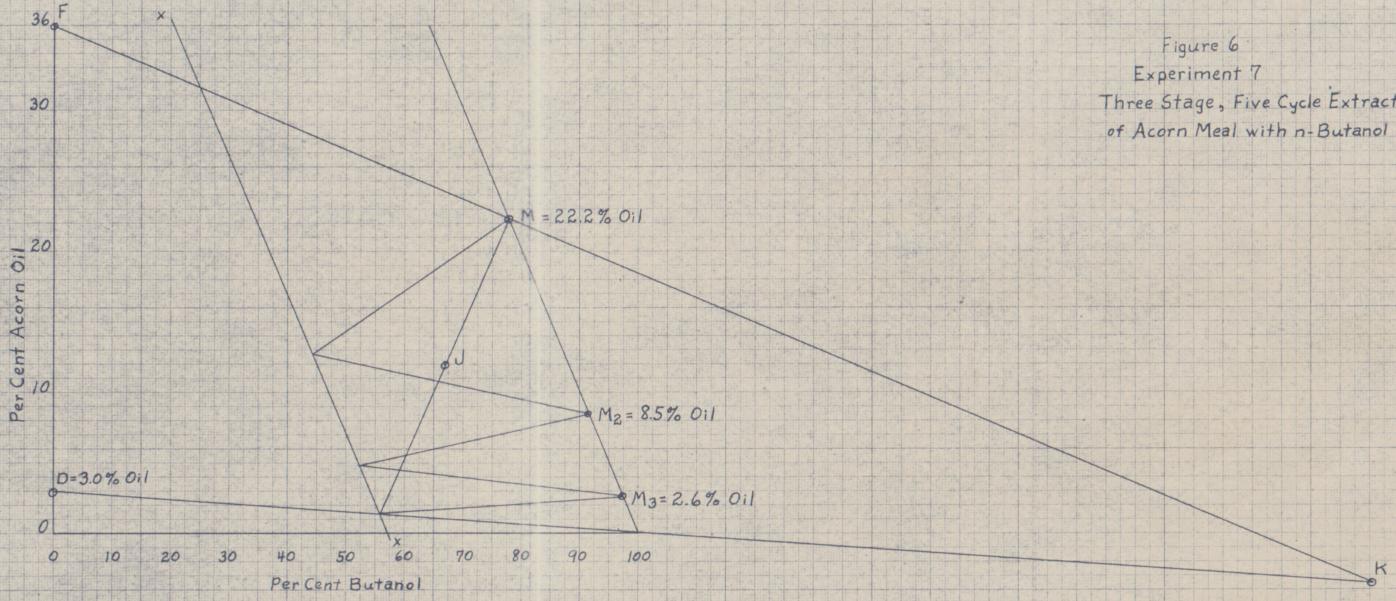


Figure 6
Experiment 7
Three Stage, Five Cycle Extraction
of Acorn Meal with n-Butanol

The raffinate contained 26.7 - 25.6 = 1.1 grams of oil. The feed contained 14.4 grams of oil so that 14.4 - 1.1 = 13.3 grams of oil had been extracted, or 13.3/14.4x100 = 92.4 per cent of oil was experimentally extracted.

The theoretical solvent-free raffinate, D, in Fig. 6 contained 3.0 per cent of oil and calculating as before 94.0 per cent of the oil should have been extracted according to theory.

The average weight of the raffinate is 56.9 grams. This raffinate consists of 25.6 grams of inert material and 31.3 grams of liquid of the composition M_3. M_3 contains 3.39 per cent acorn oil by analysis and hence has a specific gravity of 0.832, from Fig. 5. There are then 31.3/0.832 = 37.6 ml. of liquid in the average underflow.

(1) Acorn oil, Per cent	(2) Sp. G. from Fig. 5	(3) Weight Liquid in underflow, Grams	(4) Weight underflow, (3)+25.6 Grams	(5) Inert, Per cent	(6) Solvent, Per cent
0.0	0.830	31.2	56.8	45.1	54.9
2.0	0.831	31.2	56.8	45.1	52.9
5.0	0.833	31.3	56.9	45.0	50.0
10.0	0.837	31.4	57.0	44.9	45.1
15.0	0.840	31.6	57.0	44.9	35.2
25.0	0.848	31.9	57.2	44.7	20.3

The values of per cent inert in colum 5 and per cent solvent in column 6 are those used to plot the xx line in Fig. 6.

Determination of Equilibrium Time of Contact. The length of time required to bring the systems investigated to equilibrium was determined. Equilibrium was established immediately in the artificial systems with sand as the solid phase.

Experiments were conducted to bring about equilibrium in the acorn oil and cocoa butter systems. Solids and solvent were mixed in the proportions used in the experiments. These mixtures were shaken for 5, 10 and 30 minutes and then settled for two minutes. Supernatant liquid was drawn off the settled solids and concentration changes were measured by evaporation of a known quantity of liquid to constant weight, or by determining its specific gravity. There was a slight increase in solute concentration, (or change in specific gravity), between 5 and 10 minutes shaking time, but no difference between the 10 and 30 minute samples. Ten minutes was selected as a satisfactory mixing time and this plus the settling time gave twelve minutes as sufficient to establish equilibrium.

B. PILOT PLANT STUDY OF THE SOLVENT EXTRACTION OF OIL FROM ACORNS

Plan of Investigation

Two pilot plant extraction units were planned for operation. The first of these was to employ a centrifuge to separate underflow from overflow using the same extraction scheme on a pilot plant scale as had been used in the laboratory extractions, Fig. 2. A continuous extractor was to be built as the second extraction unit. Such experimentation as was necessary was to be conducted in connection with the design and construction of this continuous unit.

It was planned to remove the acorn shells in a commercial manner and to make a sufficient study of acorn shelling to demonstrate the relative amounts of meats and shells which could be expected.

All experiments were to be carried out in such a way as to make possible a comparison between the experimental results and those calculated by solvent extraction theory.

The continuous extractor was to be used to extract both acorn oil and cocoa butter so that a comparison might be made between the extractability of these two oils.

n-Butanol was selected as the solvent to be used in these pilot plant extractions. None of the usual oil extraction solvents such as methylene chloride or hexane were suitable for these extractions because of their volatility. Operation of the centrifuge created an air blast which would evaporate very considerable quantities of any volatile solvent. Toxic or flammable solvents would be too dangerous to use with the centrifuge or with the continuous extractor. n-Butanol is not very volatile, its vapor pressure is 4.3 mm. of mercury at 20°C. and 18.6 mm. at 40°C.; it would not be dangerous to use, its flash point is 35°C.; it is a satisfactory solvent for acorn oil, as was shown by experiment 7; and it could be obtained in the quantities required.

Suitable procedures were to be worked out for solvent recovery and production of crude acorn oil. It was planned to recover butanol from mixtures of acorn oil and butanol by vacuum distillation and to remove traces of solvent from the oil by vacuum steam distillation. Some of the crude acorn oil was to be refined as a matter of interest.

An acorn expeller run was planned to process 300 to 400 pounds of acorn meats in one of the Anderson Duo Expellers at Rockwood's plant.

The usual constants; specific gravity, index of refraction, acid number, saponification number and iodine number (WIj's); were to be determined on the different acorn oils produced.

Experiments on Continuous Extractors. Experimentation was necessary before a satisfactory continuous extractor could be constructed. The first such apparatus constructed consisted of a pyrex column four inches in inside diameter by three feet long. This column was mounted vertically between two steel plates supported in an angle iron frame. Connections were made to the column through these supporting plates in such a way that solvent was admitted to the bottom of the column and miscella was taken off at the top. Oil-bearing meal was fed in at the top, settled through the rising solvent and was collected in a container underneath the column. This container was connected to the column through a gate valve which could be closed while the container was emptied of liquid and settled solids. The meal settled so rapidly that most of the extraction took place in the container below the column.

The first pyrex column extractor was modified by the introduction of baffles to retard the fall of oil-bearing meal. These baffles were slotted disks cut from tin cans and mounted between spacers on an axial shaft supported by the upper column plate. The baffles did slow down the rate of solid's travel through the extractor but not sufficiently to give much extraction in the column. In addition to its poor performance as an extractor this apparatus had some other drawbacks.

It was difficult to balance solvent in and miscella out so as to maintain a constant liquid stream. The solvent inlet was governed by a valve. The miscella outlet was a siphon with a valve in the siphon leg. The arrangement for extracted solids discharge was awkward. This pyrex column extractor was abandoned.

The second continuous extractor was patterned as closely as possible after the one at Rockwood and Company.[15] It consisted of a twenty foot length of two inch pipe bent in the form of a U. A cut out was made on the top of the center of the bend. A short section of two inch pipe was carefully fitted to this hole and welded to the long section. This short pipe was threaded at the top to accommodate a flange fitting. The flange fitting was drilled to fit the flange for a two inch pyrex column, which was thus attached to the short pipe. The entire apparatus was mounted in a vertical position in a pipe frame support with the short pipe and pyrex column in the center parallel to the sides of the U. A drive sprocket wheel was installed above the ascending leg of the U; an idler wheel above the descending leg. A motor, speed reducer, drive chain and the sprocket wheels were supported on a metal table top above the extractor. A continuous chain formed of No. 45 malleable detachable links with C-1 flights every fourth link was installed in the U pipe.

Solids were fed to the bottom of the U through the pyrex column. Solvent was fed in on the ascending side of the chain. Miscella was drawn off above the solid level from the pyrex pipe. A sketch of this first model of the continuous extractor is presented in Fig. 7.

There was no difficulty in elevating sawdust fed to the chain through the center pipe and this material discharged readily at the top of the ascending leg. A test run was made with solvent and crushed cocoa expeller cake. The mechanical performance of the extractor was satisfactory for a short time, but in a little while the solids packed against the chain on the upsweep of the U and the chain jammed. No solid feed rate could be found which would prevent this jamming.

The design was modified by tipping the U so that the solids were not carried up such a steep slope. After functioning satisfactorily for a few minutes the chain jammed again and broke the shaft in the reducer. This speed reducer was a small one of the type used in the operation of flashing electric signs and was not very strong. The speed reducer was repaired and the extractor tipped still more--as much as possible on

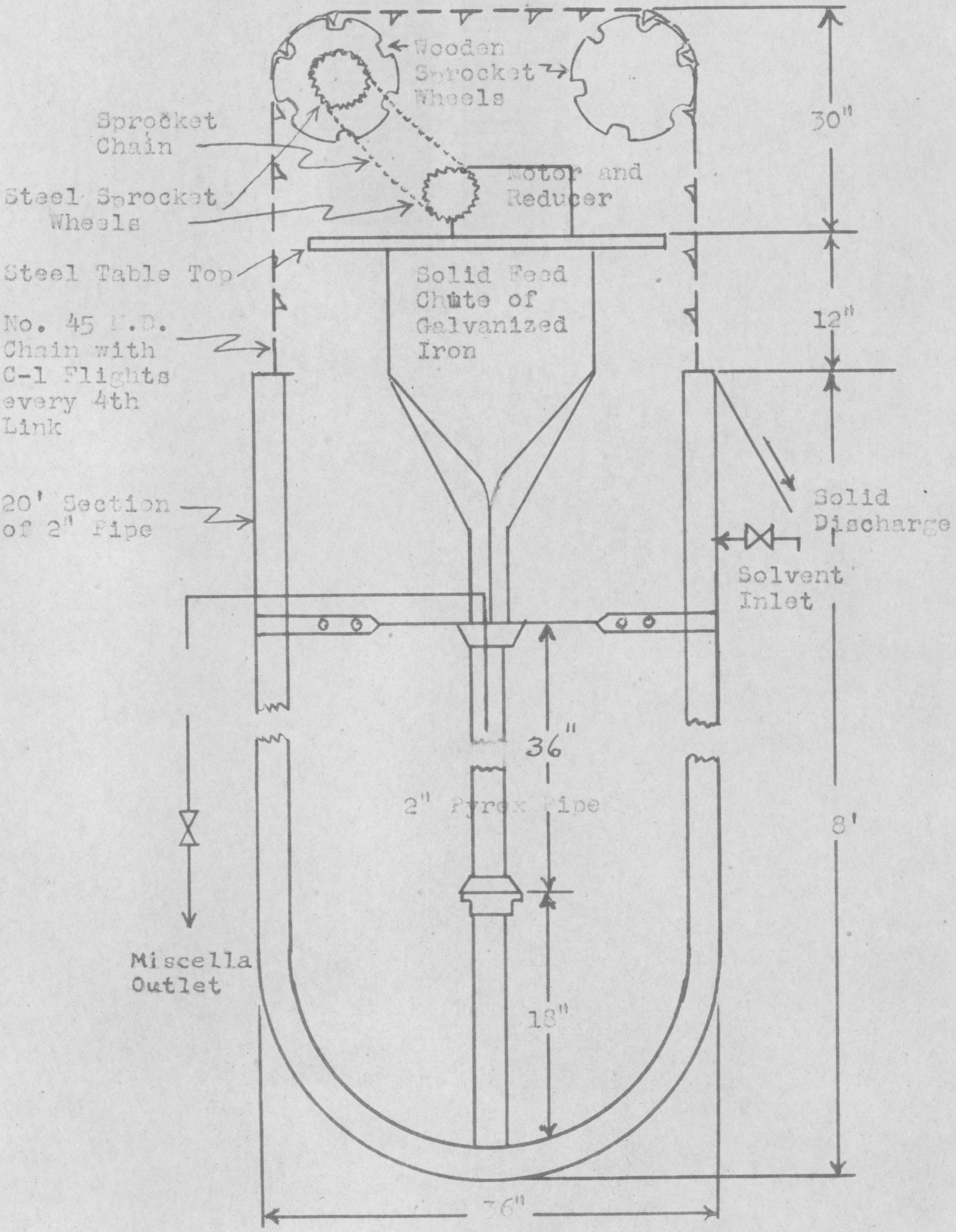


Figure 7.

The Continuous Extractor - First Model.

this pipe frame support. Each time the extractor was moved the supports for the sprocket wheels had to be changed and the motor drive readjusted. The ascending leg was now at an angle of about 50° with the horizontal plane. The performance of the extractor was not improved by this last change. The chain jammed as before and the speed reducer shaft was broken again. It was thought that a stronger drive might solve this problem. A much stronger speed reducer was procured and installed. This time the chain stuck as before but instead of breaking any part of the drive the extractor was lifted up with a man standing on it and the three-quarter inch pipe supports for the drive sprocket wheel were bent. The chain could not be pried out of the pipe with a heavy bar until the packed solids were flushed out of the pipe with water. Apparently this chain working in this duct will not elevate this type of feed through a very high angle.

The U shaped extractor was dismantled and considerably altered in design. One of the legs of the U was cut off and the other was unbent. This new extractor was mounted temporarily and tried out. The chain elevated the solids satisfactorily at this new low angle. Appreciable extraction took place. The mounting was made permanent and pilot plant extractions of acorn oil and of cocoa butter were made with this extractor.

Materials

Acorns. These were obtained from two sources: R. A. Morgen, Jr. of Gainesville, Florida; and C. F. Brown of the Anderson Hardware Company, Anderson, South Carolina. The Florida nuts were from the Live Oak, Quercus Virginiana, and a Scrub Oak, Quercus catesbaei. The South Carolina acorns were from the Spanish Oak, Red Oak and White Oak.

Alcohol, Ethyl Alcohol, pure 95%, U. S. Industrial Chemicals Corp.

Benzene, A.R., Thiophene free, Mallinckrodt Chem. Co.

n-Butanol, Normal Butyl Alcohol, Commercial Solvents Corp. This solvent had the following specifications:-

Specific Gravity: 0.810 to 0.813 at 20°C./20°C.

Distillation Range:

Below 115°C. .... none

Above 118°C. .... none

Flash Point: 35°C.

Iodine, A.R., Mallinckrodt Chem. Co.

Potassium Bichromate, A.R., Mallinckrodt Chem. Co.

Potassium Hydroxide, A.R., Mallinckrodt Chem. Co.

Potassium Iodide, A.R., Mallinckrodt Chem. Co.

Potassium Thiosulphate, A.R., Mallinckrodt Chem. Co.

Starch, Soluble, Potato, J. T. Baker Chem. Co.

Wij's Solution, J. T. Baker Chem. Co.

Apparatus.

Acorn Sheller. The first equipment required in processing the acorns for oil was some type of sheller. The one used in this investigation was built by the J. H. Lehman Company of New York for Rockwood and Company of Brooklyn, New York. It had been used to remove the shells from cocoa beans.

This apparatus is shown in Figs. 8 to 14. Fig. 8 is a view of the hull discharge side with the discharge port cover (a) in place. Fig. 9 shows the feed end; feed hopper (b), drive from the main shaft (c) to the crushing rolls (e). Fig. 10 shows the product discharge side with the fan housings (f) in place. In Fig. 11 the fan housings have been removed to show the fans (g). The motor (j), motor drive to main shaft (c) and the drive (k), main shaft (c) to fan shaft (i) are shown in Fig. 12. Fig. 13 and Fig. 14 are photographs of drawings of the sheller giving the major details of construction and the principle dimensions.

In operation of the sheller acorns of the correct size, less than one half inch in diameter, are placed in the feed hopper (b). The motor (j) is started and the component parts of the sheller revolve, the rolls (l) at about 70 r.p.m., the revolving screen (m) at 80 r.p.m., and the fans (g) at 1100 r.p.m.

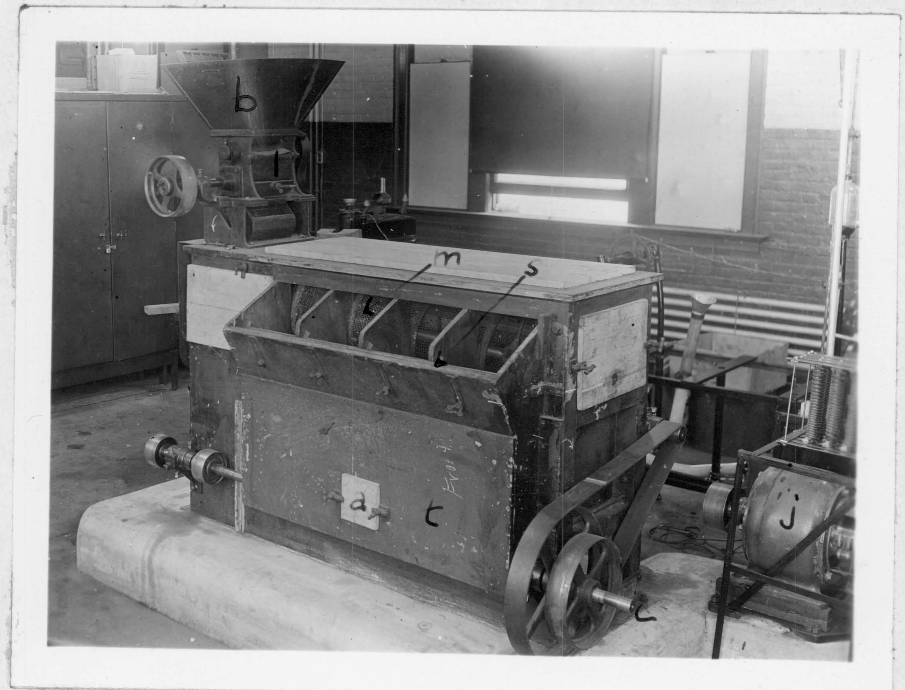


Figure 8

Acorn Sheller from the Hull Discharge Side.

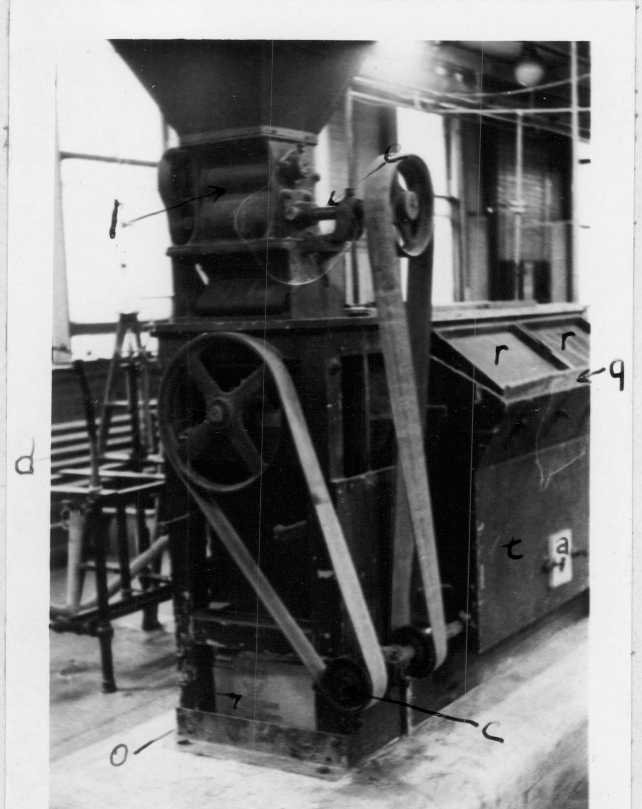


Figure 9

Acorn Sheller from the Feed End.

The acorns, crushed by the rolls, fall into the revolving screen (m). The screen has four different screen sections each about eleven inches long. The screens are approximately 3/32" mesh, 5/32" mesh, 1/4" mesh and 5/16" mesh. The fine material, mostly dust and hull fragments, passes through the finest screen and falls through an opening (n) at the bottom of the sheller. The box (o) placed to collect this material can be seen in Fig. 9 and Fig. 10. Material of the larger sizes moves down the trommel and all but the oversize falls through one or another of the screens. All material but that through the 3/32" screen falls on inclined decks (p) each sloping toward a fan (g) with an air blast from that fan at its lower end blowing up the slope. The heavy meat fragments travel down the slope against the air blast and are discharged into boxes (h) placed beneath the lower ends of the chutes. The lighter shell fragments are blown up the slope to strike against an inclined baffle (q) at the upper end of the chute. The baffles are shown raised in Fig. 9. In order to keep down the amount of dust sent out into the room by the sheller, screens were placed across the air discharge ports (r). These screens are in place in Fig. 9.

After striking the baffles the light material drops down into space (s) between the outside sheathing of

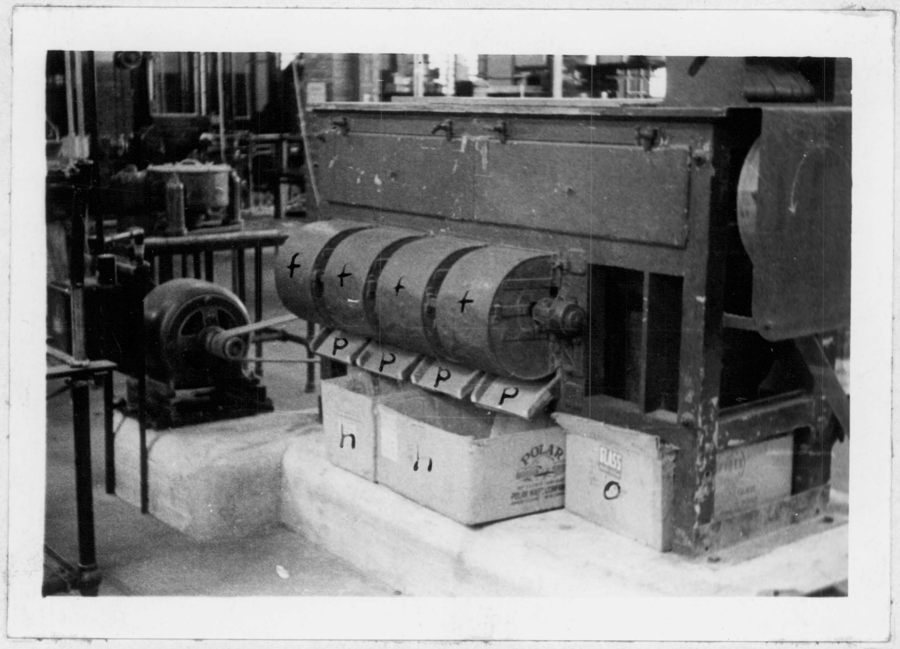


Figure 10

Acorn Sheller from the Product Discharge Side.

Figure 11

View of the Acorn Sheller Showing the Fans.

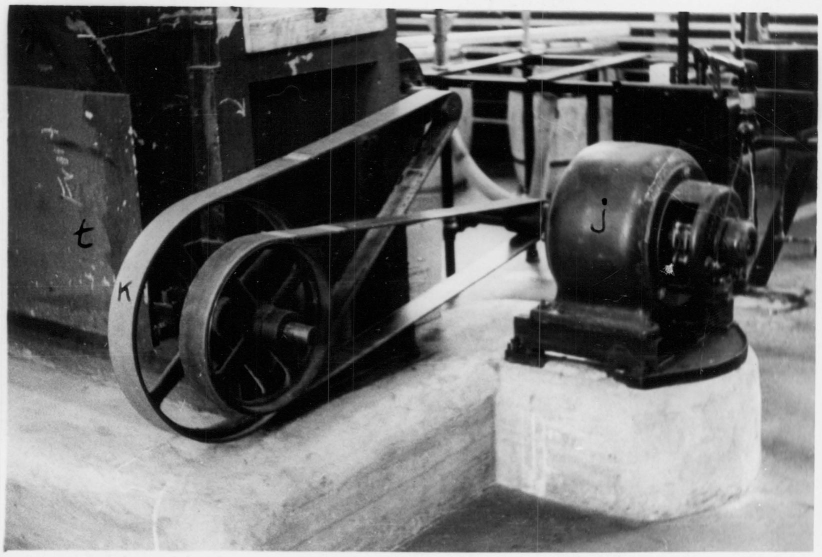


Figure 12

Motor and Drive to the Main Shaft and the Fan Shaft of the Acorn Sheller.

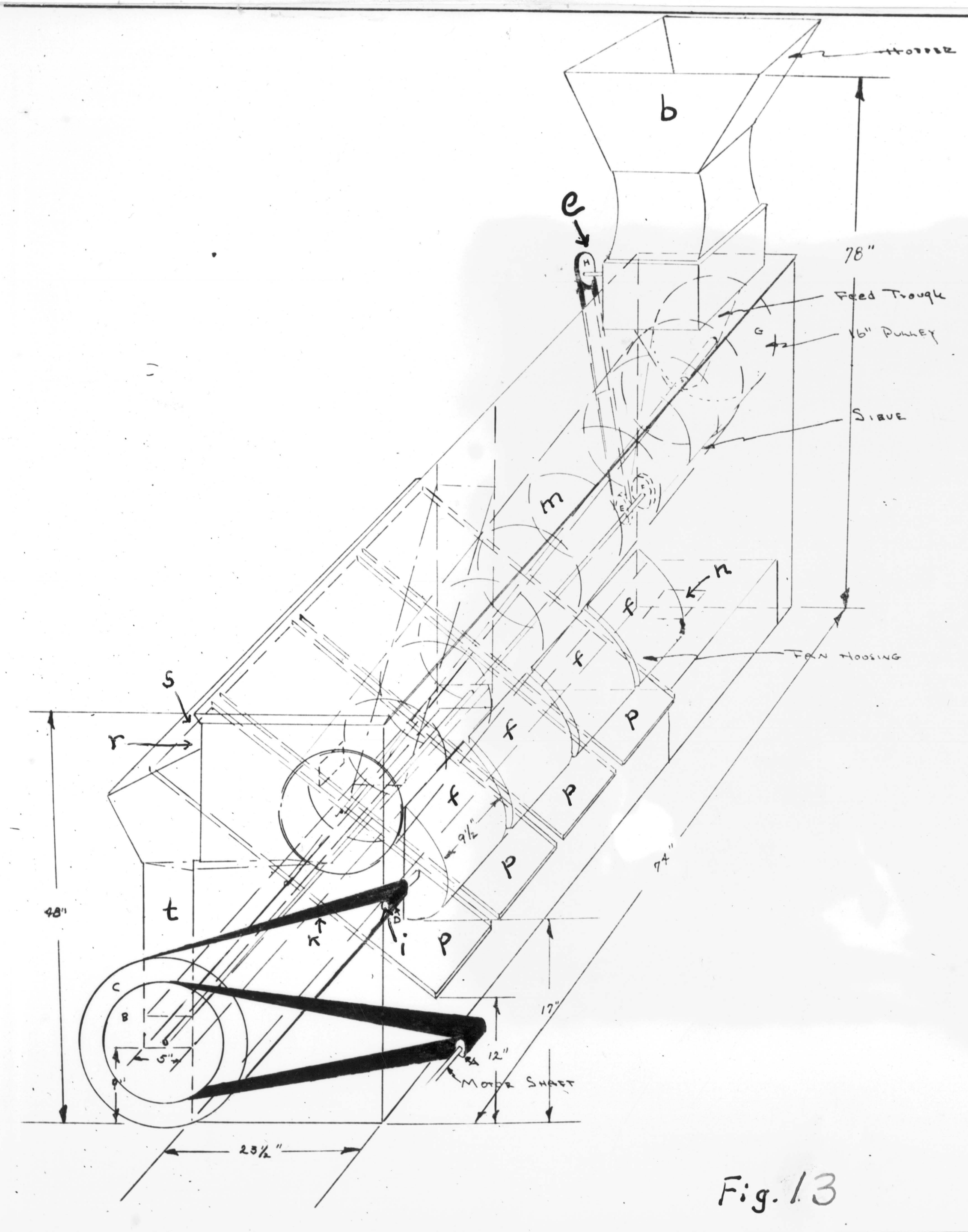


Fig. 13

Isometric Sketch of

Acorn Sheller

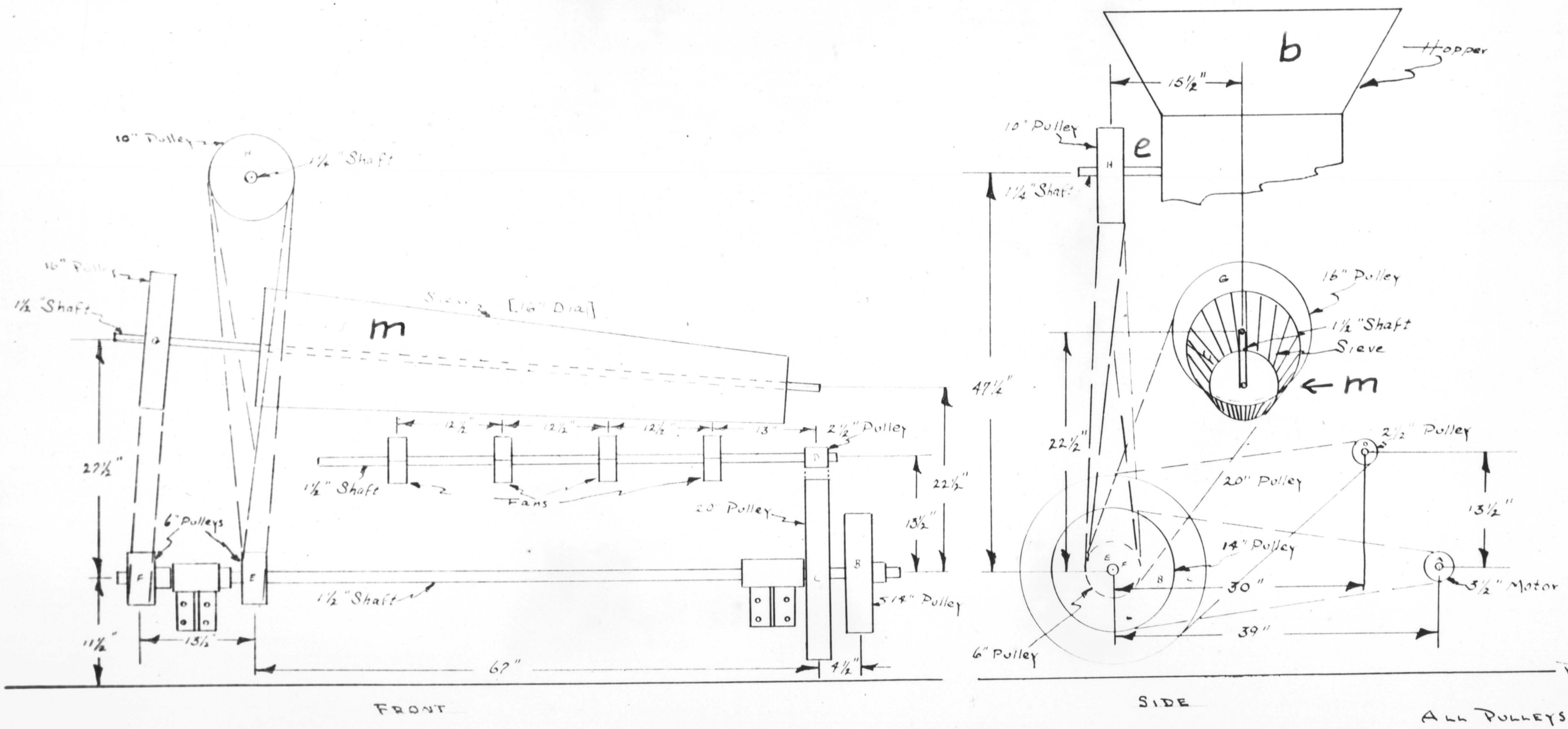
in

Chem. Eng. Lab.

Ch. E. 7-8

ACORN in SHELLER

Chem. Eng. Lab.



ALL PULLEYS WITH 3" WIDTH

——— INDICATES BELTING.

SCALE 3/32" = 1"

See Isometric Sketch

Figure 14.

the machine and the inclined decks. This space (s) is shown in Fig. 13. The dead space (s) is the top of the hull collector (t) which is a narrow box along the hull discharge side of the sheller. It shows in Figs. 8, 9, and 13. The bottom of this box slopes on both sides to the shell discharge opening (a), the cover of which appears as a light square of unpainted wood about the center of the side in Fig. 8. As operation continues shells build up in this collector and are removed as necessary to keep the shell bin (t) from filling up.

The screen sized product is collected in boxes (h) on the fan side of the machine. The oversize is cleaned of dust and fine particles, but often contains large pieces of meat still adhering to shell. This material was sometimes re-run through the sheller until a shell free product was obtained. The rolls on this apparatus are not adjustable and it was found that the best practice was to crush this oversize in another roll mill before passing it back through the winnower and fanner, (this type of sheller is known as a winnower and fanner).

Rolls. The roll mill, which was used to crack acorns, to crush expeller cake and acorn fragments is illustrated in Fig. 15. It is a two roller mill manufactured by the Sturtevant Mill Company of Boston, Mass., number TR 32.

Air Separator. A Raymond Laboratory Mechanical Air Separator, serial number 41344, was used to separate acorn shells from acorn meats. This separator was made by the same company as the hammer mill. It is shown in Fig.16.

Oil Expeller. This machine was used at Rockwood and Company, Brooklyn, N. Y. It was employed to expel acorn oil and to provide an expeller cake for extraction study. The equipment in Rockwood's plant is an older model of the Anderson Duo Expeller as described in the October, 1940 bulletin, "The Anderson Duo Expeller", of the V. D. Anderson Company, Cleveland, Ohio.

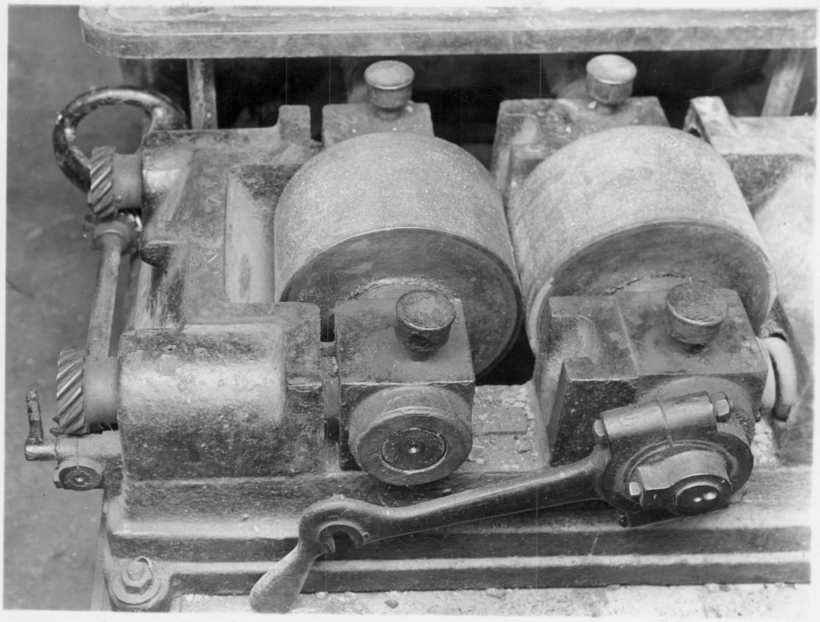


Figure 15

Roll Mill with the Cover Removed to Show the Two Rolls.

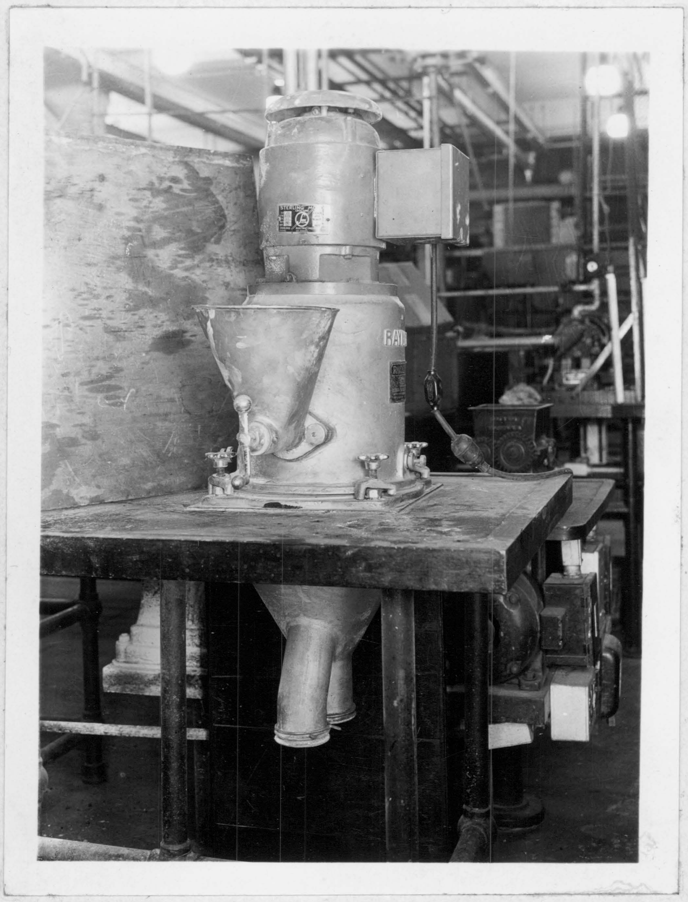


Figure 16

The Raymond Laboratory Air Separator.

Continuous Extractor. The continuous extractor, the evolution of which was described on pages 54 - 58 loc. cit., is illustrated by Figs. 17 to 23. Fig. 17 and Fig. 18, are views of the extractor lengthwise from either end. In Fig. 19, the Jeffrey-Traylor Feeder (F) is in position. Fig. 20, shows the details of the drive--motor to cone pulley shaft, belt to another cone pulley, second cone pulley to a reducer work, reducer worm to gear wheel, gear wheel to sprocket wheel bolted to it, sprocket wheel to sprocket chain, chain to second sprocket wheel. The second sprocket wheel is bolted to the large chain drive wheel (D).

The construction and operation of this extractor can best be explained by the figures and the following:-

Key to the Illustrations of the Continuous Extractor.

Key Letter	Item
A	Five gallon drum.
B	Two liter aspirator bottle.
C	Length, 28-3/4 feet, No. 45 malleable detachable chain with No. 45 C-1 flights every fourth link.
D	10 inch, 18 toothed, sprocket wheel for No. 45 M.D. chain.
E	Rotameter, size No. 1. Schutte-Koerting, Philadelphia, Pa. Rotameter No. 386025.
F	Jeffrey-Traylor No. 1-B Feeder, No. 5582; Jeffrey Mfg. Co., Columbus, Ohio.

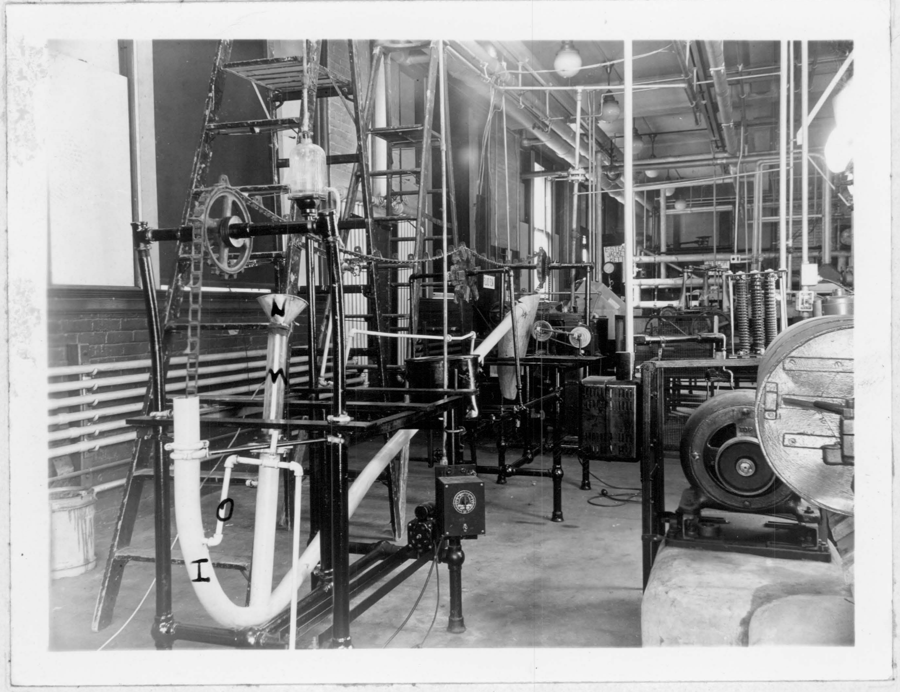


Figure 17

The Chain Extractor from the Miscella Discharge End.

Key to the Illustrations of the Continuous Extractor, (continued).

Key Letter	Item
G	Eastern Centrifugal Pump, Model D-10, with fittings for 1/4 inch pipe. Eastern Mfg. Co., New Haven, Conn.
H	1/6 horsepower motor, geared to a reducer so that the output speed is 16 2/3 r.p.m.
I	2 inch std. galv. steel pipe.
J	Jeffrey regulator for vibratory feeder.
K	5, 4, 3, 2 inch four step cone pulley.
L	100:1 worm gear speed reducer.
M	14 inch section of 2 inch pyrex pipe.
N	Solid feed inlet.
O	Miscella outlet.
P	Solvent inlet.
Q	Extracted solids discharge.
S	A 20 inch section of 2 inch pipe welded to I. This is called the silo.

Other Items

6	1/4 inch globe valves.
3	1/4 inch floor flanges.
2	Steel laboratory table frames.
28	feet of 1/4 inch galv. steel pipe.
13	1/4 inch elbows.
4	1/4 unions.
2	1/2 inch pitch, 1/8 inch width sprocket wheels, one is 5 inches in diameter with 32 teeth, the other is 6 inches in diameter with 34 teeth.
1	54 inch length of 1/2 inch pitch sprocket chain.

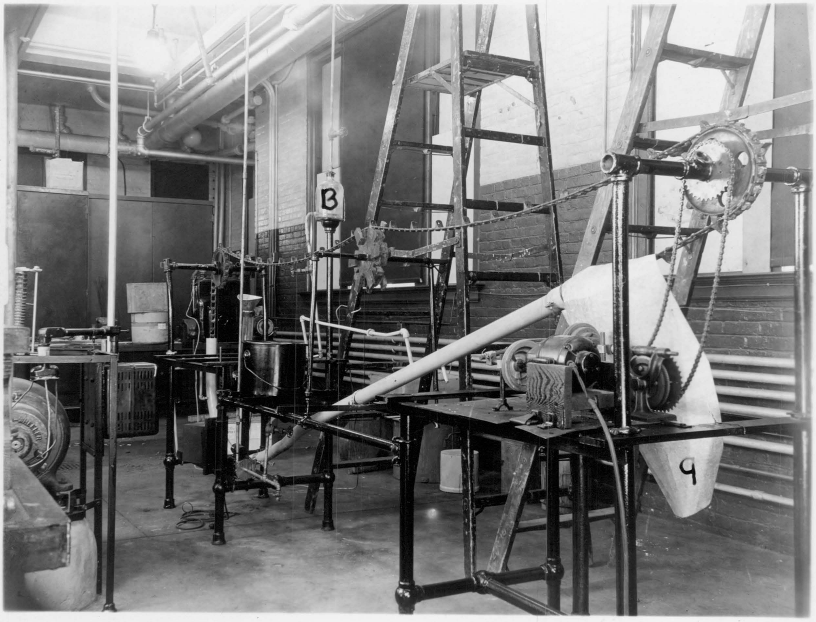


Figure 18

The Chain Extractor from the Raffinate Discharge End.

Continuous Extractor. Operation. The operation of this unit was as follows:- The lower of the two five gallon drums (A) was filled with solvent. This solvent was pumped up to the upper five gallon drum (A) and allowed to run by gravity into the extractor, entering at (P).. The flow was controlled according to the reading of the rotameter (E). The two liter leveling bottle (B) was installed above the rotameter (E) in order that the flow might be measured without interrupting operation. A liter was carefully marked on this bottle and during each run the rotameter reading was checked against this measured liter. At the beginning of a run the system was filled with solvent until liquid overflowed from the miscella outlet (O).

Solid was fed in from the Jeffrey-Traylor Feeder (F), either with the chain at the end of the extractor, (N in Fig. 21, or at the top of the silo, N in Fig. 17 and in Fig. 19), falling through liquid to the chain at the bottom of the bend. The chain picked up the solid at the bottom of the bend and carried it up the slope against a counterflow of fresh solvent from (P). Above (O) the solids were drained until they were carried out of the extractor duct. The chain ran almost horizontally from the end of the duct (I) to the chain drive wheel (D) so that most of the extracted material fell from the chain on to the discharge apron,

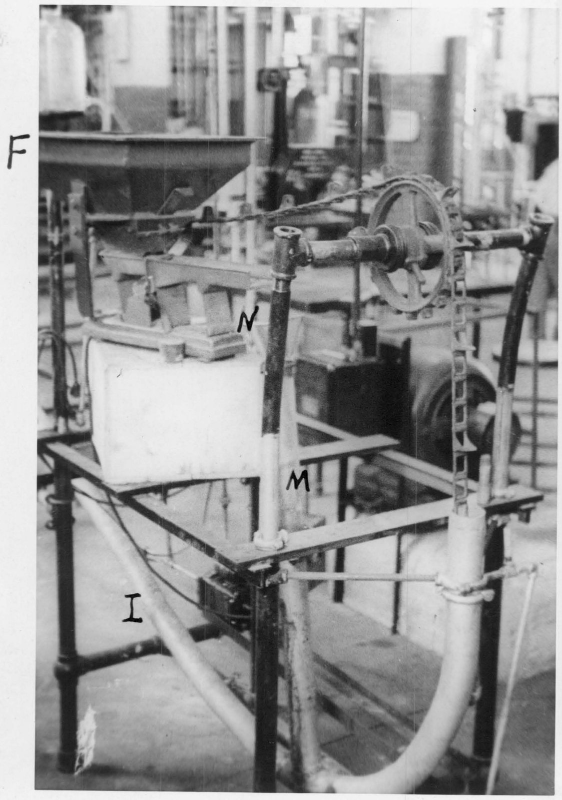


Figure 19

The Chain Extractor - Feed to Silo with Feeder in Place.

(q in Figs. 18, 20, 21), and was directed by this apron to a pail below it. Such material as adhered to the chain was brushed off with a test tube brush.

Miscella was withdrawn, either from near the top of the silo, (O in Fig. 21), or from near the top of the bend into which the chain was running, (O in Fig. 17). In the experiments designated as Series I feed and miscella take-off were as shown in Fig. 21. In the experiments under Series II the feed was in with the chain, at (N) in Fig. 21, with miscella taken off near the top of the silo at (O). The Series III experiments had solid feed to the top of the silo at (N) and miscella take-off at (O) as shown in Figs. 17 and 19.

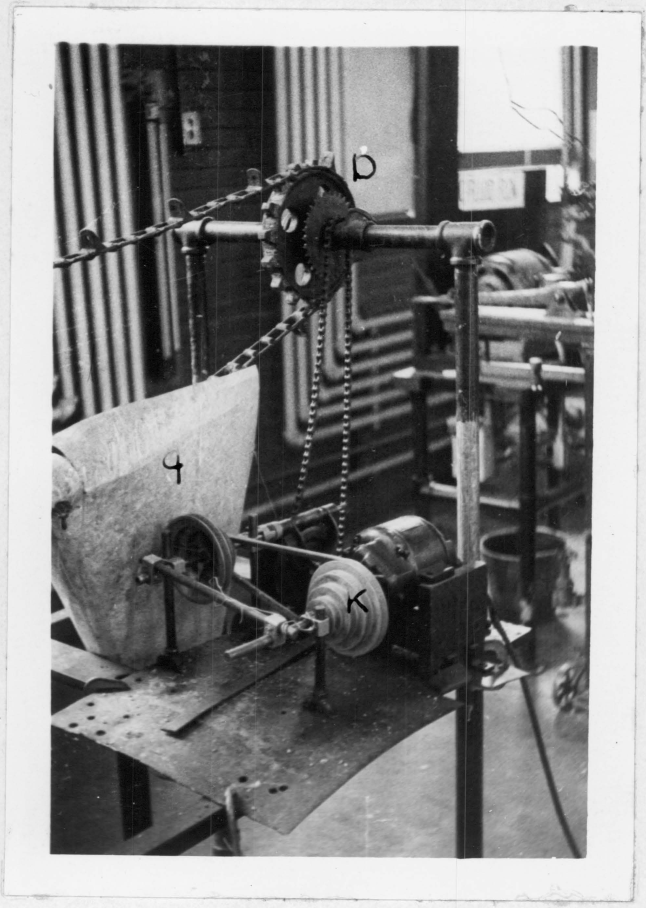


Figure 20

The Chain Extractor, Close-up of Chain Drive.

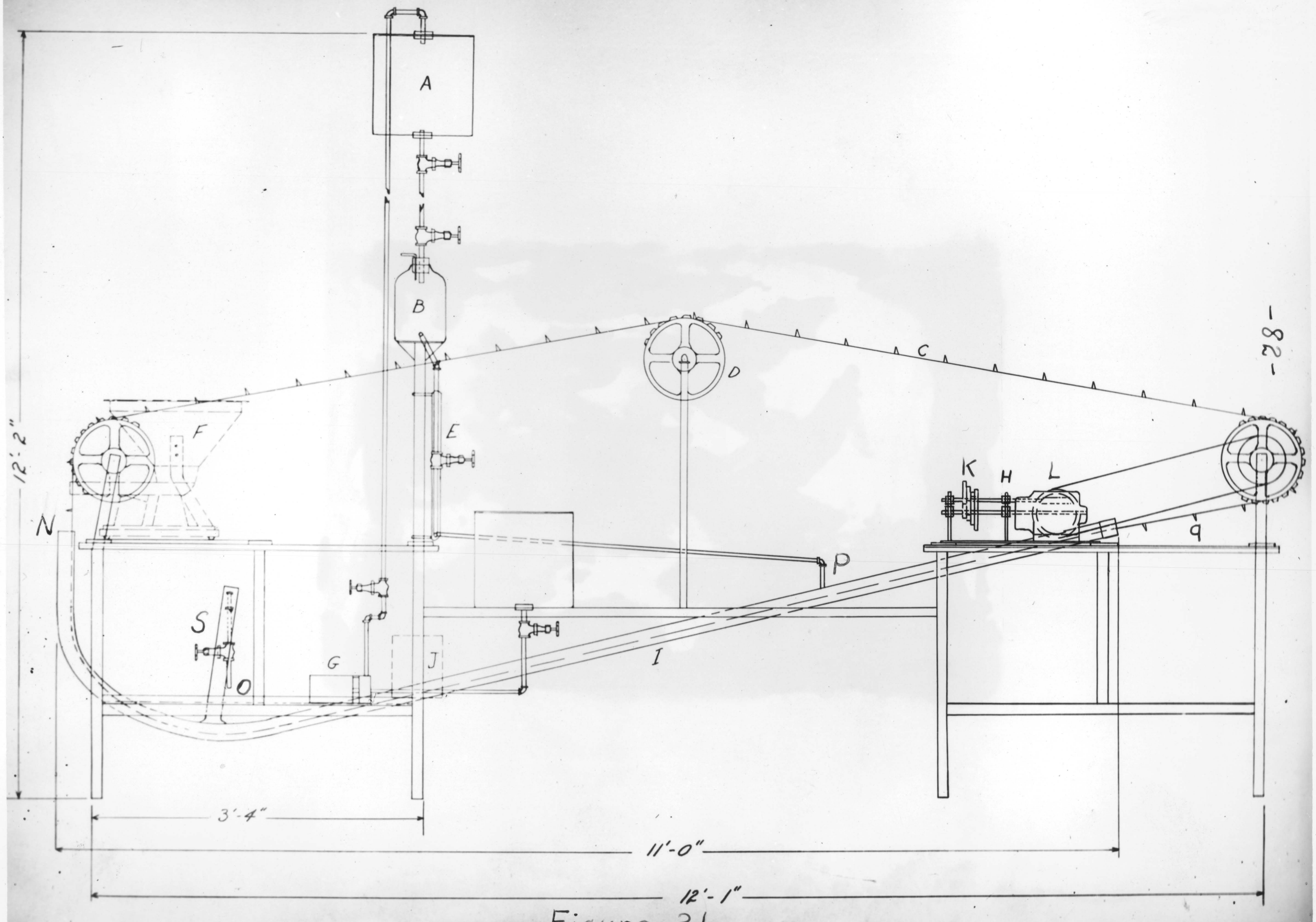


Figure 21.
Side View of Extractor

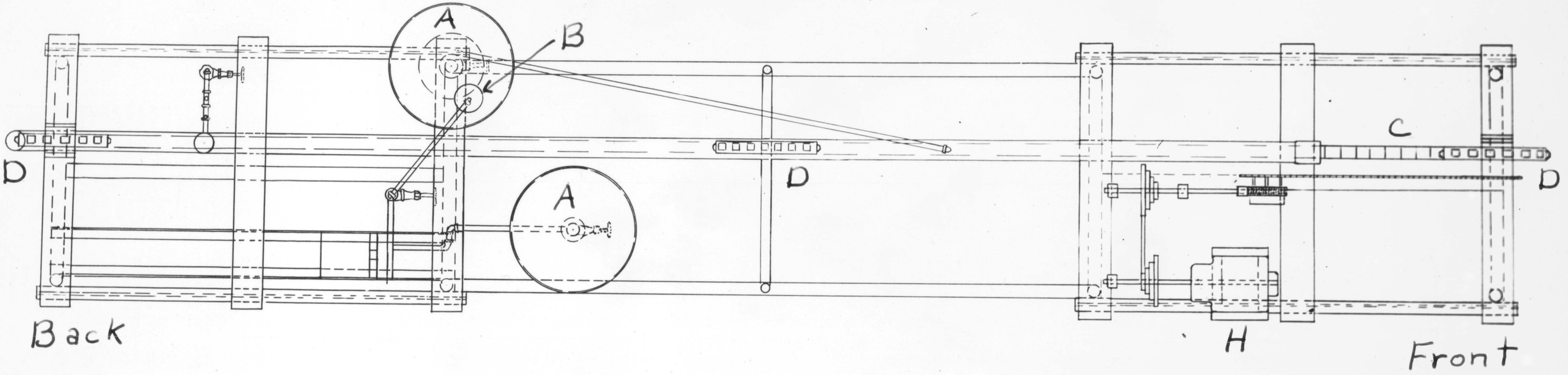
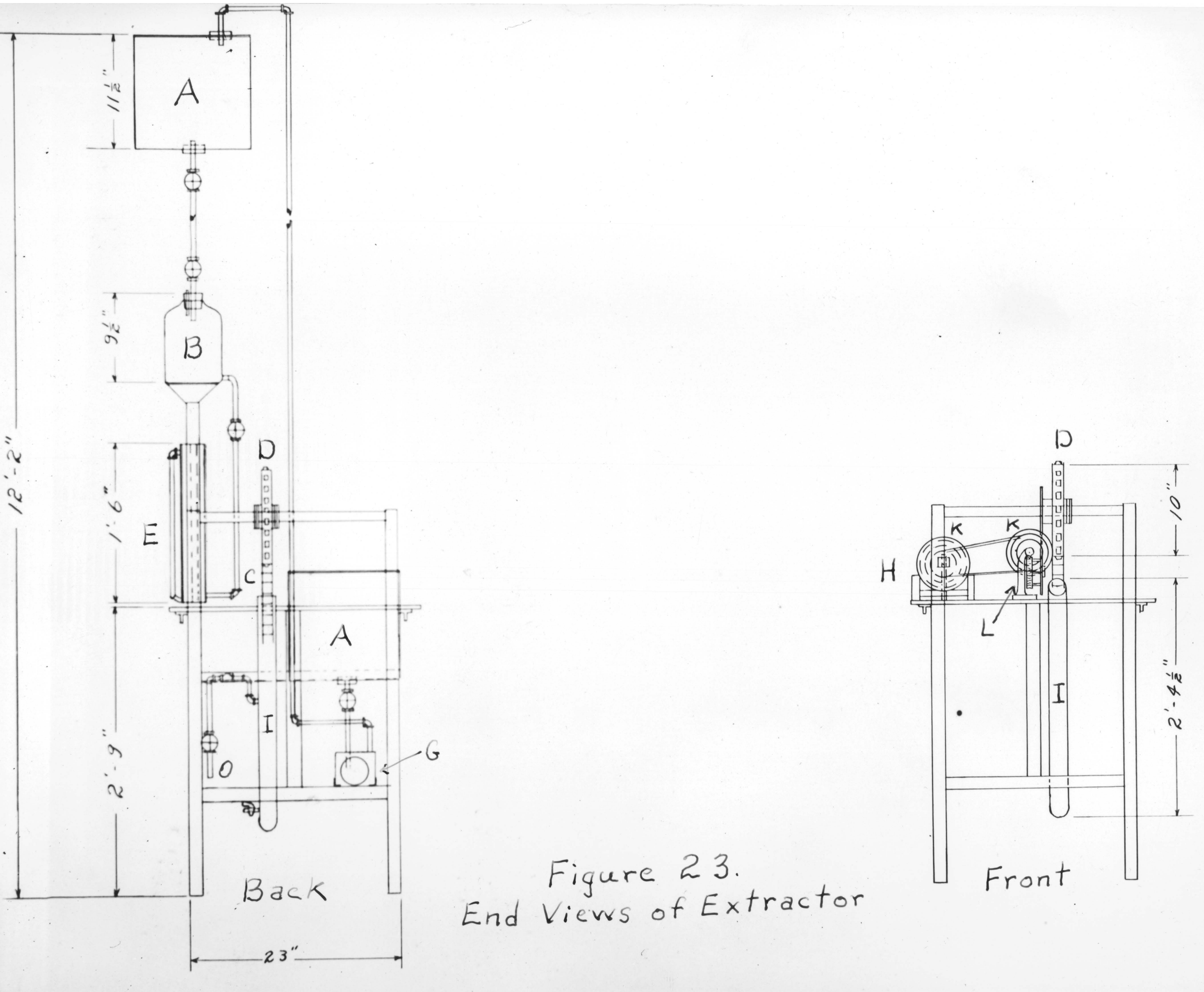


Figure 22
Top View of Extractor



Back

Front

Figure 23.
End Views of Extractor

Centrifuge. The centrifuge extractions were made with a Tolhurst Centrifugal, Serial No. T-7893; 12 inch basket; basket speed 2100 r.p.m.; the Tolhurst Centrifugal Division, American Machine and Metals Company, East Moline, Illinois. The machine appears in Fig. 24.

Ball Mill Jars. Porcelain ball mill jars of one gallon capacity similar to Eimer and Amend's No. 8-390 were used to mix solvent and solid in the centrifuge extractions.

Jar Mill. The porcelain jars were rotated in a double motor driven jar mill similar to the one furnished by Paul O. Abbe Inc.

Still. A steam jacketed vacuum still was used to recover solvent from the miscellas. This was a complete unit including condenser and vacuum receiver. It was made by the F. J. Stokes Machine Company of Philadelphia, Pa. and is their number 84260. This still was piped so that steam could be blown into the charge. This equipment is shown on the left in Fig. 25.

Vacuum Dryer. Solvent was recovered from the raffinate in a J. P. Devine Company's No. 1468 Vacuum Dryer. This dryer appears to the right of the vacuum still in Fig. 25.

Figure 24

The Tolhurst Centrifugal.

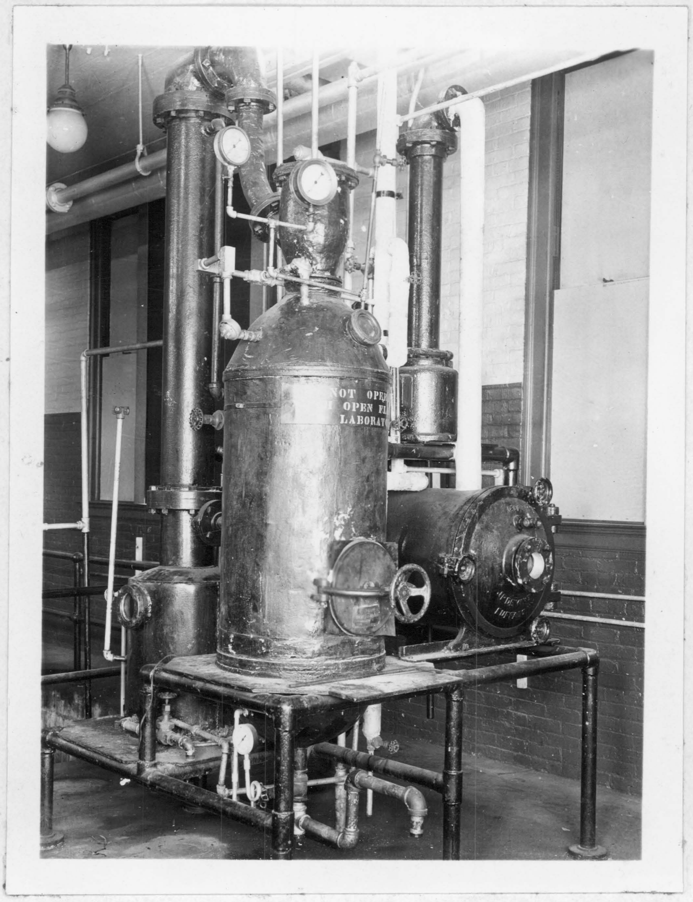


Figure 25

The Steam Jacketed Vacuum Still

and

Vacuum Dryer.

Vacuum Pump. The still and dryer are both connected to the same vacuum pump which was supplied by the Stokes Company with the still. They are also connected with a Kinney Manufacturing Company's VSD, 5x5, High Vacuum Pump. The Stokes pump was customarily used with this equipment, but during a period in which it was out of commission the Kinney pump took its place.

Procedure

Preparation of Material for Extraction. The first step in the preparation of acorns for most of the experimentation was sorting. There is a great variation in the oil content of the acorn meats depending on the condition of the nuts. Kinney[35] analysed sprouted nuts and found no oil in them. The oil content of wormy nuts depends on the extent of worm damage. Sound nuts were found to contain 36.0 to 40.0 per cent oil as determined by soxhlet analysis with n-butanol.

Sorting 140 pounds of the acorns of Quercus catesbaei from Gainesville, Florida gave: 104.4 pounds, (74.6 per cent), sound nuts; 10.8 pounds, (7.7 per cent), sprouted nuts; and 24.8 pounds, (17.7 per cent), wormy nuts. Sorting 78.75 pounds of acorns from the White, Red and Spanish Oak from Anderson, South Carolina gave: 32.4 pounds, (41.2 per cent) sound nuts; 21.5 pounds, (27.3 per cent), sprouted nuts; and 24.8 pounds, (31.5 per cent), wormy nuts.

The second step in the experimental procedure was the removal of the acorn shells. This was done by hand, (if the quantity of material required was not large), by crushing the nuts in the rolls and separating meat from hull in the air separator, or by passing the nuts through the acorn sheller. The acorns processed in the sheller were not sorted.

The acorn meats obtained by removing the shells were in large fragments which could not be penetrated by solvent. In order to prepare a feed which could be penetrated by solvent the shelled meats were either ground in the Raymond Mill, Fig. 1, to produce acorn meal of which 83.2 per cent passed through a standard 35 mesh sieve and two per cent was retained by an 8 mesh sieve, or taken to Rockwood and Company and run through one of their Anderson Duo Expellers to produce an acorn expeller cake. This expeller cake was crushed in the two roll mill and screened in the revolving screen of the acorn sheller to produce material retained by a 1/8 inch mesh screen and passed by a 1/4 inch mesh screen.

Expelling Acorn Oil. Mr. W. T. Clarke, Chief Chemist of Rockwood and Company, made arrangements for an experimental acorn run at his company's plant. The acorn meats, 366.5 pounds, produced by shelling acorns in the winnower and fanner were run through an Anderson Duo Expeller. There was material enough for a 65 minute run and 8.0 pounds of acorn oil were produced along with 355 pounds of acorn expeller cake.

The expeller feed was analysed by soxhlet extraction with Skellysolve A and the expeller cake was analysed similarly. The feed contained 13.25 per cent acorn oil while the cake showed a content of 11.0 per cent of this same oil. A material balance over the expelling operation, based on these analyses, shows a loss of 1.2 pounds of acorn oil in this operation.

There were:

366.5x0.1325=48.6 pounds of oil in the feed

366.5 - 48.6=317.9 pounds of inert material in the feed

and,

317.9x0.11/0.89=39.4 pounds of oil in the expeller cake

or,

48.6 - 39.4=9.2 pounds of oil were expelled.

There were 8.0 pounds of oil collected, so that:

9.2 - 8.0=1.2 pounds of oil lost in this operation.

The data on production of acorn meal is given in the quantitative flow sheet, Fig. 25, Preparation of Acorn Meal.

Fig. 26, Preparation of Acorn Expeller Cake, is a quantitative flow sheet of the operations employed in the production of this type of solvent extractor feed.

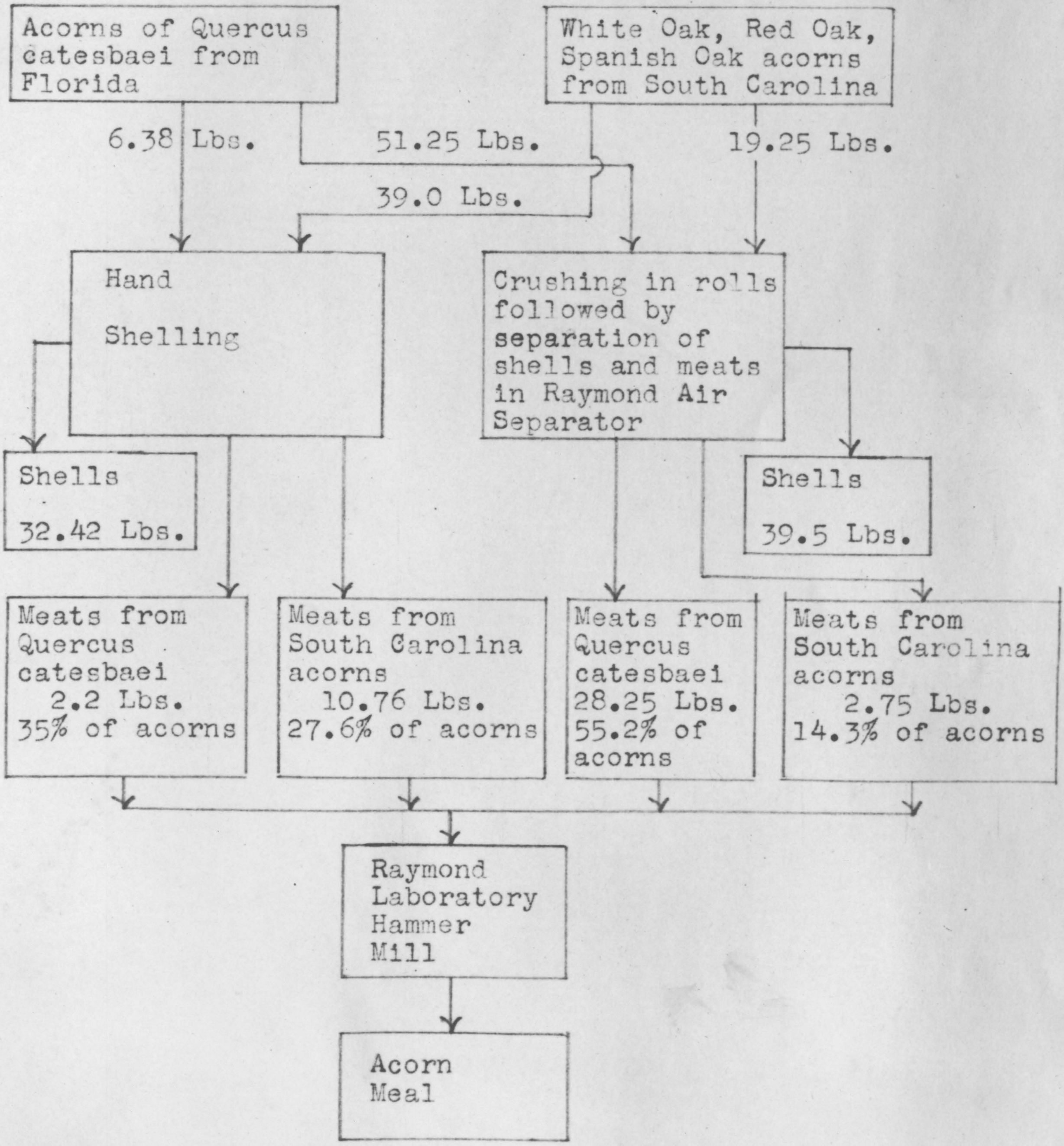


Figure 26.

Preparation of Acorn Meal.

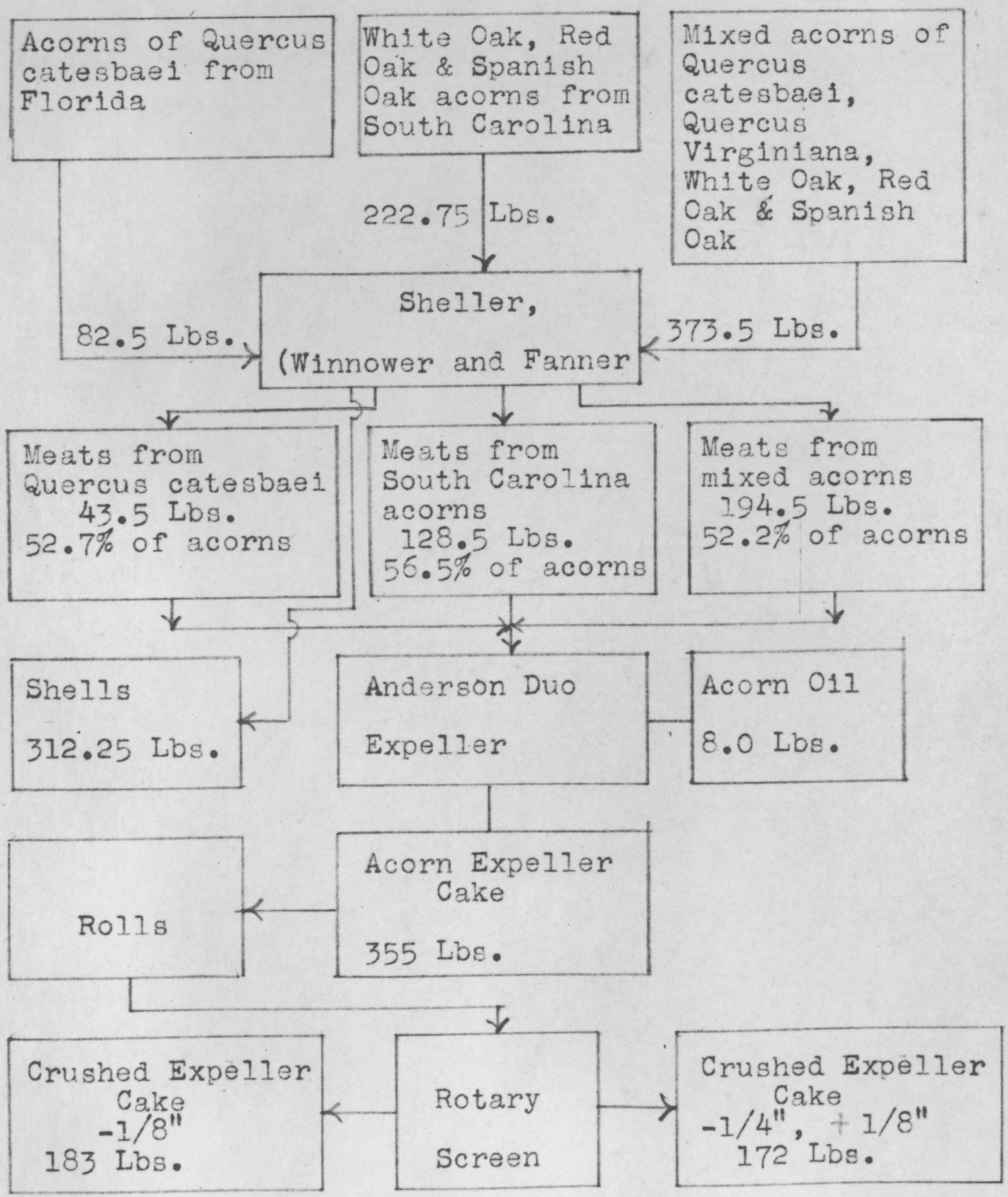


Figure 27.

Preparation of Acorn Expeller Cake.

Pilot Plant Extractions Using a Centrifuge. The extraction scheme was the same as that shown in Fig. 2, page 34, loc. cit. Feed and solvent, or underflow and intermediate liquor were placed in an empty ball-mill jar and rotated in the ball mill for over an hour in experiments 8 and 9, or for half an hour in experiment 10. A flow diagram for a three stage centrifuge extraction is given as Fig. 28.

After mixing the requisite length of time the contents of the jar were transferred to the basket of the centrifuge which had been lined with a piece of filter cloth. Liquid and solid were separated by centrifuging until the flow of liquid from the centrifuge was negligible. Both streams were weighed before being passed on to the next stage or out of the system.

Experimental Conditions. The experimental conditions for this group of experiments are given in Table IX, Experimental Conditions for Centrifuge Extractions.

Extraction Data. The extraction data for these experiments is presented in the quantitative flow sheets, Figs. 29, 30, and 31.

Results of Centrifuge Extractions. The results of these experiments are tabulated in Table X, Results of Centrifuge Extractions.

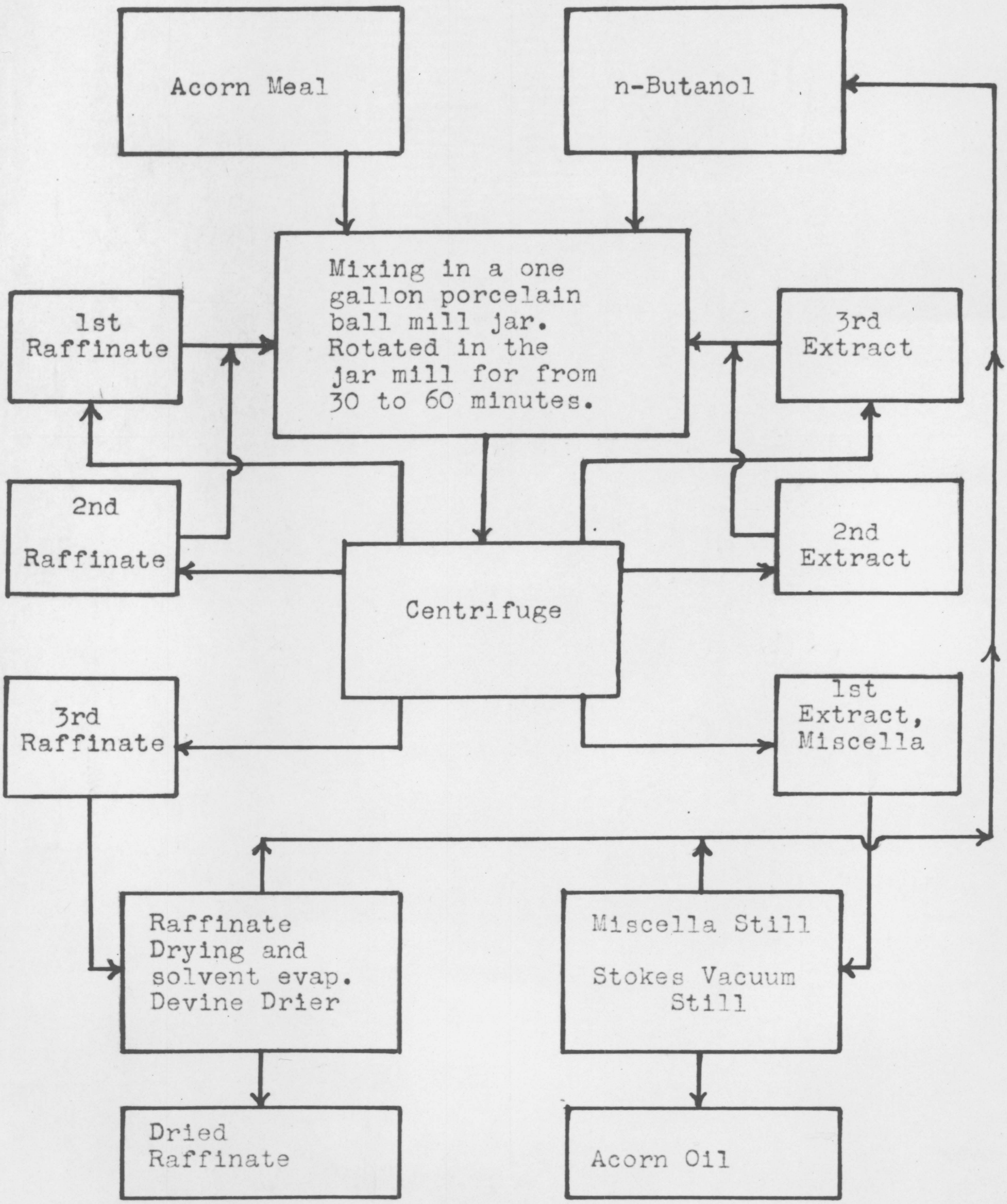


Figure 28.

Flow Diagram of a Three Stage Centrifuge Extraction.

TABLE IX.

Experimental Conditions for Centrifuge Extractions.

Experiment number	8	9	10
System	inert, acorn oil, butanol	inert, acorn oil, butanol	inert, acorn oil, butanol
No. of stages	3	2	2
No. of cycles	3	3	3
Temp., °C.	25	25	25
Extraction time, hours	1.0	1.0	0.5
Feed:-			
Weight, Lbs.	2.0	2.0	4.0
Solute, Per cent	40.0	36.0	38.6
Inert, Per cent	60.0	64.0	61.4
Solvent:-			
Weight, Lbs.	4.0	4.0	4.0
Solvent, Per cent	100	100	100
J, Mixture of feed and solvent:-			
Solute, Per cent	13.33	12.00	19.3
Solvent, Per cent	66.67	66.67	50.0
Inert, Per cent	20.00	21.33	30.7
Miscella, Lbs.	3.81	3.28	4.07
Weight ratio, solvent to feed	2.0	2.0	1.0

TABLE X.

Results of Centrifuge Extractions

Experiment number	8	9	10
Solute in miscella, experimental, Per cent	18.63	18.4	28.6
Miscella, weight, Lbs.	3.44	3.5	3.94
Oil in miscella, Lbs. oil extracted	0.64	0.65	1.13
Oil in feed, Lbs.	0.80	0.72	1.54
Oil experimentally extracted, Per cent	80.0	89.5	73.0
Solute in miscella, theoretical, Per cent	22.10	19.3	36.0
Oil theoretically extracted, Per cent	95.0	93.7	92.2
Difference between per cent experimentally extracted and per cent theoretically extracted	15.0	4.2	19.2
Difference, Per cent, (Difference divided by per cent oil theoretically extracted)	15.8	4.5	20.8

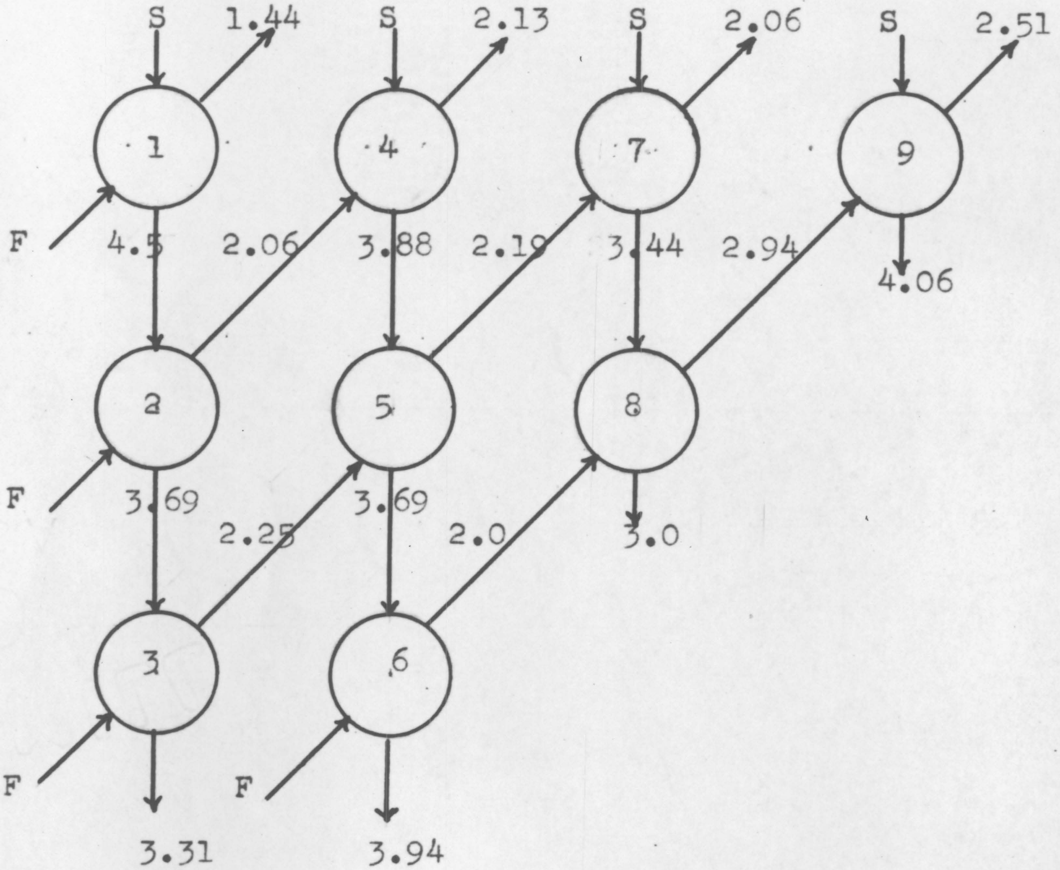


Figure 29.

Quantitative Flow Diagram of 1st Centrifuge Extraction, Experiment Number 8.

F = 2.0 lb. acorn meal. S = 4.0 lb. n-butanol.

All figures are pounds. Overflows are vertical lines. Underflows are diagonal lines. M-6 (miscella) is 18.63 per cent acorn oil. M-8 (intermediate liquor) is 5.80 per cent acorn oil. M-9 (intermediate liquor) is 1.54 per cent acorn oil.

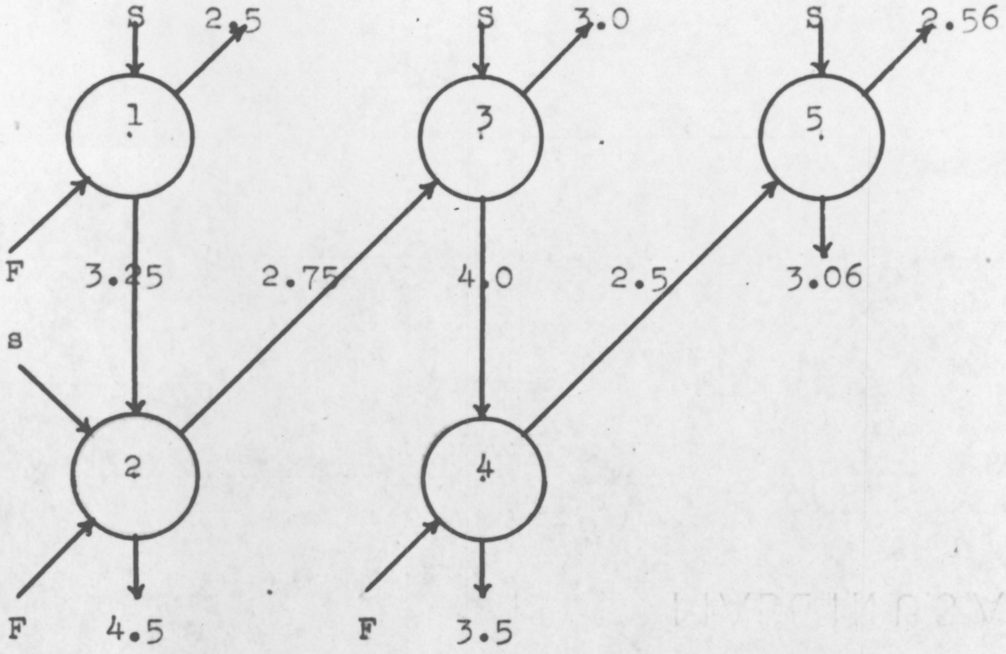


Figure 30.

Quantitative Flow Diagram of 2nd Centrifuge Extraction.
Experiment Number 9.

F = 2.0 lb. acorn meal. S = 4.0 lb. n-butanol.

Overflows, miscellas, are vertical lines. Underflows, raffinates, are diagonal lines. All figures are pounds. s = 1.0 lb. n-butanol added to make up for solvent evaporated in centrifuging the material from the 1st stage. M-4 (miscella) is 18.4 per cent acorn oil. M-5 (intermediate liquor) is 4.1 per cent acorn oil.

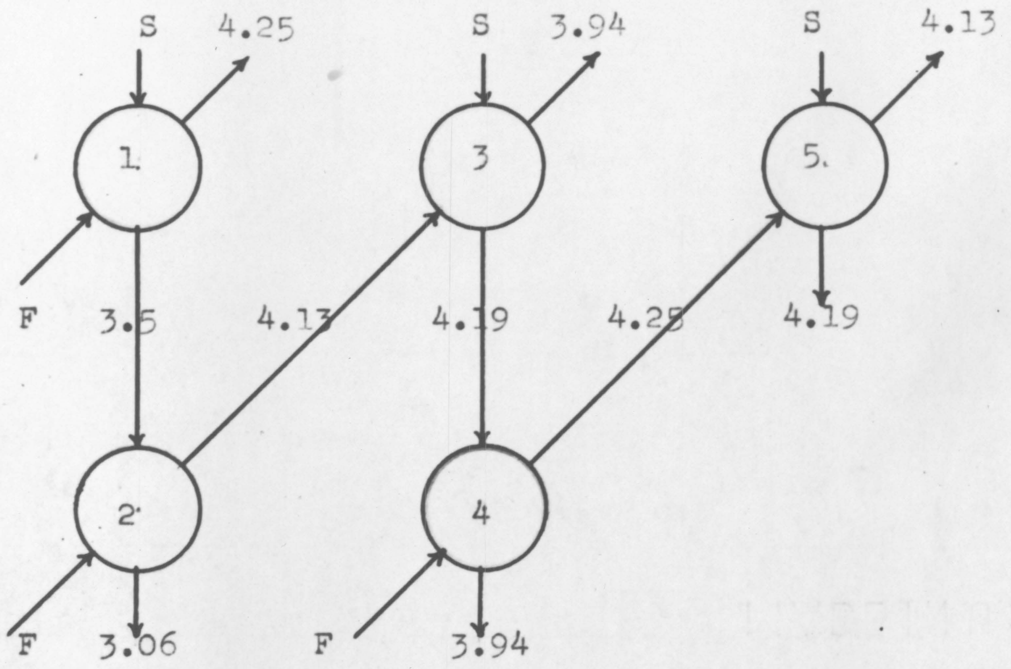


Figure 31.

Quantitative Flow Diagram of 3rd Centrifuge Extraction.
Experiment 10.

F = 4.0 lb. acorn meal. S = 4.0 lb. n_butanol.

M-4 (miscella) is 28.6 per cent acorn oil.

M-5 (intermediate liquor) is 12.7 per cent acorn oil.

Overflows, miscellas, are vertical lines. Underflows, raffinates, are diagonal lines. All figures are pounds.

Analytical. The feeds were analysed by soxhlet extraction with n-butanol. Solutions of acorn oil and butanol were analysed by distilling the solvent from a weighed sample in a tared distilling flask and drying the residue to constant weight at 135° C. Raffinates were analysed by evaporating solvent from a weighed sample to constant weight at 135°C. and soxhlet extraction with n-butanol of a weighed sample of this dried raffinate.

Theoretical Underflow. The theoretical underflow, or xx line, was calculated in the same way as before in experiment 7, pages 44-46, loc. cit. Theoretical underflows are given in Table XI, Theoretical Underflows in the Centrifuge Extractions.

Calculations. The graphical calculations led to the theoretical extractions given in Table X. These constructions were made in a manner identical with the illustration given with experiment 7. The calculations of actual and theoretical extraction in these experiments were based on the oil content of the miscella rather than on the amount of unextracted oil. The method of calculation is indicated in Table X.

Pilot Plant Extractions with the Continuous Extractor. Three series of experiments were conducted with the continuous extractor. As has been described under the operation of this extractor, pages 78-80 loc. cit., the manner of feeding this unit and taking miscella from it was different in each of these series. Series I were extractions of cocoa expeller cake with n-butanol; Series II, acorn meal with n-butanol; Series III, acorn expeller cake with n-butanol.

Extraction Procedure. The extractor was operated for one hour before taking any data in order that equilibrium might be established between the inlet and outlet streams. During this time liquid and solid feed were adjusted so that material was neither building up in the extractor nor being withdrawn faster than it was being added. After equilibrium had been attained samples and data were taken for the length of the continuous run. The experimental conditions for these experiments are given in Table XII, Experimental Conditions for the Continuous Extractions. The weight of solvent fed was controlled by the rotameter reading and measured by means of the calibrated bottle. The rate of solid fed was regulated by the speed controller of the Jeffrey-Traylor Feeder. Solid was added to the hopper of this feeder a quarter of a pound at a time so that the rate

TABLE XII.

Experimental Conditions for the Continuous Extractions.

Experiment	Series	Feed	Length of run, Minutes	Solvent fed, Lbs.	Solid fed, Lbs.	Raffinate removed, Lbs.	Miscella out, Lbs.
I	I	Crushed cocoa expeller cake	120	8.0	4.0	8.4	4.4
2			120	8.0	4.0	6.3	6.3
3			30	4.0	2.0	2.7	2.4
4	II	acorn meal	60	4.0	2.0	3.6	1.5
5			210	16.2	7.0	14.7	8.4
6			120	10.5	4.0	6.7	6.3
7			120	8.6	4.0	7.6	3.3
8			120	5.3	4.0	7.7	3.1
9	III	crushed acorn expeller cake	20	2.4	0.9	1.3	1.8
10			120	7.2	4.6	6.4	5.8
11			90	4.0	4.0	3.4	4.1

of feed could be checked during the run. The raffinate was collected in a pail on a scale and weighings were made every 15 minutes. The miscella was collected in gallon jugs, also on a scale, and weighings of this stream were likewise made at 15 minute intervals.

The experimental conditions were checked by a material balance. This material balance is given in Table XIII, Material Balances on the Continuous Extractions.

Analytical Procedure. There was a considerable amount of fine inert material carried over with the miscella in the Series I and Series II experiments, but not in those of Series III. This fine material was filtered out of a weighed sample of the miscella through a tared filter paper. The paper was dried to constant weight at 135°C. and the per cent of fine material in the miscella thus determined.

Another weighed sample of the miscella was distilled from a tared distilling flask. The residue was dried to constant weight at 135°C. and reported as oil plus fine material, (oil only in the Series III experiments).

The composition of the miscella was calculated from these two determinations. Miscella compositions are given in Table XIV, Analytical Data for the Continuous Extractions.

TABLE XIII.

Material Balances on the Continuous Extractions.

Experiment	(1) Material in, feed & solvent, Lbs.	(2) Material out, raffinate & miscella, Lbs.	(3) Difference, (1) - (2), Lbs.	(4) Difference, Per cent
1	12.0	12.8	-0.8	6.7
2	12.0	12.6	-0.6	5.0
3	6.0	5.1	0.9	15.0
4	6.0	5.1	0.9	15.0
5	23.2	23.1	0.1	0.4
6	14.5	13.0	1.5	10.3
7	12.6	10.9	1.7	13.5
8	9.3	10.8	-1.5	16.1
9	3.3	3.1	0.2	6.1
10	11.8	12.2	-0.4	3.4
11	8.0	7.5	0.5	6.3

Per cent difference is (3)/(1)x100.

TABLE XIV.

Analytical Data for the Continuous Extractions.

Experiment	Solute in feed, Per cent	Inert in miscella, Per cent	Solute in miscella, Per cent
1	11.5	1.27	4.33
2	11.5	0.79	3.34
3	11.5	2.18	3.88
4	38.6	1.01	8.7
5	38.6	1.30	13.4
6	38.6	2.91	8.7
7	38.6	3.01	9.6
8	38.6	2.2	11.2
9	17.8	-	5.4
10	17.8	-	9.4
11	17.8	-	12.3

The feed was analysed by soxhlet extraction with n-butanol and the compositions of the feeds are included in Table XIV.

Calculations. The experimental per cent extracted was calculated from the feed and the miscella. Graphical calculations of the amount of theoretical extraction showed less than one theoretical stage in this extractor so that a much simpler calculation was employed for this set of experiments. This calculation is illustrated with the data from Experiment 10.

Specimen Calculation. Theoretical Extraction in One Stage. In Experiment 10:- There were 7.16 pounds of solvent fed plus 0.82 pounds of oil, (in solid feed), equal to 7.98 pounds of total liquid into the system. There were 5.84 pounds of miscella removed so that 5.84/7.98 is approximately the fraction of the oil which was extracted. The precise fraction would be the volume of liquid in the miscella divided by the volume of liquid entering the extractor. There is little difference in these two fractions, however, and the simpler approximate calculation is used for these experiments.

Results of Continuous Extractions. The results of these continuous extractions are presented in

Table XV, Results of Continuous Extractions. Experimental extraction is compared in this table with theoretical extraction in one stage. Pounds oil extracted is pounds liquid removed, from Table XII, times per cent oil in miscella, from Table XIV. Pounds oil in feed is per cent solute in feed, from Table XIV, times pounds feed, from Table XII. Per cent oil experimentally extracted is pounds oil extracted divided by pounds oil in feed times 100. Pounds liquid into system equals pounds oil in feed plus pounds solvent fed. Theoretical per cent oil extracted equals pounds miscella divided by pounds liquid into system times 100.

Per cent of oil experimentally extracted is plotted against solvent-solid feed ratio in Fig. 32 for the extractions of acorn meal and acorn expeller cake. Increasing the amount of solvent relative to the feed increased the extraction of oil from the acorn meal, which would generally be expected. An increase in the solvent-feed ratio, however, decreased the extraction of oil from the acorn expeller cake, which is contrary to general expectation. The solvent-solid ratio does not take into account other factors in extraction, particularly the ratio of liquid to solid in the underflow. Solvent extraction theory takes account of both these factors, solvent-solid ratio and liquid-solid

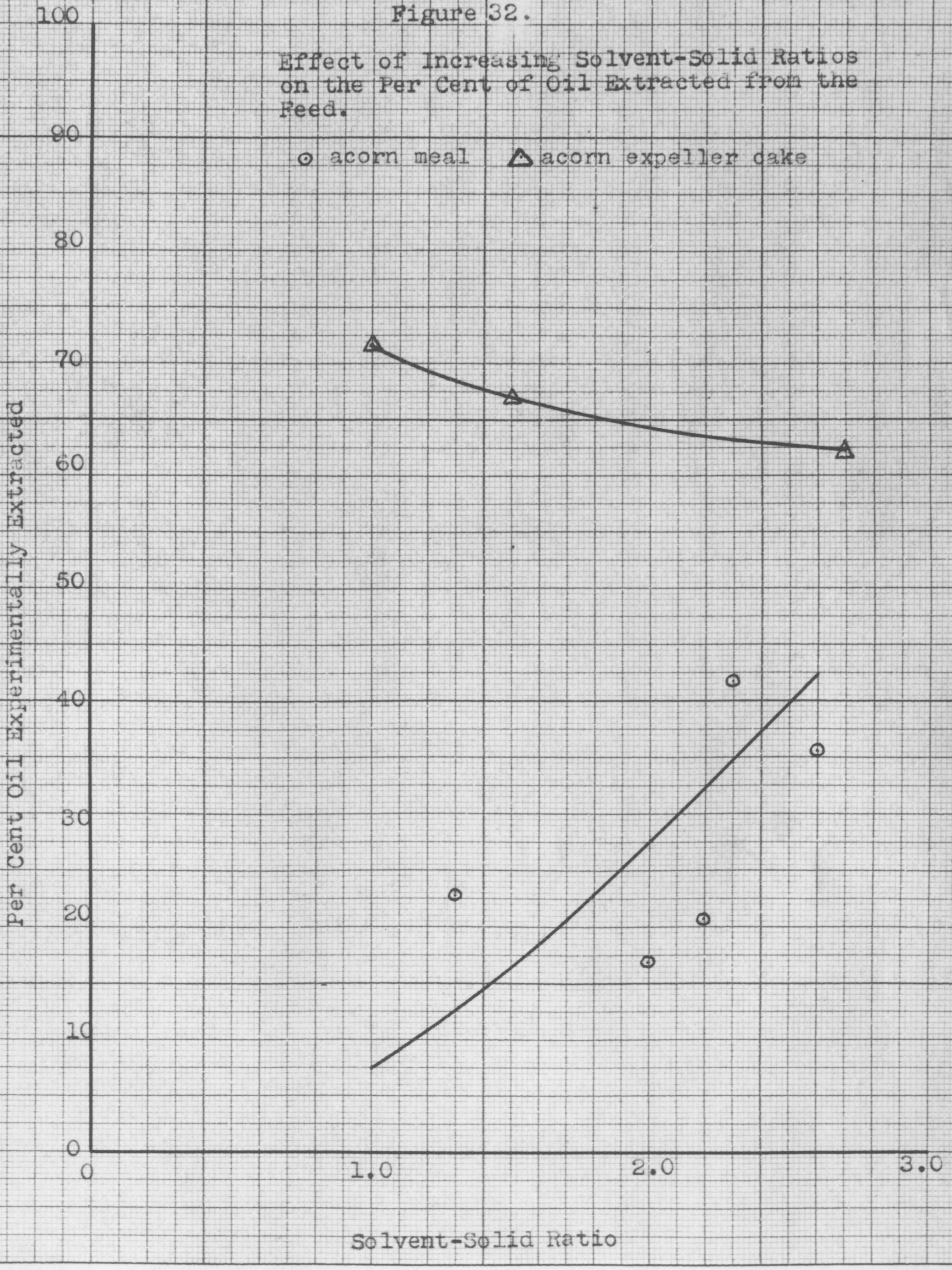
TABLE XV.

Results of the Continuous Extractions.

Experiment	Oil extracted, Lbs.	Oil in feed, Lbs.	Oil experimentally extracted, Per cent	Liquid into system, Lbs.	Oil extracted, theoretical, Per cent	Ratio, solvent to feed
1	0.19	0.46	41.3	8.46	52.0	2.0
2	0.21	0.46	45.6	8.46	74.5	2.0
3	0.09	0.23	39.2	4.23	57.8	2.0
4	0.13	0.77	16.9	4.77	31.5	2.0
5	1.13	2.70	41.8	18.90	44.5	2.3
6	0.55	1.54	35.8	12.04	52.2	2.6
7	0.32	1.54	20.8	10.14	32.5	2.2
8	0.35	1.54	22.8	6.84	45.4	1.3
9	0.10	0.16	62.3	2.56	70.3	2.7
10	0.55	0.82	67.0	8.02	72.3	1.5
11	0.51	0.71	71.8	4.71	87.0	1.0

Figure 32.

Effect of Increasing Solvent-Solid Ratios on the Per Cent of Oil Extracted from the Feed.



ratio in the underflow. The per cent oil experimentally extracted in all these experiments is plotted against the theoretical extraction to be expected with one ideal stage in Fig. 33, Comparison between Experimental and Theoretical Extraction. Fig. 33 shows that solvent extraction theory indicates the extraction trend much more accurately than does the solvent-feed ratio.

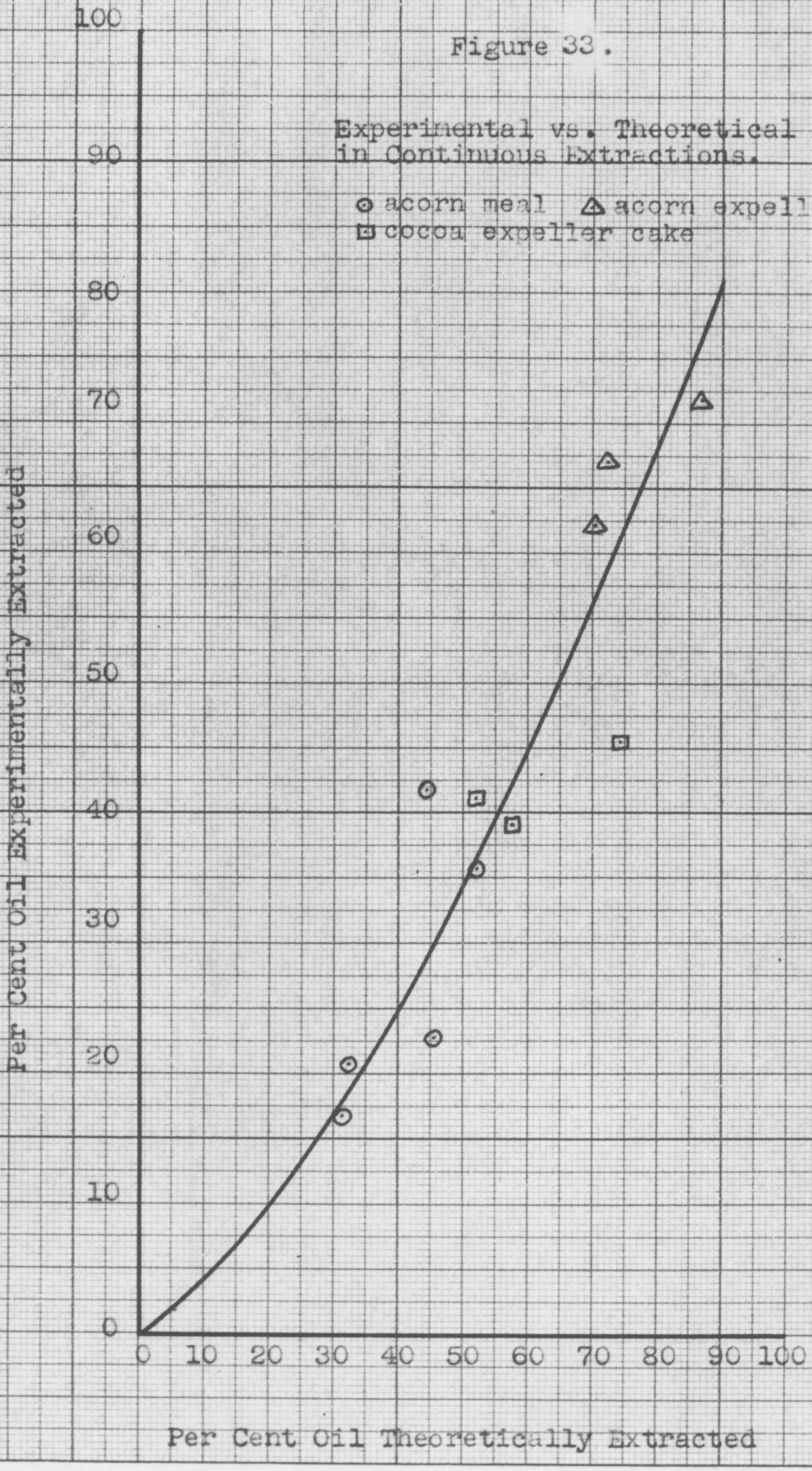


Figure 33.

Experimental vs. Theoretical Extraction in Continuous Extractions.

Solvent Recovery. Acorn oil-butanol mixtures from the various extractions were allowed to accumulate until at least five gallons of this material was on hand. The mixture was charged into the batch still of Fig. 25 and butanol was distilled under vacuum. This solvent was re-used for extraction. The residue in the still was steam distilled for 15 to 30 minutes to remove traces of solvent. The gate valve at the bottom of the still was then opened to discharge crude acorn oil and water into a bucket placed beneath it. The still was steamed out until no more oil appeared in the discharge.

Purifying Crude Acorn Oil. This crude acorn oil contained solid material and much of it was emulsified with water. It was allowed to stand until two distinct layers separated. The upper of these layers, the oil layer, was washed free of solid material and tannins in a large separatory funnel. When the lower layer was no longer dark in color washing was stopped. The upper layer was collected as crude water washed butanol extract.

A rough test was made to refine some of this water washed butanol extract. 425 grams of it were mixed with 139 ml. of 0.242 N-NaOH and treated according to the procedure for refining cottonseed oil. 262 grams of refined oil were obtained. No attempt was made to recover oil from the foots.

TABLE XVI

The Constants of Acorn Oils Produced by Pilot Plant Operations.

Sample	Specific gravity at 25°C.	Index of refraction at 25°C.	Acid number	Saponification number	Iodine number (Wij's)
First oil collected in expelling oil from mixed acorns, Filtered	0.903	1.4676	30.8	191	111
Last oil collected in expelling oil from mixed acorns, Decanted	0.907	1.4669	29.5	192	105
Water washed butanol extract from Quercus catesbaei	0.907	1.4677	5.60	190	106
Refined butanol extract from Quercus catesbaei	0.903	1.4684	2.6	188	107

IV. DISCUSSION

Introduction. Discussion of the work of this thesis logically divides into two sections; the first concerned with the extraction of oil from acorns; the second dealing with the development and use of solvent extraction theory. This discussion is therefore divided into two parts as follows:

A. Solvent Extraction of Oil from Acorns.

B. The Development and Use of Solvent Extraction Theory.

The purpose of the work discussed in the first section was the practical one of producing acorn oil; involving collecting acorns, preparing them for extraction, extracting the oil, recovering solvent and obtaining acorn oil from solvent-oil mixtures.

The philosophy of solvent extraction theory underlying Elgin's graphical method for calculation of leaching operations was not changed but the method of applying that philosophy to solvent extraction was modified to such an extent that it is desirable to discuss this theory in detail. The second discussion section develops solvent extraction theory as it was applied to the experimental extractions. The use of this theory is illustrated by sample calculations and by discussion of the experimental data presented in this thesis.

A. SOLVENT EXTRACTION OF OIL FROM ACORNS

The possibility of using acorns for food has often been discussed in the literature, but, except in times of scarcity of other foods, acorns have been utilized only by wild animals or by semi-domestic pigs. There are some references to the possible uses of acorn oil, but there is no record of any large scale work with this material. This investigation is concerned with handling a quantity of acorns, 847 pounds, to disclose what particular problems there are in processing this material for oil; to demonstrate a practical method of obtaining acorn oil; and to relate solvent extraction theory to experimental extractions.

There are three general methods for obtaining oil from oleaginous seeds; pressing, squeezing the oil from the oil-bearing seeds by applying a pressure to this material in a hydraulic press; expelling, again pressure but in this operation applied to the material by forcing it through a narrowing slotted barrel by means of a screw, (the oil flows out through the slots in the barrel); solvent extraction, dissolving the oil from the material in a suitable solvent, separating the solids from the oil-bearing solvent, miscella, and recovering the oil by distillation of the solvent from the oil in the miscella.

Solvent extraction was selected as the most promising method for obtaining oil from acorns since it can be applied to any oil-bearing material no matter what its oil content.

Acorns. One of the purposes of this thesis was to determine what type of material could be obtained by offering a price for acorns. Inquiries showed that three cents a pound would be sufficient inducement to produce a supply of acorns adequate for experimental purposes. The Boy Scouts of Gainesville, Florida and the Anderson Hardware Company of Anderson, South Carolina were the only two suppliers who collected acorns at this figure. There were 361 pounds of acorns sent from Florida and 485.5 pounds from South Carolina. Acorns were ordered from Arkansas, Virginia and New York State, but none were received from these localities.

It is the author's opinion, based on his attempts to get acorns and on his personal observation, that acorns are seldom as abundant as popularly supposed and that gathering them in quantity is not easy.

The nuts which were supplied were of poor quality. The best lot obtained, the Scrub Oak acorns from Florida, consisted of 75 per cent of sound nuts and 25 per cent of acorns which were either wormy or sprouted. The quantity of oil which may be produced from sprouted or wormy nuts depends on the extent of growth or of worm damage. Most of the wormy nuts which were examined contained no meats at all. Fully sprouted nuts contain less than one per cent of oil.[39] The South Carolina acorns were only 41 per cent sound nuts.

Before an acorn oil mill could be established on a commercial basis an extensive educational campaign would have to be conducted in order to acquaint prospective acorn harvesters with the type of material required for oil extraction. The nuts must not be allowed to lie on the ground to become moist and sprout. It is necessary that they be gathered as they fall and stored in dry cribs.

Preparation of Acorns for Extraction. Most of the acorns were prepared for extraction by removing the shells in a winnower and fanner. This machine had been built by the J. H. Lehman Company of New York for Rockwood and Company and had been used to remove the shells from cocoa beans. Since the acorns were shelled without difficulty at a rate of about 200 pounds per hour no new type of equipment needs to be designed for processing acorns.

There are a number of methods of preparing seeds for oil extraction. The most satisfactory of these, according to the experience of soya oil producers, is to prepare the seed as a thin flake; the thinner the better. These flakes are readily penetrated by solvent but hold their shape after oil removal so that drainage of miscella from extracted solids is rapid. Attempts to produce acorn flakes were unsuccessful, using such equipment as was available. Rockwood and Company have had good success in extracting crushed expeller cake, sized to be retained by an eighth inch mesh screen and passed by a half inch mesh screen. Expelling is a hot pressing operation which produces a porous cake, probably due to the formation of steam within the material passing through the expeller. Solvent penetrates the porous expeller cake fragments easily and these fragments, like the soybean flakes, do not break up on removal of oil. The least desirable method of preparing material for oil extraction is to grind it finely enough so that solvent can penetrate the particles of oil-bearing material. Grinding produces a large per cent of fine flour, evident after oil-removal, which cannot be handled by any of the commercial extractors described in the literature as being in current use.

Acorn expeller cake was prepared by using an

Anderson Duo Expeller at Rockwood's plant on the acorn meats from the winnower and fanner. This expeller cake was crushed and the material retained by an eighth inch screen and passed by a quarter inch screen was extracted.

At least 300 pounds of acorn meat were required for one expeller run so that most of the acorns were used for this experiment. The nuts were not sorted, which would have resulted in a feed containing considerable more oil, but would have departed from the purpose of processing the material as received and not as selected for the highest possible yield of oil. Carefully selected acorns contain up to 40.0 per cent of butanol extractable material whereas the material fed to the expeller contained only 13.3 per cent of such material.

The results of the expeller run show that acorn meats can be handled by an Anderson Duo Expeller. A good many runs would be required to establish optimum expelling conditions. During the first part of the 65 minute run the acorn meat was fed as it was. The first cake was crumbly and not firm. Water was added to the meat during the second part of the run and a much stronger and harder expeller cake was formed.

A centrifuge might well be used as an interstage filter in an extraction scheme designed to handle fine material. Acorn meal was prepared for extraction in such a scheme by grinding the meat in a Raymond Laboratory Hammer Mill No. 40127. In order to avoid fines the grinding was done through the coarsest screen, (one quarter inch), supplied with this mill. Some of the ground material, 14.2 per cent, was too large to pass a 35 mesh screen and hence could not be expected to extract well.

Method of Extraction and Choice of Solvent. Two extractors were used in processing acorns on a pilot plant scale. The first of these consisted of a mixing tank, (a one gallon porcelain ball mill jar), for solvent and feed, followed by a Tolhurst No. T-7893 centrifuge to separate extracted solids and miscella. Extraction followed Elgin's pseudo-countercurrent extraction scheme.[20] Hunter [36] shows that such a scheme gives a deviation of 3 to 10 per cent, depending on the stage, from a truly countercurrent extraction when 5 cycles are used with 4 stages. He demonstrates that this deviation becomes less than 2 per cent for all stages with 10 cycles. Three and four cycles were employed with two and three stages in these centrifuge extractions. A considerable deviation from a truly countercurrent process is therefore to be expected.

The second extractor consisted of a continuous chain made up of No. 45 malleable detachable links with No. 45 C-1 flights every fourth link moving through a 2 inch pipe. The flights carried the solid material up a 25° slope against a counterflow of solvent.

Neither of these extractors was solvent tight so that no volatile nor dangerous solvent could be used with them. The usual commercial oil solvents are low boiling hydrocarbons (mainly hexane) and their chlorinated derivatives. These solvents are both volatile and dangerous; the hydrocarbons because of their flammability; the chlorinated hydrocarbons because of their toxicity. n-Butanol was selected as solvent because:-- it is not very volatile (vapor pressure of 4.3 mm. of mercury at 20°C. and 18.6 mm. at 40.0°C.); it was not dangerous to use; preliminary experiments indicated that it was a satisfactory solvent for acorn oil; and it could be obtained in the quantities required.

Centrifuge Extractions. The centrifuge extractions, as shown in Table XI, removed from 73.0 to 80.0 per cent of the oil in the feed. A higher yield might have been obtained from a more finely subdivided feed. The results prove, however, that acorn oil can be extracted from acorn meal using the extraction in Fig. 28.

Continuous Extractions. It was difficult to obtain consistent results with the continuous chain extractor. This was due to the tendency for solid material to hold up in the pipe and to progress irregularly through the system. This difficulty was particularly noticeable with acorn meal which packed against the sides of the pipe so that the chain moved through a square duct composed of solvent-wet meal. This was an unstable condition. At times more material went into the system than was discharged. Again, after the extractor had been running some length of time and was loaded with solid material, a reduction in feed rate did not result in a corresponding reduction in discharge rate. It was found possible to reach a rather unstable equilibrium by cleaning the system well before a run; filling it with solvent and establishing the solvent feed rate; and then feeding in the solids at the selected rate for the run for a period of about an hour. Under these conditions fairly consistent results were obtained.

In experiments 1 and 2 the feed conditions were the same, 4.0 pounds of solvent and 2.0 pounds of solid were fed to the extractor per hour. Extraction in these two experiments, 41.3 and 45.6 per cent respectively, is about the same. The feed rate was double in experiment 3, i.e., 8.0 pounds of solvent and 4.0 pounds of solid being fed to the extractor per hour. Extraction was somewhat worse--39.2 per cent. The material balance, Table XIV, shows that material was being retained by the extractor in experiment 3.

The solid feed rate was kept constant at 2.0 pounds per hour in experiments 4, 5, 6, 7 and 8 and the solvent feed was varied from 2.6 to 5.2 pounds per hour. Plotting solvent-solid ratios against per cent extraction in Fig. 32, shows that increased extraction results from increasing this ratio, as would be expected. Extraction varied from 16.9 per cent to 41.8 per cent in these runs with acorn meal.

The per cent of oil extraction from crushed acorn expeller cake was the highest obtained from any feed to the continuous extractor, varying from 62.3 to 71.8 per cent of the oil in this cake. Solvent-solid ratios for the acorn expeller cake experiments, 9, 10, 11, are plotted against per cent extraction in Fig. 32. Contrary to what would be expected, the greatest extraction results from the lowest solvent-solid ratio.

Characteristics of Acorn Oils. Table II shows that acorn oil, as reported by previous investigators has a specific gravity at 25°C. of 0.908 to 0.914, an index of refraction of 1.4594 to 1.4725, also at 25°C. The saponification numbers of acorn oils vary from 188.4 to 199.3; iodine numbers (Wijs) from 83.0 to 100.7 have been reported; acid numbers range from 4.5 to 22.2. The acorn oils resulting from this experimental work had specific gravities of 0.904 to 0.908 at 25°C., indexes of refraction (at 25°C.) of 1.4669 to 1.4684, acid numbers of 2.6 to 30.8, saponification numbers from 188 to 192 and iodine numbers (Wijs) of 105 to 111. The iodine numbers of the acorn oils produced by the pilot plant experiments are higher than any listed by other investigators. The other constants indicate that this acorn oil is similar to that produced by other workers.

B. SOLVENT EXTRACTION THEORY

Introduction. Solvent extraction theory is concerned with methods of calculation of the results of hypothetical extractions. These postulated extractions may be practically realized, if it is possible to carry out actual extractions under conditions similar to those hypothecated in the derivation of the method of calculation.

A modified derivation of a theoretical method for calculation of the results of solvent extractions is presented. This method is based on the consideration of a solvent extraction as a ternary system consisting of solvent, solute and inert carrier solid. The derivation is prefaced by a discussion of those properties of triangular diagrams which are used in it.

Properties of Triangular Diagrams. There are certain properties of triangular diagrams which pertain to the derivation of a graphical method for the solution of leaching problems. These are illustrated by Figure 34, in which the corners of the triangle ABC refer to pure components; specifically for oil extraction, A is 100 per cent solvent, B is 100 per cent oil and C is 100 per cent inert carrier solid. All possible mixtures of A and B are represented by the side AB, of B and C by the side BC, and of C and A by the side AC. Points within the triangle represent mixtures of all three components; such a point is P representing a mixture of a per cent of a, b per cent of B and c per cent of c. c is a perpendicular from P to AB, b a perpendicular from P to AC and a a perpendicular from P to CB; a + b + c = 100 per cent.

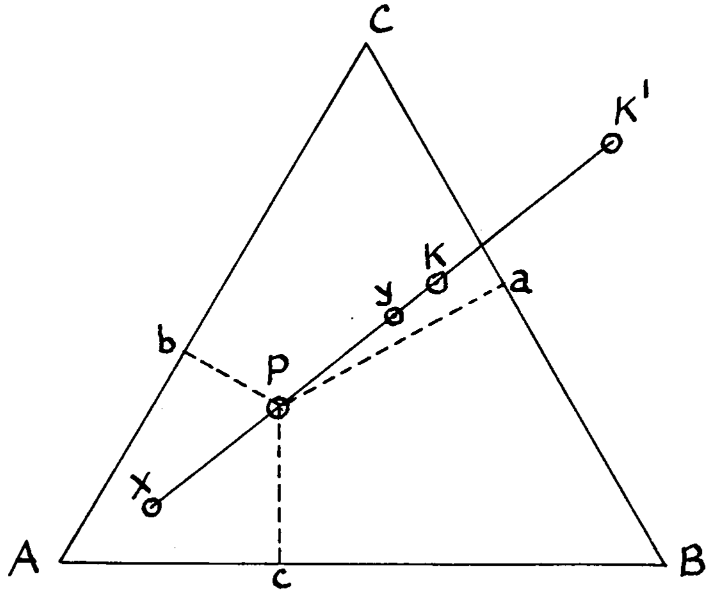


Figure 34.

Properties of Triangular Diagrams.

The mixture P may be divided into two other mixtures, x and y, whose compositions are represented by the ends of the straight line xPy. P may be considered as the result of mixing x and y and in this case the per cent composition of the mixture can be located in two ways. P lies on a straight line connecting x and y. If W_x is the weight of the mixture of composition x and W_y is the weight of the mixture of composition y, $xP/yP=W_y/W_x$, so that, P can be located by dividing xy into two segments in the ratio W_y/W_x. P can also be located arithmetically from the known weights and compositions of the mixtures x and y.

Suppose that the composition of the mixture K obtained by subtracting x from y is desired. If y is greater than x, K will lie within the triangle. If y is less in weight than x, it will be an imaginary mixture and its composition will be represented by a point outside the triangle, K'. In either case y may be considered as a mixture derived by the addition of K or K' and x, and as before:-

$$xy/Ky = W_K/W_x \quad , \quad xy/K'y = W_{K'}/W_x$$

where,

$$W_K = Wy - Wx \quad , \quad W_{K'} = Wy - Wx$$

The arithmetic method could be applied to the location of such points as K, it would be difficult to apply to points such as K'.

Considering the addition, or subtraction of pure components to mixture P; addition of A will produce mixtures lying along PA between P and A; subtraction of A, by evaporation of solvent, will produce mixtures whose compositions lie along AP extended beyond P; addition or subtraction of B will give compositions along a line through P and B; addition or subtraction of C will give a point on a line through P and C.

These are special cases of the division of the mixture P into a mixture and a pure component or the production of a new mixture by the addition of a mixture and a pure component; compositions would be calculated as for points such as P and K.

In order to illustrate these properties of triangular diagrams some specific cases are presented in Figure 35, Three Component Mixtures.

Example 1. Acorn oil is being removed from acorn meal by extraction with n-butanol. This acorn meal consists of 20.0 per cent oil and 80.0 per cent inert material. One pound of the meal, the solid feed, is mixed with 0.75 gallon of an overflow consisting of 10.0 per cent acorn oil and 90.0 per cent butanol. The specific gravity of this overflow at the temperature of the extraction is 0.90. What is the composition of the resulting mixture?

Solution:-

$$\text{The 0.75 gallon of overflow} = \frac{(.75)(231)(62.4)(.90)}{1728}$$

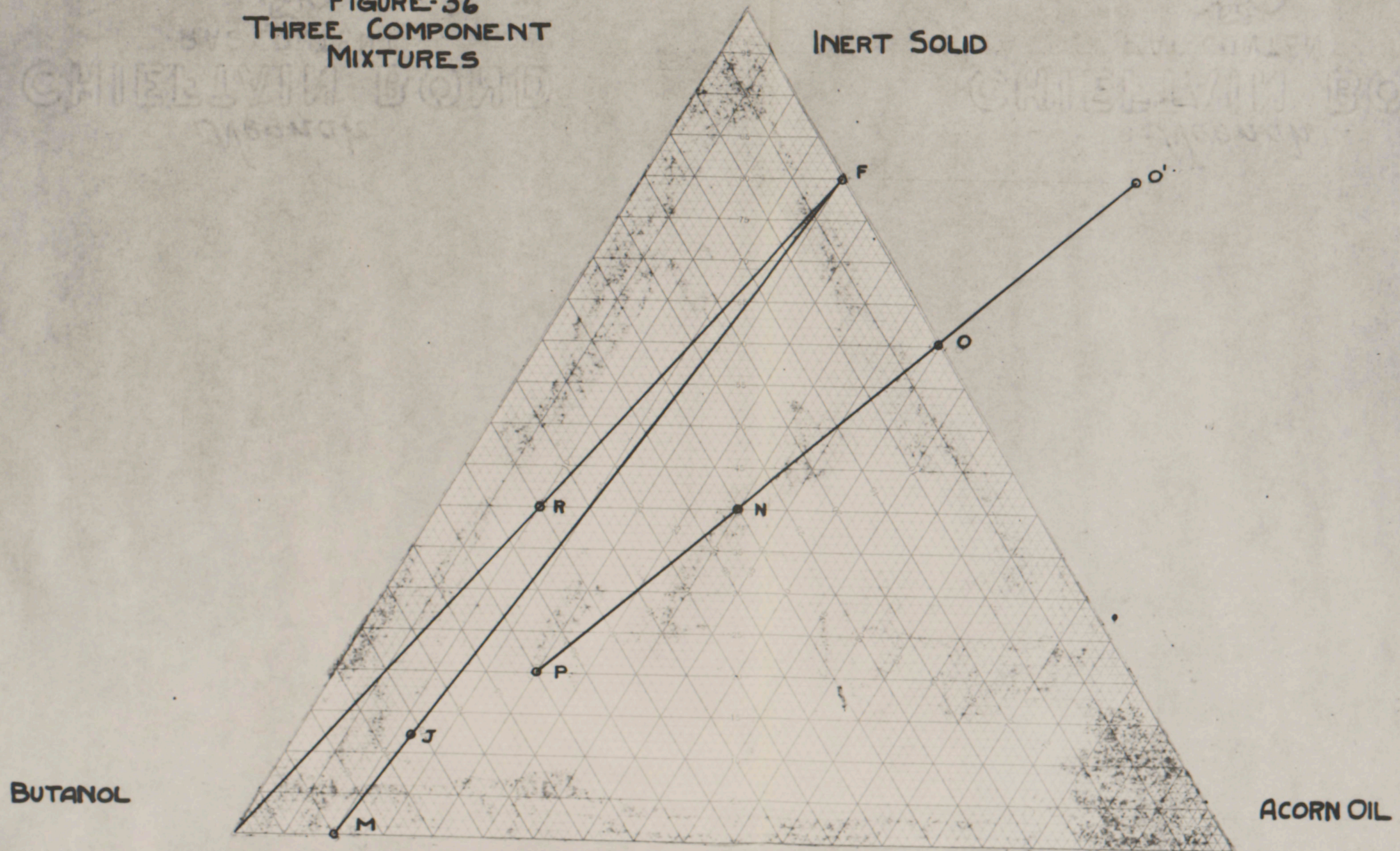
$$= 5.625 \text{ pounds}$$

Locate F in Figure 35 at the per cent composition of the acorn meal.

Locate M at the composition of the miscella, overflow. Connect F and M. The resulting mixture is represented by point J on the line FM located so that:

$$FJ/MJ = 5.625/1.0$$

FIGURE-36
THREE COMPONENT
MIXTURES



FM is 200 mm. in length, MJ + JF = 200 mm. JF = 5.625MJ, MJx6.625 = 200, MJ = 30.2 mm. and JF = 169.8 mm., measuring MJ and thus locating J, the coordinates of J, as read from the diagram are:-

Acorn oil	11.5	per cent
Inert	12.0	" "
Butanol	76.5	" "
	100.0	per cent

Calculating the composition of J from the per cent compositions and amounts of F and M :-

F consists of,

1.0x0.20 = 0.20 pounds of acorn oil
1.0x0.80 = 0.80 pounds of inert material

M consists of,

5.625x0.10 = 0.56 pounds of oil
5.625x0.90 = 5.07 pounds of butanol

J consists of,

0.20+0.56 =	0.76	pounds of acorn oil
	0.80	pounds of inert material
	5.07	pounds of butanol
	6.63	pounds

or,

J is,

11.5 per cent acorn oil
12.0 per cent inert material
76.5 per cent butanol

This second calculation is exact. The graphical solution is as exact as the care used in the construction and in reading the diagram.

Example 2. The underflow in an acorn oil extraction is analysed and found to contain 40.0 per cent inert material, 10.0 per cent acorn oil and 50.0 per cent solvent, butanol. What is the composition of this underflow after evaporation of the solvent?

The solution may be graphical:-

R in Fig. 36 corresponds to this underflow. AR extended to CB, locating point F, 20.0 per cent oil and 80.0 per cent inert material, gives the composition of the solvent free underflow.

The solution may be mathematical:-

Removal of solvent from 100 pounds of underflow leaves a mixture of 10 pounds of oil and 40 pounds of inert material, with a per cent composition of,

10/50x100 = 20 per cent acorn oil

40/50x100 = 80 per cent inert material

Example 3. P consists of 20 per cent acorn oil, 20 per cent solid and 60 per cent butanol. N has the composition 40 per cent inert material, 30 per cent butanol and 30 per cent acorn oil.

(a) What would be the composition of the mixture O produced by subtracting 1.0 pound of P from 2.0 pounds of N?

(b) What would be the composition of the mixture O' produced by subtracting 2.0 pounds of P from 1.0 pound of N?

The solution of Example 3(a) may be graphical:-

In this case the process of subtraction of one mixture from another may be considered as the addition of a negative amount, thus subtraction of 1.0 pound of P from 2.0 pounds of N will give 1.0 pound of O. N can be produced by addition of 1.0 pound of O to 1.0 pound of P and N must therefore divide the line OP into segments such that,

PN/ON = 1/1, and since PN = 61 mm., ON = 61 mm.

The coordinates of O are:-

40.0 per cent acorn oil
60.0 per cent inert material

as read from Fig. 36.

The solution of Example 3(a) may be mathematical:-

0.2 pound of acorn oil
0.20 pound of inert material
0.60 pound of butanol

are to be subtracted from,

0.80 pound of inert material
0.60 pound of butanol
0.60 pound of acorn oil

leaving the mixture O consisting of,

0.60 pound of inert material = 60 per cent
0.40 pound of acorn oil = 40 per cent
0.0 pound of butanol

The solution of Example 3(b) must be graphical. Such a mixture as O' would be negative or imaginary and would be represented by a point outside the limits of the triangle. The point corresponding to O' may be located as follows:-

Subtraction of 2.0 pounds of P from 1.0 pound of N will give -1.0 pound of O', or N would be produced by addition of -1.0 pound of O' to 2.0 pounds of P. N must therefore divide O'P into segments such that,

$PN/O'N = -1/2$, and since $PN = 61$ mm.,

$-O'N = 122$ mm.

While this imaginary point can be, and is, located in Fig. 36 as O', its composition cannot be read on this diagram.

Solvent Extraction Theory. A graphical method for predicting the results of leaching operations has been derived by J. C. Elgin. This method makes use of the properties of triangular diagrams which have been discussed. The graphical calculation requires:-

(1) The system consists of solute, solvent and inert carrier solid. An inert carrier solid is defined as a solid phase of negligible solubility in the solvent.

(2) The solute is neither absorbed nor adsorbed by the carrier solid.

(3) The solute is removed solely by physical solution in the leaching solvent and no chemical reaction occurs.

(4) Equilibrium is attained in every stage so that the concentration of solution remaining with the solid is identical with that of the solution withdrawn.

Elgin demonstrates theoretically that, if these four assumptions are valid, and leaching conditions have been established, either practically or hypothetically, it is possible to calculate, either the extent of the leaching to be expected with a definite number of leaching stages, or the number of leaching stages required to effect a desired degree of leaching.

The extraction of oil from oil-bearing material is a special case of leaching. In general the oil to be extracted is miscible with the solvent in all proportions and there are no regions within the triangle representing more than one liquid phase nor any areas of saturated solutions. The most interesting case, from a commercial standpoint, is that of continuous countercurrent extraction and a modification of Elgin's derivation for this case is presented here.

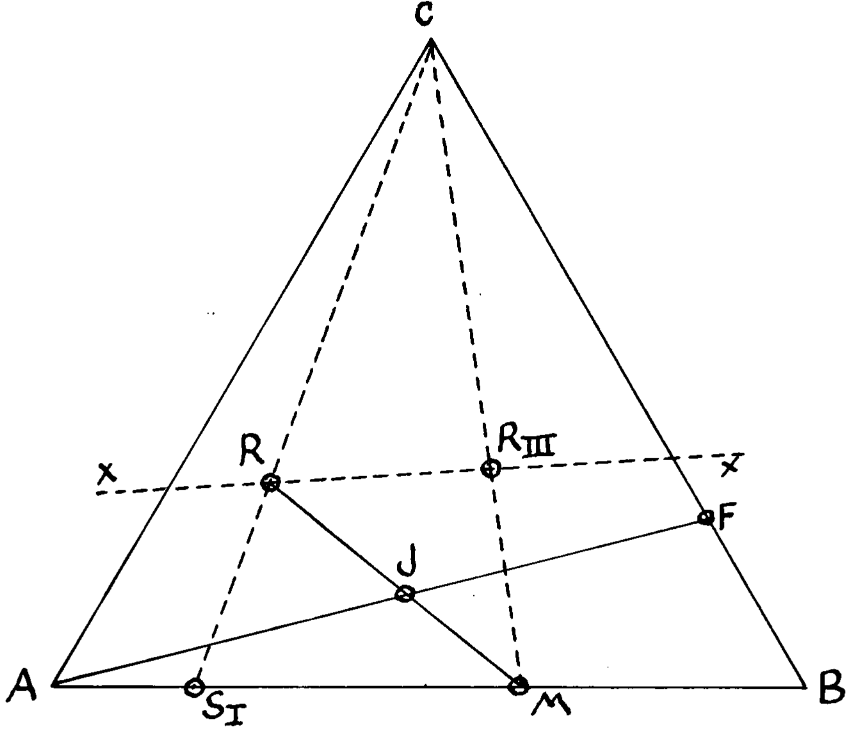


Figure 37

Triangular Diagram for Three Stage Countercurrent Extraction.

Suppose than an oil-bearing material consisting of oil and inert material, its composition represented by F in Figure 37, Triangular Diagram for Three Stage Countercurrent Extraction, is extracted with S pounds of solvent, composition A in Figure 37, in a three stage countercurrent process as shown in Figure 38, Three Stage Countercurrent Extraction.

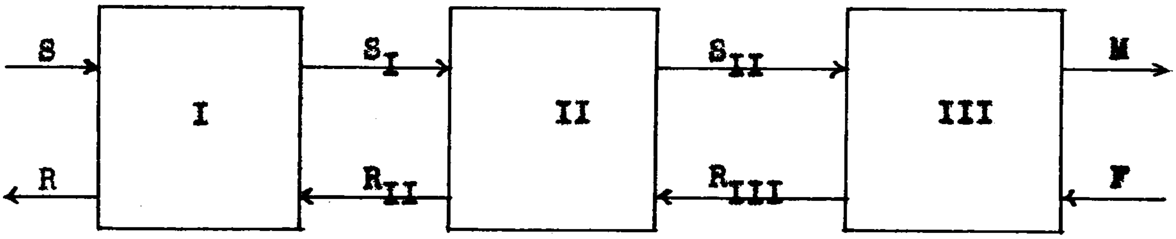


Figure 38.

Three Stage Countercurrent Extraction

When this system is in equilibrium,

$F + S = M + R$

F = pounds of oil-bearing material, of composition F in Figure 37.

S = pounds of solvent, of composition A in Figure 37.

M = pounds of miscella, of composition M in Figure 37.

R = pounds of extracted solid + residual oil + inert material, of composiion R in Figure 37.

The extraction is carried out so that:-

F pounds of feed plus S pounds of solvent enter the system per unit of time and M pounds of miscella plus R pounds of raffinate leave the system in this same unit of time. Equilibrium is established in each stage so that the composition of the liquid in the underflow is the same as that in the overflow.

There may or may not be inert solid in the overflow. This development is for the case in which there is no inert solid in the overflow and the composition of the overflow varies from some point to be determined on AB to M, also on AB. The weights and compositions of the overflows from the first and second stages are represented by S_I and S_{II}. The weights and compositions of the underflows are represented by R_{II} and R_{III}, (Both as shown in Figures 37 and 38).

The oil, inert solid and solvent entering the system in F + S must leave in M + R; therefore, if the composition of the mixture F + S is represented by J, R amd M will lie at opposite ends of the straight line RJM in Figure 37. The composition of J is calculated from the composition and quantities of the two feed streams, F and S; or, considering terminal conditions in the extraction of Figure 38, the mixture J formed by addition of F to S is divided into the two mixtures M and R so that J must be the intersection of AF, (the composition of S is A), and MR; therefore by drawing MR and AF, J may be located graphically.

The compositions of R, R_{II} and R_{III} depend on the quantity and composition of liquid in the underflow associated with I, the number of pounds of inert solid (composition C) which is the same in F, R, R_{II} and R_{III}. The composition of the underflow in the usual oil extraction can be represented by such a line as xx in Fig. 37. The liquid M is of the same composition as that in the underflow R_{III}. R_{III} can then be obtained from M by the addition of inert solid, I pounds, and is therefore located on the line MC at the intersection of MC with xx. The overflow S_I is of the same composition as the liquid in R and its composition is that obtained from R by removal of inert solid, so that S_I is located by the extension of CR to AB. Thus, making use of the properties of triangular plots, knowing the composition and amounts of the feed streams in an oil extraction, as well as the relation between solid and liquid in the underflow, it is possible by establishing the composition of M (or R, or R_{III} or S_I) to determine the composition of R, J, R_{III} and S_I.

Material balances over the system and over each stage are:-

1. $S + F = M + R$
2. $S + R_{II} = R + S_I$
3. $S_I + R_{III} = R_{II} + S_{II}$

4. $F + S_{II} = M + R_{III}$

5. $R - S = F - M$

6. $R = F - M + S$

7. $S - R_{II} = F - M + S + S_{I}$

8. $R_{II} - S_{I} = F - M$

9. $S_{I} + R_{III} = F - M + S_{I} + S_{II}$

10. $R_{III} - S_{II} = F - M$

In these equations the letter identifying the stream stands for both its weight and its composition. Thus S means pounds of S and also pounds of Sx100 per cent, where all components are considered. If only one component (oil) were considered, the equations would be:-

Sx(per cent of oil in S) + Fx(per cent of oil in F) = Mx(per cent oil in M) + Rx(per cent of oil in R).

Thus the subtraction of the overflow from any stage from the solids carrying stream entering that stage gives a constant value equal to the feed stream minus the miscella. In general this value will be negative since the feed stream is usually smaller than the miscella. It is represented by a point K lying outside the triangle (indicating that this is an imaginary mixture), but having the same characteristics as points within the triangle, e.g., representing a mixture of the three components, A, B, and C.

K can be located from the compositions and weights of F and M, or at the intersection of RS and FM, extended. $R_{II}S_I$ and $R_{III}S_{II}$ also meet in point K.

The underflow is the stream carrying solids. In the usual extraction all inert solid, I, entering in the feed moves from stage to stage in the underflow and the quantity of inert solid is the same in all stages. When this is the case, and the volume of the underflow is constant, as it usually is in a countercurrent process, the composition of all possible underflows may be represented by a line such as xx in Fig. 37. The weight of the oil-solvent mixture in the underflow will depend on the specific gravity of that liquid so that; if the volume of the liquid associated with the I pounds of inert solid is known, along with the variation in specific gravity of oil-solvent mixtures, points defining the line xx may be calculated.

The proportion of liquid and solid in the underflow in any particular extraction would usually be established experimentally. The liquid solid ratio might, however, be postulated, and, if information concerning the amount of liquid likely to be carried along with the solid were available, this postulate could be carried out in practice. As examples:-

1. Sand settles compactly in kerosene and could

be freed of lubricating oil by a kerosene extraction, (mixing feed and solvent, settling solid, pouring off miscella, adding fresh solvent and repeating), with an underflow of 100 ml. of liquid to 100 grams of sand. This underflow is practicable since experience with this system has shown that when a mixture of oil, kerosene and sand is allowed to settle and then the liquid is poured off, 1.0 gram of sand will retain 0.3 ml. of kerosene-oil.

2. Filter paper scrap could not be freed of lubricating oil by a kerosene extraction with an underflow of 100 ml. of liquid to 100 grams of scrap. Experience with this system has shown that 3.0 ml. of kerosene-oil will be retained per 1.0 gram of filter paper scrap. The extraction of oil from filter paper scrap would require ten times as much liquid in the underflow as would the extraction of oil from sand.

Where the underflows cannot be represented by a single line such as xx, they can be represented by a series of such lines, one for each underflow if each is different.

The utility and application of this graphical method of calculation is illustrated by the following examples:-

Case I-A. The underflow is of constant volume. There is no solid material in the miscella. The specific gravity of oil-solvent mixtures increases with increasing oil content.

The extraction of acorn oil from acorn meal with n-butanol can be carried out in such a way as to be an illustration of this case. Suppose that such an extraction follow Fig. 39, and that it is desired to know the number of stages required to produce an extraction of 95 per cent of the oil from the feed. The graphical calculation is shown in Fig. 40, The Extraction of Case I. F is the feed, 40 per cent acorn oil, 60 per cent inert solid. S is 250 ml. of solvent, (250x0.83 = 207.5 grams). The underflow is to consist of 50 ml. of liquid plus 60 grams of inert solid. If extraction were complete, this underflow would consist only of butanol and inert solid and would be represented by the point 59.0 per cent C on AC in Fig. 40. This is one point on xx. Other points along xx may be located from Table XVII, (for which the specific gravities of butanol-acorn oil mixtures are taken from Fig. 5).

Draw the xx line using Table XVII in the following manner:-

Lay a straight edge along 5.0, 10.0, 15.0, etc., per cent oil on AB to C and locate points corresponding to 59.0, 58.9, 58.8, etc., per cent solid on these lines. It is best not to draw the lines 5.0 per cent

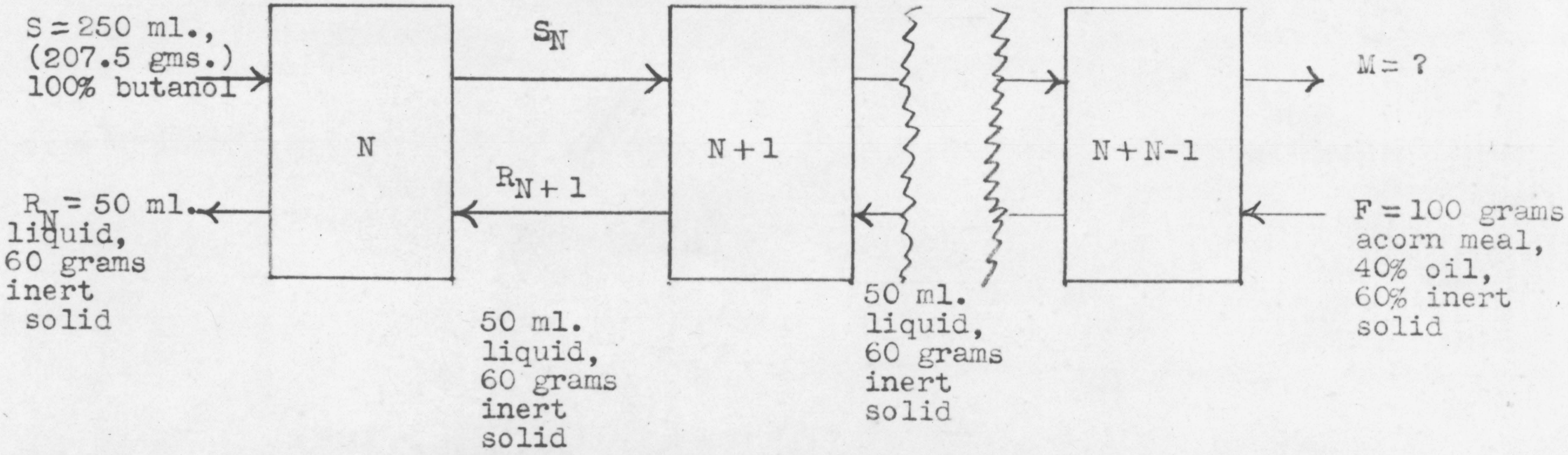


Figure 39.

The Extraction Illustrating Case I-A

oil, 95 per cent butanol, etc., to C since these added lines make the final diagram confusing.

TABLE XVII.

Variation in Per Cent Inert Solid in the Underflow of Case I with Variation in the Per Cent Oil in the Liquid Part of that Underflow.

Acorn oil in the liquid underflow, Per cent.	Sp. G. of liquid in underflow.	Weight of liquid in underflow, Grams.	Solid in underflow, Per cent.
0.0	0.830	41.5	59.0
5.0	0.833	41.6	59.0
10.0	0.837	41.7	58.9
15.0	0.840	42.0	58.8
20.0	0.843	42.2	58.7
25.0	0.848	42.4	58.6
30.0	0.851	42.6	58.5
40.0	0.859	42.9	58.3
50.0	0.866	43.3	58.0

Since 95.0 per cent of the oil in the acorn meal is to be extracted the dry composition of the raffinate is set as:-

(0.05)(40) =	2.0 grams	oil,	3.22%
	60.0 "	inert solid,	96.78%
	62.0 grams		100.00%

This is the point R_D in Fig. 40.

Locate F in Fig. 40.

Draw AR_D and its intersection, R_N, on xx locates the wet composition of the raffinate from the Nth stage.

Locate point J, the mixture of S and F.

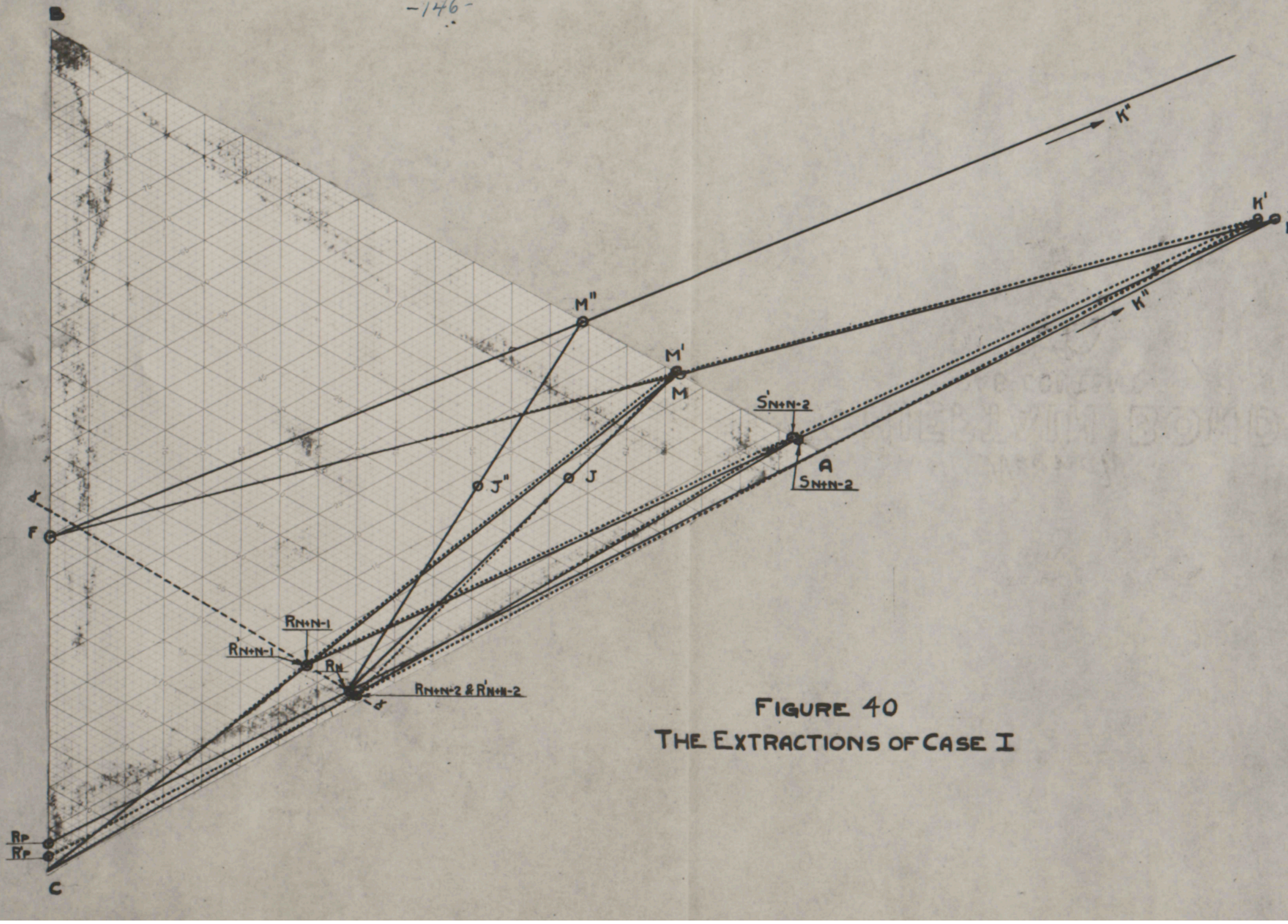


FIGURE 40
THE EXTRACTIONS OF CASE I

J

207.5	grams	butanol,S	67.5%
60.0	"	inert solid,F	19.5%
40.0	"	acorn oil,F	13.0%
307.5	grams		100.0%

The mixture J is divided by the extraction into R_N and M so that M is located by extending R_NJ to M on AB.

$F - M = R_N - S$, and FM meets SR_N at K so that K is located by extending FM and SR_N to their intersection.

Draw MC, its intersection with xx is the composition of the underflow from the N + N - 1 stage, R_{N+N-1}.

Draw $R_{N+N-1}K$, its intersection with Ab, the miscella line, is S_{N+N-2}, the composition of the overflow from the N + N - 2 stage.

Draw $S_{N+N-2}C$, its intersection with xx is the composition of the underflow from the N + N - 2 stage, R_{N+N-2}.

Since R_{N+N-2} lies to the left of R_N on xx, two stages would remove more than the required amount of oil and would be specified for this extraction.

The composition of the miscella, M, would be 18.3 per cent acorn oil, 81.7 per cent butanol. The quantities of the streams R and M may be calculated from a material balance.

Case I-B. Calculate the extraction to be expected with two stages under the same conditions as in Case I-A. Points F, J and the xx line are the same as in I-A. Two stages produce more than the extraction required in I-A so that a little richer miscella would be expected. The correct miscella composition will cause R_N and R_{N+N-2} to coincide. This miscella composition, determined by trial, is 18.7 per cent acorn oil, 81.3 per cent butanol. The construction for the extraction to be expected with two stages is shown in dotted lines in Fig. 40. The miscella of 18.7 per cent acorn oil corresponds to a solvent-free raffinate, R'_D in Fig. 40, containing 2.0 per cent acorn oil.

The total weight of this raffinate is,

60/0.98 = 61.3 grams

or,

40 - 1.3 = 38.7 grams of oil would be extracted with two stages; which is an extraction of,

38.7/40.0x100 = 96.75 per cent

Case I-C. Suppose that a richer miscella is desired and the quantity of solvent to be used is reduced to 150.0 ml.,(124.5 grams). Again it is required to calculate the number of stages which will produce an extraction of 95.0 per cent of the oil from the meal.

The composition of J becomes:-

124.5	grams	butanol, S	55.5%
60.0	"	inert solid, F	26.7%
40.0	"	acorn oil, F	17.8%
224.5	grams		100.0%

Locate this point as J' in Fig. 40.
Starting the construction as in I-A by drawing R_NJ' to M' on AB and then extending FM' and R_NA, A = S, it is found that point K lies so far from the rest of the diagram that the construction is difficult. This construction can be handled by transfer to rectangular coordinates.

There is another common construction which can also best be handled on rectangular coordinates; if a high degree of extraction is required from a feed low in oil, point M will be close to A and the lines of the resulting diagram will be so close together that it is difficult to be sure of the number of stages required or of the extraction effected by a given number of stages. This case has been illustrated by Kinney in his enlargement of the triangular plot by transferring it to rectangular coordinates. This rectangular plot is a distorted triangle, and, since any point on the ternary diagram may be located from the per cent composition of two of the three components, points are transferred to the two axis diagram by using per cent oil and per cent solvent. 100 per cent inert solid is 0.0 per cent oil, 0.0 per cent solvent. Another advantage of transfer to rectangular coordinates, aside from enlargement, lies in the ease with which different scales for the two axes may be employed. This makes the handling of such a problem as Case I-C easy.

The solution of this problem, Case I-C, may be carried out as shown in Fig. 41. There is no oil concentration greater than 40.0 per cent to be represented on the diagram so that the oil axis does not need to go beyond this point. The points in Fig. 41 all have the same significance as those in Fig. 40 and are located in the same way. The composition of the rich liquor was established as 31.0 per cent oil in Fig. 40, which agrees with M = 31.1 per cent oil in Fig. 41. Fig. 41 shows that three stages will give more than the required extraction.

Solving under the conditions of Case I-C for the extraction to be expected with three stages Fig. 41 shows M = 32.0 per cent oil and R_D = 2.0 per cent oil. There are 60.0 grams of inert solid in R_D so that $R_D = 60/0.98 = 61.3$ grams and contains 1.3 grams oil. The per cent extraction to be expected with three equilibrium extraction stages, under the postulated extraction conditions, will then be:-

$$(40.0 - 1.3)/40.0x100 = 96.8 \text{ per cent}$$

Case II. The specific gravity of oil-solvent mixtures decreases with oil concentration. The volume of the underflow is constant. Solid appears in the miscella.

Figure 41.

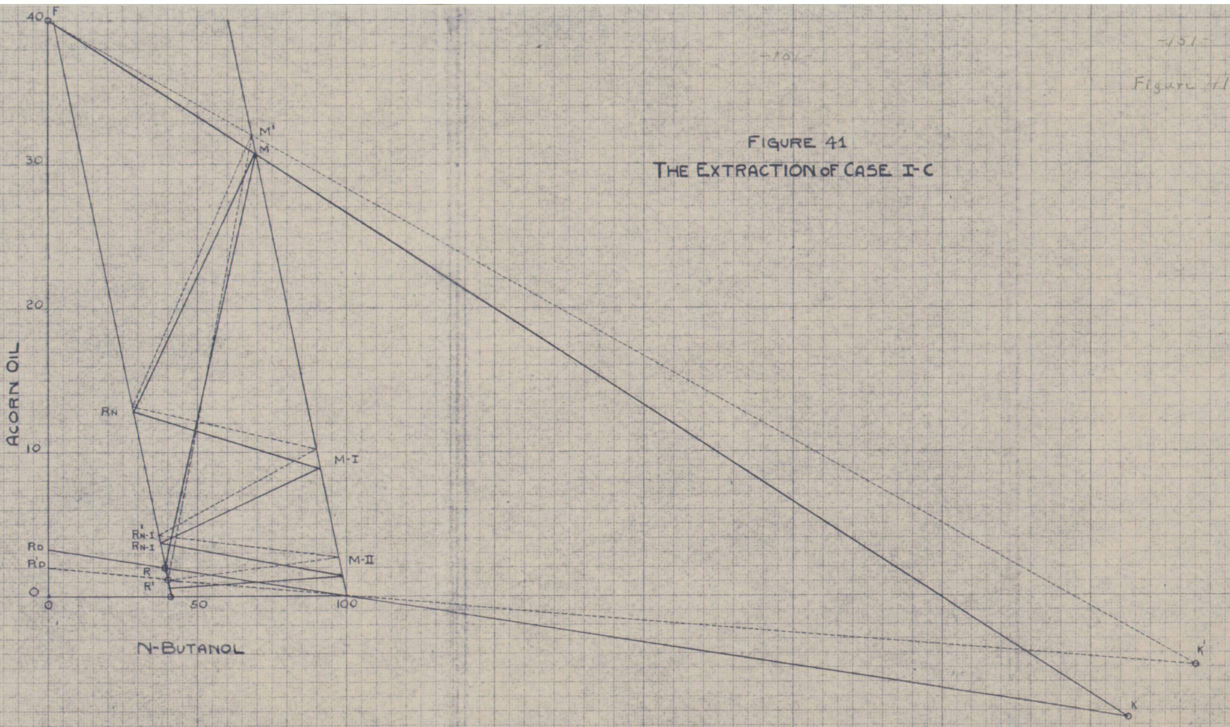


FIGURE 41
THE EXTRACTION of CASE I-C

Case II differs from Case I in that the xx line slopes up toward C. Data on the solid content of the miscella with increasing oil content in oil-solvent mixtures must be available. The miscella line will depend on this data, just as the xx line was defined by similar data on the underflow in Case I.

The triangular diagram for the solution of this case might appear like Fig. 42, Triangular Diagram for the Solution of Case II.

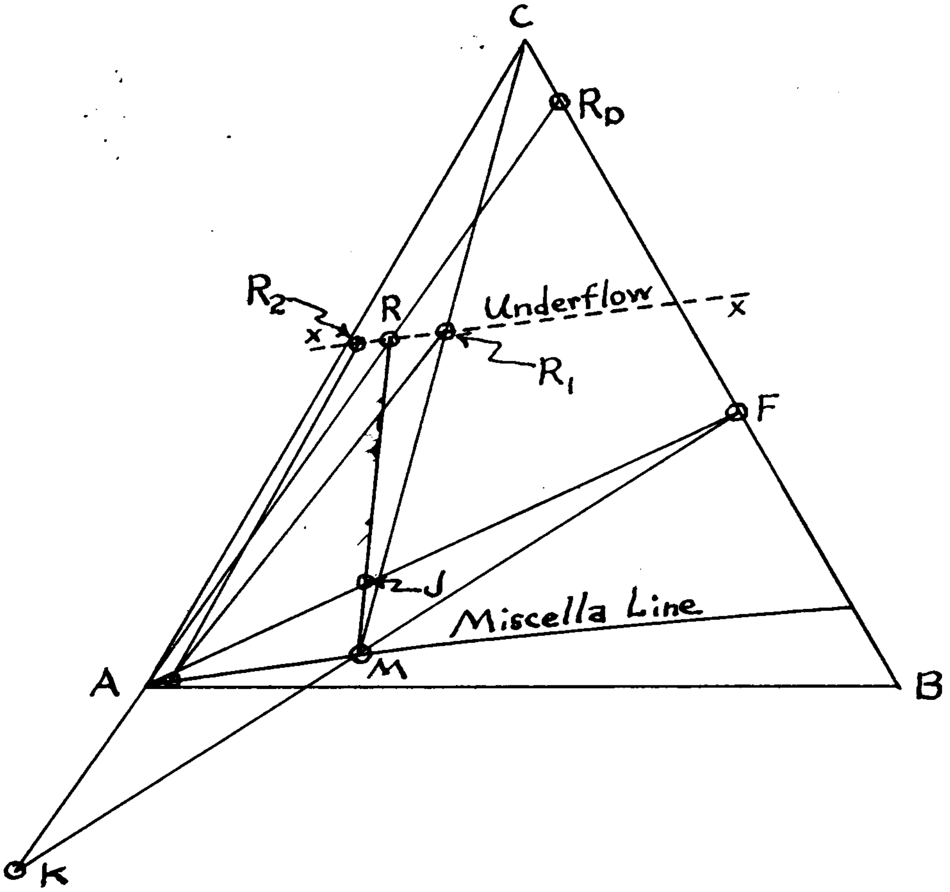


Figure 42.

Triangular Diagram for the Solution of Case II

Case III. The specific gravity of solvent-oil mixtures is substantially constant with increasing solute concentration. Solid appears in the miscella. The volume of the underflow varies from stage to stage.

Solution of this case requires the same data as Cases I and II with additional data on the variation of the underflow from stage to stage. The triangular diagram which would be required for the solution of this case is presented in Fig. 43, The Triangular Diagram for Case III. Usually the number of stages to be used would be known in this case, otherwise it would hardly be possible to have the required data on the variation of the underflow.

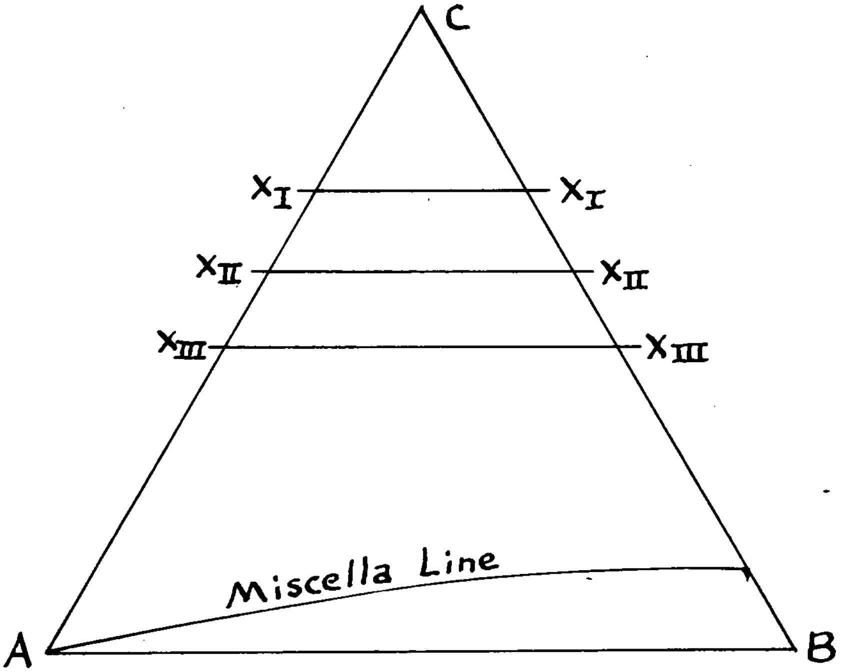


Figure 43.

The Triangular Diagram for Case III.

Illustration of Case III. Linseed oil is being extracted from crushed flaxseed, (40 per cent oil, 60 per cent inert solid), with ethyl propionate as solvent. A continuous countercurrent process of four stages is employed. 10.0 gallons of solvent and 50.0 pounds of crushed flaxseed enter the system per cycle. The underflow from the first stage is 80 per cent inert solid, from the second stage, 70 per cent; from the third, 60 per cent; and from the fourth, 50 per cent. The extraction follows Fig. 42, The Extraction Illustrating Case III.

Solid appears in the miscella according to the following table:-

Oil in Miscella, Per Cent.	Solvent in Miscella, Per Cent.	Solid in Miscella, Per Cent.
0.0	100.0	0.0
5.0	94.0	1.0
10.0	88.0	2.0
15.0	82.0	3.0
20.0	76.0	4.0
25.0	70.0	5.0
30.0	65.0	5.0
35.0	60.0	5.0
40.0	55.0	5.0

The specific gravity of ethyl propionate is 0.968. What per cent of the oil is extracted from the crushed flaxseed? What is the composition of the miscella produced by the extraction battery?

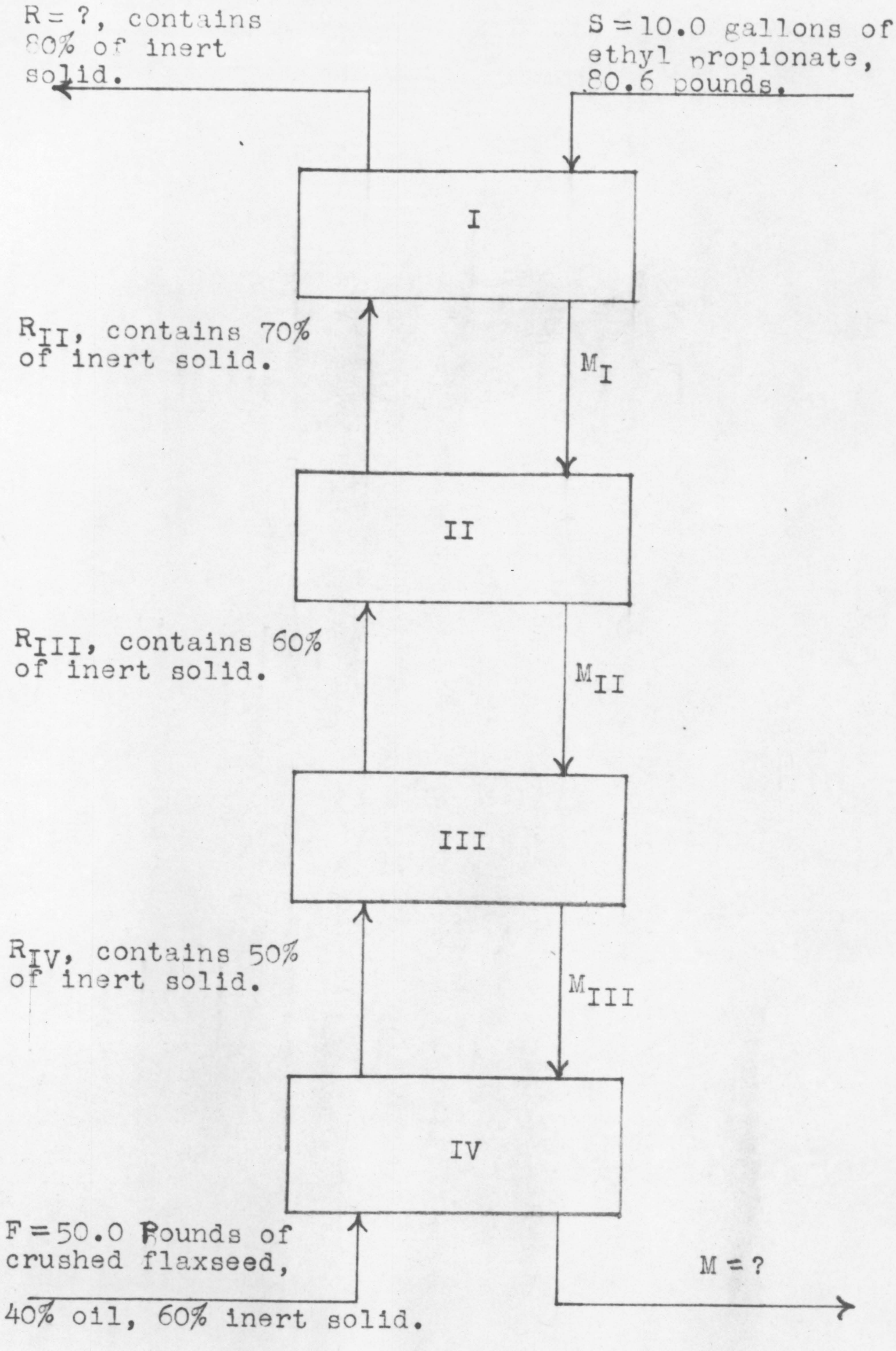


Figure 44.

The Extraction Illustrating Case III.

The solution is shown in Fig. 45, The Graphical Solution of the Problem Illustrating Case III. The miscella line is drawn from the table. Point J is:-

20.0 lb.	oil,	15.3 per cent
30.0 lb.	inert solid,	23.0 per cent
80.6 lb.	ethyl propionate,	61.7 per cent
130.6 lb.		100.0 per cent

The construction is very similar to that illustrating Case I-C. A composition is selected for R_D, which locates R at the intersection of R_D to 100 per cent ethyl propionate with the line representing the underflow from the first stage, (80 per cent inert solid). If this R corresponds to the point obtained by the intersection of M_I to 100 per cent inert solid, (0.0 per cent oil, 0.0 per cent solvent), with the underflow line for the first stage, the composition of R_D was selected correctly. If these points do not coincide, another value of R_D is chosen, etc., until a value has been found which gives this required correspondence. For this problem this value is 0.15 per cent oil, 99.85 per cent inert solid.

$R + M = S + F = 130.6$ lb., so that $R = 130.6 - M$

an inert material balance gives,

$0.8R + 0.041M = 30.0$ and substituting,

$0.8(130.6 - M) + 0.041M = 30.0$

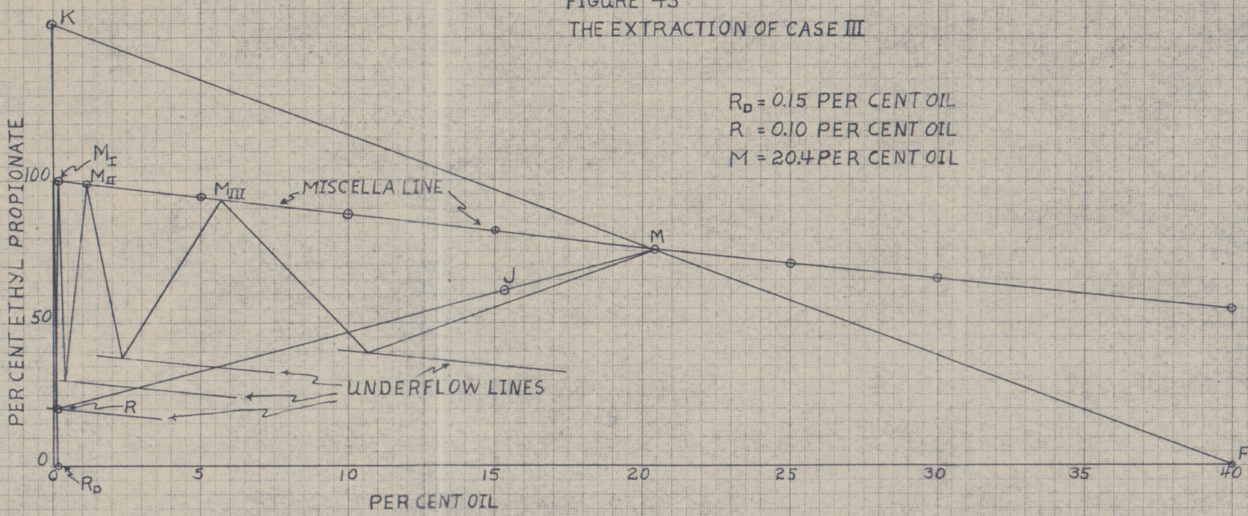
solving for M,

$M = 98.2$ lb., and $R = 32.4$ lb.

Figure 45.

FIGURE 45

THE EXTRACTION OF CASE III



The composition of R, as read from Fig. 45 is 80.0% inert solid, 0.1% oil, 19.9% ethyl propionate. Therefore 0.0324 pounds of oil are not extracted, being left in both R and R_D. 20.000 - 0.0324 = 19.9676 lb. of oil are extracted. 19.9676/20.0x100 = 99.84 per cent of the oil is extracted.

The composition of M, the miscella, is read from Fig. 45 as 20.4 per cent oil, 4.1 per cent inert solid, 75.5 per cent ethyl propionate.

These three cases cover at least the more common examples encountered in the solvent extraction of oil from oil-bearing materials. The graphical method, particularly when extended in its utility by using rectangular coordinates with different scales for the two axes, should have many important applications, if it could be shown that systems of oil-bearing material and solvent react as assumed in the derivation of this method of calculation. All of the experimental work of this thesis was carried out in such a way as to show what correlation might be expected between this solvent extraction theory and solvent extraction practice.

Extraction Theory as Related to Experimental Extractions. When the system is carefully controlled, as it was in the experiments with the artificial systems, sand, acetic acid, water of experiment 1; sand, acetic acid, dilute acetic acid of experiment 2; and sand, acetylene tetrabromide, acetone of experiments 3 and 4; the results predicted by solvent extraction theory are realized exactly, Table VIII.

The acetic acid, water, system is one in which the specific gravity increases with increasing acid concentration, although this increase is so slight that the effect of increasing gravity has little bearing on the results of a graphical calculation -- assuming constant specific gravity for solvent-solute mixtures gives almost the same result. The system, sand, acetylene tetrabromide, acetone, was selected as one in which the specific gravity of solvent-solute increases greatly with increasing solute concentration, (acetylene tetrabromide is one of the heaviest known liquids). The effect of changing gravity in this system is so great that the assumption of constant specific gravity is not admissible.

All of the small scale experiments were carried out so that the volume of liquid associated with solid in the underflow remained constant. This is the usual condition in most commercial extractions. The amount of liquid in an underflow will depend on the volume of liquid left with settled solids; or the volume of liquid retained by the solids under extraction conditions of drainage, filtering or centrifuging.

The small scale experiments with natural systems, experiments 5 and 6 with cocoa matter, cocoa-butter, methylene chloride, and experiment 7 with acorn-matter, acorn-oil, n-butanol, gave results, Table VIII, which varied slightly from those predicted by theory; 80.5 per cent extraction against a calculated 83.0 per cent, 84.5 against 86.5, 92.8 compared to 94.0 respectively for these experiments. This variation is probably due to incomplete extraction of a small part of the solids -- large particles which were not penetrated by solvent during the extraction time used. The extraction times were checked by determinations of the equilibrium time of contact for solid and solvent. These determinations were not as exact, however, as the analytical determinations made in connection with the experiments. They were based on specific gravity determinations or evaporation of solvent from small quantities of solvent-solute. More careful analysis might well show that equilibrium was not quite attained in the extraction times employed.

Equilibrium time of contact was determined by mixing solids and solvent in the proportions used in the experiments for definite periods of time, (5, 10, 30 minutes), settling for an appropriate period, two minutes, and determining the concentration of solute in solvent in the supernatant liquid, either by determining the specific gravity of this liquid, or by evaporating a known quantity of it to constant weight on a tared watch glass.

It may be, following Hunter,[36] that the deviation of the pseudo-countercurrent scheme from a continuous process was sufficient to accouht for the difference between experimental and theoretical extraction. This does not seem likely since no such divergence was observed in the artificial systems, in which extraction was carried out in the same manner.

These small scale experiments show that solvent extraction theory may be verified exactly experimentally when experimental conditions fulfill the assumptions required by that theory. They prove further that solvent extraction theory will predict the results of stage extractions with a practical accuracy for the extraction of natural oils such as cocoa butter and acorn oil. If the results of a stage extraction depart from those calculated by this theory, it is most likely that equilibrium has not been established in each stage.

Solvent extraction theory did not predict the pilot plant extractions with anything like the accuracy found in the small scale experiments. The centrifuge extractions were not carried through a sufficient number of cycles to be expected to give results approaching those which would be predicted for a continuous system. The continuous extractor showed less than one theoretical stage under the conditions of its operation. Even here, however, Fig. 33 shows a definite correlation between theory and experiment. When extraction conditions indicated a higher theoretical yield, a higher experimental yield was realized. Efficiency of solvent extraction, per cent of possible solute extracted, depends not only on the solvent-solid ratio employed, but also on the per cent of liquid in the underflow. Solvent-solid ratio indicates greater extraction in experiment 9 than in experiment 11, Table XVI and Fig. 32, which is opposite to that experimentally obtained. Solvent extraction theory shows that the extraction trend in these experiments is the one which would be expected, Fig. 33.

Solvent extraction theory provides a useful criterion by which an extraction may be judged. An extraction may be good or bad depending on whether much or little of the desired material has been removed. If the results of a bad extraction agree with those calculated by theory the fault lies, not in the manner in which the extraction was carried out, but in the extraction conditions. The extraction in experiment 1, 65.2 per cent of the solute, was not particularly good. Theory predicted an extraction of 67.2 per cent in this experiment and this agreement between theory and practice shows that the manner of carrying out the extraction was not at fault. Extraction in experiment 2, 82.6 per cent, is better than that in experiment 1 and the improvement is due to a change in the operating conditions, increase in solvent-feed ratio and an increase in the number of extraction stages.

When the results of an extraction are poorer than those predicted by theory, there is something wrong with the manner in which the extraction is carried out. Extraction in experiments 6-8 was poor, varying from 20.8 per cent to 35.8 per cent, and was more than 15 per cent lower in each experiment than that predicted by extraction theory. The character of the feed was changed in experiments 9-11 and better results, extractions of from 62.3 per cent to 71.8 per cent of the solute were obtained.

V. CONCLUSIONS

Preparation of Material for Extraction

1. There is a great variation in the oil content of acorns depending on the condition of the nuts. Sound nut meats contain 36.0 to 40.0 per cent oil. Sprouted nut meats contain some to no oil, depending on the extent of growth. The oil content of wormy nuts depends on whether all or part of the meat has been eaten.

2. There were 74.6 per cent sound nuts, 7.7 per cent sprouted nuts and 17.7 per cent wormy nuts in 140 pounds of the acorns of Quercus catesbaei from Gainesville, Florida.

3. There were 41.2 per cent sound nuts, 27.3 per cent sprouted nuts and 31.5 per cent wormy nuts in 78.75 pounds of mixed acorns from Anderson, South Carolina.

4. Cracking acorns with a hammer, removing the shells by hand and grinding the meats in a hammer mill produces 12.98 pounds of acorn meal from 45.39 pounds of nuts.

5. Cracking acorns in a two roll mill, separating the shells from the meats in a air separator and grinding the meats in a hammer mill produces 32.1 pounds of acorn meal from 73.25 pounds of nuts.

6. Passing acorns through a winnower and fanner separates the meat from the hulls. 682 pounds of acorns yields 366.5 pounds of acorn meats.

7. Expelling part of the oil from 366.5 pounds of acorn meats in an Anderson Duo Expeller gives 8.0 pounds of acorn oil and 355 pounds of expeller cake.

8. Crushing 355 pounds of expeller cake in a two roll mill and screening the crushed cake yields 172 pounds of material which is passed by a quarter inch screen and retained by an eighth inch screen.

Extraction of Acorn Oil

1. Acorn oil can be extracted to the extent of 92.8 per cent from acorn meal on a small scale employing n-butanol as solvent and using a three stage pseudo-countercurrent extraction scheme. 250 ml. wide-mouthed bottles can be used as mixing vessels and a Buechner funnel can be used to separate liquid from solids.

2. Acorn oil can be extracted from acorn meal on a pilot plant scale employing one gallon porcelain ball mill jars as mixing vessels and a Tolhurst T-7893 centrifuge to separate solids from liquid. 5.7 pounds of oil can be obtained from 26.0 pounds of acorn meal using n-butanol as solvent; an extraction of 57.0 per cent of the oil in the meal.

3. Acorn oil can be extracted from acorn meal using a continuous extractor in which the solid material is carried up a 25° slope in a two inch pipe, against a counterflow of solvent, by No. 45 C-1 flights and No. 45 malleable detachable links. This meal is not a suitable feed for this extractor since it packs against the sides of the pipe and is not moved continuously through the extractor. 2.47 pounds of oil can be obtained from 21.0 pounds of acorn meal using n-butanol as solvent; an extraction of 29.4 per cent of the oil in the meal.

4. Acorn oil can be extracted with n-butanol from the plus one eighth inch minus one quarter inch screen sized crushed expeller cake in the continuous extractor. This feed is suitable for this extractor. It does not pack against the sides of the pipe and moves continuously along with the chain. 1.16 pounds of acorn oil can be extracted from 9.5 pounds of expeller-cake, 68.6 per cent of the oil in the cake.

Solvent and Oil Recovery

1. Solvent can be removed from mixtures of acorn oil and n-butanol by vacuum distillation followed by vacuum steam distillation.

2. The oil can be freed of water soluble impurities and suspended solids by washing with water.

This washing gives an oil with an acid number of 5.6.

3. The acid number of the water-washed oil can be reduced to 2.6 by alkali refining.

4. n-Butanol can be recovered from solvent wet extraction residue by vacuum drying in a J. P. Devine Company's No. 1468 vacuum dryer.

Extraction Theory Applied to the Extraction of Acorn Oil

1. Extraction theory predicts an extraction of 94.0 per cent of the oil present in the meal for the three stage small scale extractions, which compares favorably with the 92.8 per cent extraction experimentally realized.

2. Extraction theory indicates an extraction for the centrifuge extractions which is within 4.5 per cent of that realized in the experiment which agrees best with that theory and which is 20.8 per cent above that obtained in the experiment which gives the worst agreement between theory and practice.

3. Extraction theory cannot be applied to a continuous extractor until the number of theoretical stages in that extractor has been determined. Operated as it was, in the extraction of acorn oil, there was less than one theoretical stage in this extractor.

The Relation between the Extraction of Cocoa Butter and the Extraction of Acorn Oil

1. Cocoa butter can be extracted on a small scale from crushed expeller cake in a three stage pseudo-countercurrent operation using both Skellysolve C and Methylene chloride as solvents. In the first case 80.5 per cent of the cocoa-butter present in the feed is extracted, compared to 83.0 per cent extraction predicted by solvent extraction theory. The second case gives 84.5 per cent extraction, compared with a theoretical 86.5 per cent. Solvent extraction theory predicts the extraction to be expected with one solvent as well as with another.

2. Pilot plant extractions of 12.7 pounds of expeller cake containing 1.46 pounds of cocoa-butter with n-butanol as solvent using the continuous extractor produce 0.57 pounds of cocoa-butter, an extraction of 39.0 per cent.

3. Acorn oil is extracted as readily as is cocoa-butter, using the same solvent and the same apparatus. The extraction of cocoa-butter is commercially successful; hence the extraction of acorn oil is a practical operation.

VI. SUMMARY

The experimental work of this thesis is divided into three parts, Laboratory Extractions to Illustrate Solvent Extraction Theory, Pilot Plant Extractions of Cocoa-butter, and Pilot Plant Extractions of Acorn Oil.

Laboratory Extractions to Illustrate Solvent Extraction Theory. The graphical method of leaching calculations derived by Elgin[17] and modified by Kinney[38] was illustrated in its application to solvent extraction by using it to predict the results of laboratory scale extractions.

The first series of such experiments dealt with artificial systems in which all of Elgin's assumptions were valid. The first of these artificial systems was sand, acetic acid, water. A two stage pseudo-countercurrent extraction of 100 grams of a mixture of 25 per cent water, 25 per cent acetic acid and 50 per cent sand with 50 grams of water, gave an experimental extraction of 67.2 per cent of the acetic acid. This agreed exactly with a graphical calculation for a theoretical extraction under similar conditions. A three stage pseudo-countercurrent extraction of 125 grams of a mixture of 40 per cent water, 20 per cent acetic acid, 40 per cent sand with 100 grams of

2.5 per cent acetic acid gave an experimental extraction of 82.6 per cent of the acetic acid present in the original mixture, in agreement with the calculated theoretical extraction.

The second of the artificial systems was sand, acetylene tetrabromide and acetone. A three stage pseudo-countercurrent extraction of 100 grams of a mixture of 25 per cent sand with 100 ml. of acetone gave an experimental extraction of 92.8 per cent of the acetylene tetrabromide in the mixture. A similar four stage extraction of the same amount of this mixture with the same amount of acetone gave an experimental extraction of 95.0 per cent of the acetylene tetrabromide. These experimental values agreed exactly with graphical calculations for theoretical extractions under conditions similar to those of these experiments.

The second series of laboratory extractions dealt with natural systems in which Elgin's assumptions might or might not be valid. The first of these natural systems was Skellysolve C, cocoa-butter, inert cocoa-material. A three stage pseudo-countercurrent extraction of 50 grams of solid material containing 8.19 per cent of cocoa-butter and 75 ml. of Skellysolve C with 100 ml. of Skellysolve C gave an extraction of 80.5 per cent of the cocoa-butter, as compared with 83.0 per cent predicted by a graphical calculation for a theoretical extraction under similar conditions.

A second cocoa-butter extraction was similar to the first except that methylene chloride was used as the solvent instead of Skellysolve C. The same amount of solid material, 50 grams, containing 7.0 per cent of cocoa-butter and 75 ml. of methylene chloride. 84.5 per cent of the cocoa-butter was extracted as compared with 86.5 per cent predicted by calculation.

Acorn oil was extracted from acorn meal with n-butanol in a three stage pseudo-countercurrent process with a Buechner funnel used as an interstage filter. 40.0 grams of meal was shaken with 80.0 grams of solvent for 15 minutes; the mixture was then poured into the Buechner funnel and filtered dry. The solid material was removed from the funnel to be extracted twice more, following the pseudo-countercurrent scheme. The meal contained 36.0 per cent of acorn oil and 92.8 per cent of this oil was experimentally extracted, compared to an extraction of 94.0 per cent predicted by a graphical calculation for a theoretical extraction under the experimental conditions.

n-Butanol was found by this experiment, and other preliminary experiments, to be a satisfactory solvent for the removal of acorn oil from acorn meal. It was selected for the large scale extraction studies because it has a comparatively high flash point, 90°F., it is not toxic, it can be removed from solvent oil-mixtures without great difficulty, and it could be obtained in the quantities necessary for this work.

<u>Pilot Plant Extraction of Cocoa butter</u>. Four pilot plant extractions of cocoa butter from crushed expeller cake were made. These extractions were carried out to test the performance of the continuous chain extractor and to provide data which would enable a comparison to be made between the extraction of cocoa butter from cocoa expeller cake and of acorn oil from acorn meal and acorn expeller cake.

The crushed cocoa expeller cake was produced by passing cocoa beans through the Anderson Duo Expeller cycle shown in Fig. 46. It is the same material that Rockwood and Company have successfully extracted since 1938. The expeller cake was supplied by this company.

12.7 pounds of cocoa expeller cake were extracted with 24.0 pounds of n-butanol to produce

0.58 pounds of cocoa-butter, an average extraction of 38.8 per cent of the cocoa-butter in the feed.

Pilot Plant Extraction of Acorn Oil. Acorn oil has been produced on a pilot plant scale from 752.5 pounds of acorns. The process employed in this pilot plant study consists of three steps: preparation of acorns for extraction, extraction of acorn oil, and, solvent and oil recovery. The operations constituting these three steps are presented in the quantitative flow diagrams; Fig. 46, Preparation of Acorns for Extraction; Fig. 47, Extraction of Acorn Oil; and Fig. 48, Solvent and Oil Recovery. The results of the pilot plant operations are given in these same flow diagrams.

The acorns were obtained in as nearly a commercial manner as possible by offering a price of three cents a pound for them. Three hundred and sixty-one pounds of the nuts of Quercus catesbaei and Quercus Virginiana were procured from Gainesville, Florida. Five hundred pounds of a mixture of White, Red and Spanish Oak acorns came from Anderson, South Carolina.

The following equipment was used in the operations shown in Fig. 46:-

Rolls, Sturtevant No. TR 32 Two Roller Mill.

Hammer Mill, Raymond No. 40127 Laboratory Hammer Mill.

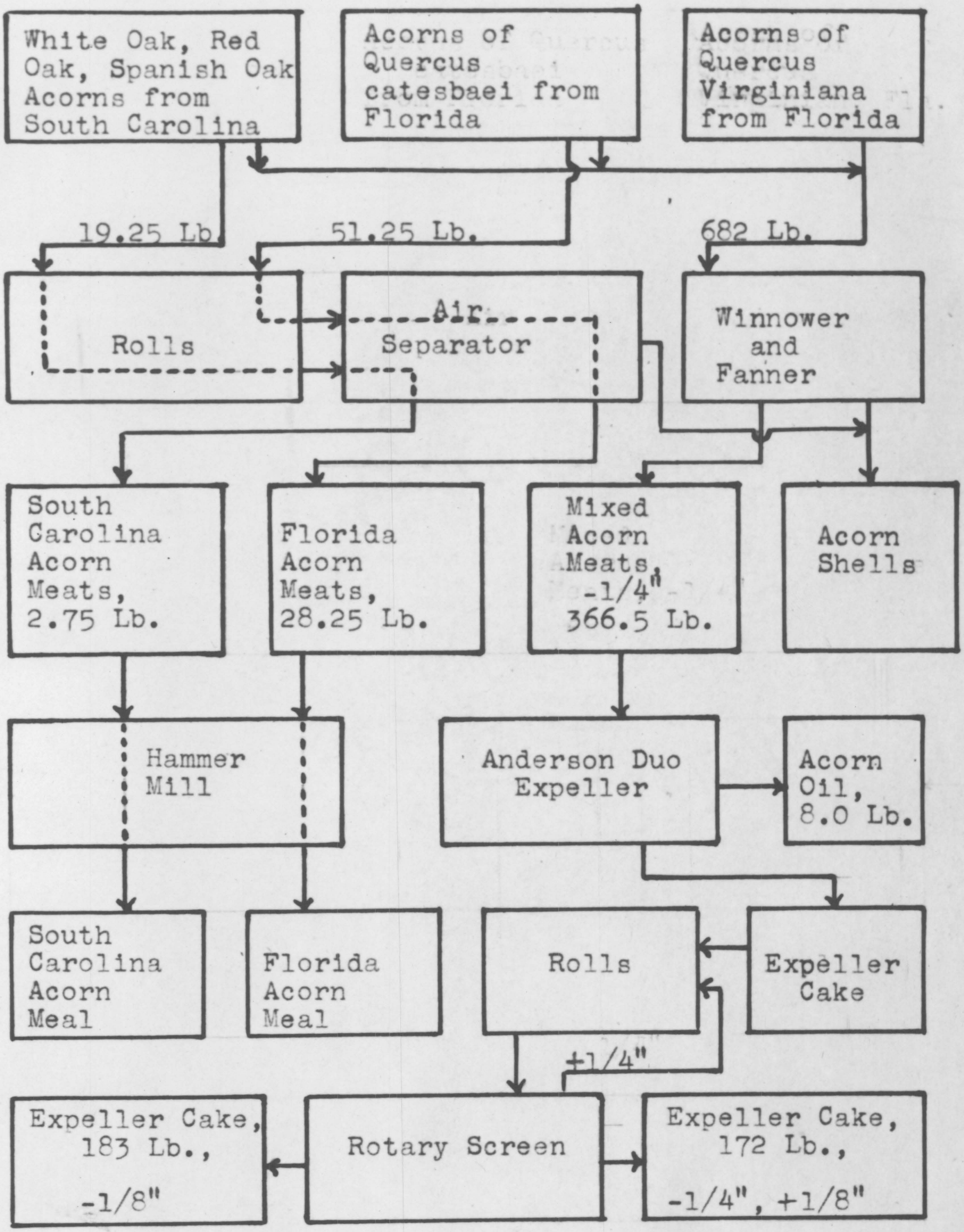


Figure 46.

Preparation of Acorns for Extraction.

Air Separator. Raymond No. 41344 Laboratory Mechanical Separator.

Winnower and Fanner. Built by J. H. Lehman for Rockwood and Company. This machine combines a roll for cracking and crushing the nuts with a revolving screen for separation of different sized particles and an air blast for blowing the light hull fragments away from the heavier nut meats.

Duo Expeller. A V. D. Anderson Company's Duo Expeller.

The equipment shown in Fig. 47 is:-

Centrifuge Extractor. A mixer, an Eimer and Amend No. 8-390 porcelain ball mill jar of one gallon capacity. This jar was rotated in a double motor driven jar mill, as furnished by Paul O. Abbe Inc. Solids were separated from solvent in a Tolhurst No. T-7893 centrifuge.

Continuous Extractor. This apparatus was constructed as part of the work of this thesis. It consisted essentially of a fourteen foot length of two inch standard galvanized steel pipe bent so that a short section was vertical with the horizontal plane and a long inclined section beyond the bend made an angle of about

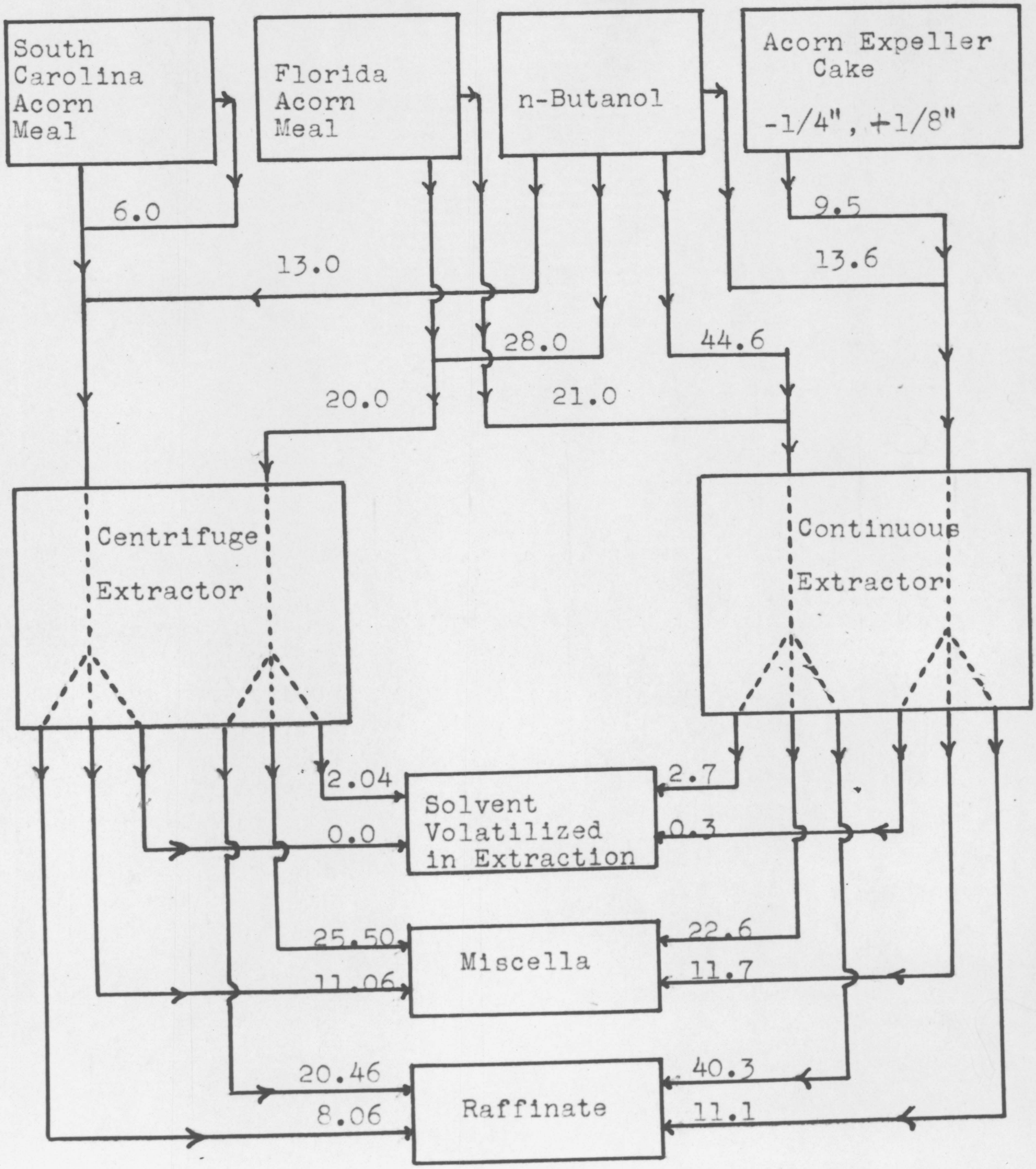


Figure 47.

Extraction of Acorn Oil

(All figures are pounds)

25° with this plane. A 28¾ foot continuous chain made up of No. 45 malleable detachable links with No. 45 C-1 flights every fourth link ran in at the top of the vertical section, up the inclined section and out at the top of this latter section. The extraction section, that part of this incline from the bottom of the bend to the solvent inlet, was 6½ feet long. The solid material being extracted was carried up the incline by the chain against a counterflow of solvent. There was a 3½ foot drainage section above the solvent inlet. The chain carried the solids through this drainage section before running out of the pipe and dropping the drained solids onto a discharge apron. The miscella flowed out of the vertical section at the solvent inlet level.

The equipment used in the steps represented in Fig. 48 is:-

<u>Still</u>, F. J. Stokes Co. vacuum still with condenser and vacuum receiver, No. 84260.

<u>Vacuum Dryer</u>, J. P. Devine Co., No. 1468.

<u>Vacuum Pump</u>, Kinney Mfg. Co. VSD, 5x5 Vacuum Pump.

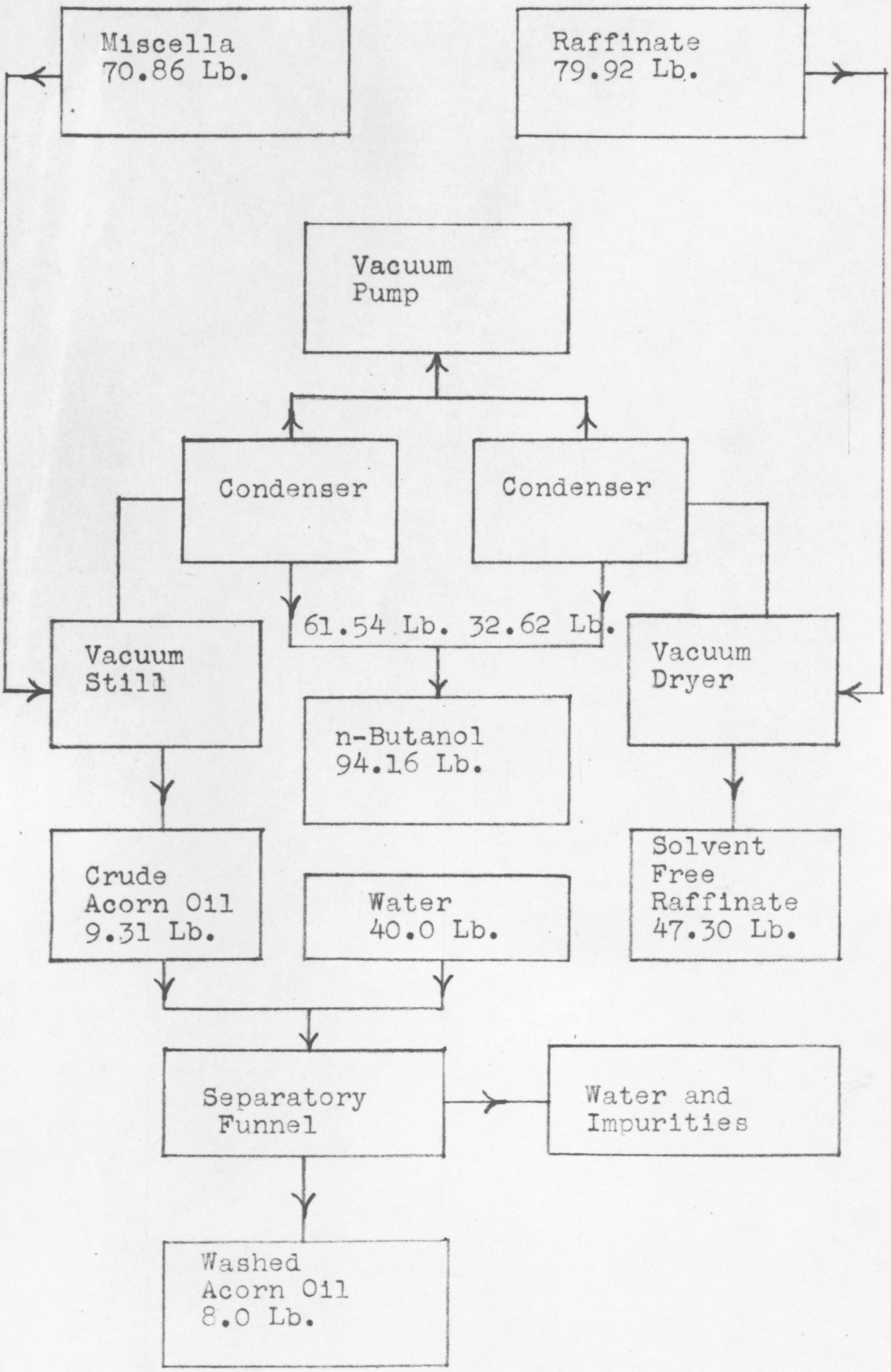


Figure 48.

Solvent and Oil Recovery

Separatory Funnel. Three two liter laboratory separatory funnels, glass.

The miscella was distilled under a vacuum of 25 inches of mercury. Solvent, n-butanol, was recovered by this operation. The still was equipped so that steam could be blown through the charge and traces of solvent were removed from the acorn oil by steaming out under vacuum. After this operation a 2 inch gate valve at the bottom of the still was opened and the residue was discharged. This residue divided into two layers, an upper acorn oil layer, and a lower water layer. The acorn oil was freed of impurities such as iron tannate and suspended solids by washing with water until the wash water was uncolored.

Approximately three gallons of crude acorn oil were produced by these pilot plant operations, (about half of this oil resulted from work reported in this thesis, and the rest came from acorn meal and acorn expeller cake processed in preliminary experiments).

A sample of this crude acorn oil from Quercus catesbaei had the following characteristics:-

Specific gravity at 25°C., 0.907, index of refraction at 25°C., 1.4677, acid no. 5.6, saponification number 190 and iodine number (Wijs') 106.

It was refined to give an oil of:-

Specific gravity at 25°C., 0.903, index of refraction at 25°C., 1.4684, acid number 2.6, saponification number 188 and iodine number (Wijs') 107.

In addition to the oil prepared by the pilot plant extractions, there were eight pounds of oil collected from the expelling operation with the V. D. Anderson Duo Expeller at Rockwood and Company. This expelled oil was filtered to free it from a small amount of solid material to give an oil of:-

Specific gravity at 25°C. of 0.907, index of refraction at 25°C. of 1.4669, acid number of 29.5, saponification number 192 and iodine number (Wijs') 105.

A total of 861 pounds of acorns were handled in these studies of acorn oil extraction. Of this total 752.2 pounds were processed in pilot plant experiments. The difference between these two figures, 108.5 pounds, represents material used in preliminary studies and wormy or sprouted nuts which were discarded. Not all of the acorn meat obtained from the 752.5 pounds of nuts was extracted to produce acorn oil. Only 23.1 pounds of crushed expeller cake, of the 172 pounds available for extraction, were used.

Acorn oil was extracted from 49.1 pounds of acorn oil-bearing material to give 9.32 pounds of crude acorn oil.

Acorn oil was expelled from 682 pounds of acorn meat to give 8.0 pounds of crude acorn oil.

VII. BIBLIOGRAPHY

1. Andès, L. E., Vegetable Fats and Oils, 4th Edition, p. 259-273. D. Van Nostrand Co., New York, (1925).

2. Association of Official Agricultural Chemists, Official and Tentative Methods of Analysis, 2nd Edition, p. 281. A. O. A. C., Washington, D. C., (1925).

3. Allis-Chalmers Plant Flow Sheet, Soybean Oil Extraction with n-Hexane. Chem. and Met. Eng., 48, 128-131, (Sept. 1941).

4. Badger, W. L. and McCabe, W. L., Elements of Chemical Engineering, p. 427-434. McGraw-Hill Book Co., New York, (1936).

5. Baker, E. M., Simplifying the Calculation of Countercurrent Extractions. Chem. and Met. Eng. 42, 669-671, (Dec. 1935).

6. Baker, J. L. and Hulton, H. F. E., Analytical Examination of Acorns and Horse Chestnuts. Analyst, 42, 351-355, (1917).

7. Bighouse, H. H., Apparatus for Extracting Oils from Oleaginous Materials. U. S. Patent 2,096,728, Oct. 26, 1937.

8. Bilbe, C. W., Continuous Solvent Extraction of Vegetable Oils. Mechanical Engineering, 63, 357-360, (1941).

9. Bonotto, M., Process for Removing Solvent from Solvent-Treated Material. U. S. Patent 2,086,180, July 6, 1937.

10. Bonotto, M., Process for Extracting Oils and Fats from Materials Containing the Same. U. S. Patent 2,112,805, March 29, 1938.

11. Bonotto, M., Process and Apparatus for Extraction of Oils, Fats and Other Soluble Constituents from Materials Containing the Same. U. S. Patent 2,156,236, April, 25, 1939.

12. Brown, F. C., Acorns Near Anderson, South Carolina. Private Communication, December 1942.

13. Cypers, J. F., Scheu, G. and Jones, W. T., Continuous Solvent Extraction Apparatus. U. S. Patent 2,278,647, April 7, 1942.

14. Disque, F. C., Hydrogenation of Acorn Oil. Brooklyn, New York. Private Communication. June, 1942.

15. Elgin, J. C., Graphical Calculation of Leaching Operations. Trans. A. I. Ch. E., 32, 451-471, (1936).

16. Elgin, J. C., "Extraction" in Chemical Engineers' Handbook, p. 1219, Perry, J. H., Editor, 2nd Edition. McGraw-Hill Book Co., New York, (1941).

17. Evans, T. W., Countercurrent and Multiple Extraction, Ind. Eng. Chem., 26, 860-864, (1936).

18. Figura, V., The Food Value of Acorns and the Possibility of Their Utilization as Food in the Human Diet. Atti. accad., Lincei 23, 707-710, (1936). Original not seen. Chem. Abst. 31, 1511, (1937).

19. Freeman, A. F. and McKinney, R. S., Tung Oil by a Solvent Process. Oil, Paint and Drug Reporter 140, 5, 38, 45, (1941).

20. Freeman, A. F. and McKinney, R. S., Tung Oil Produced by a Solvent Process. Oil, Paint and Drug Reporter 139, 3, 45 (1941).

21. Garrett, F. T., Encyclopedia of Practical Cookery, Vol. I., p. 3. J. Arnot Penman, New York, (1899).

22. Getman, F. H. and Daniels, F., Outlines of Theoretical Chemistry, p. 197, 6th Edition. John Wiley and Sons, New York, (1940).

23. Goss, W. H., Modern Practice in Solvent Extraction, Chem. and Met. Eng., 48, 80-83, (April 1941).

24. Griffin, R. C., Technical Methods of Analysis, 1st Edition, p 231. McGraw-Hill Book Co., New York, (1921).

25. ibid., p. 232.

26. Haeseler, K., Factice from Acorn Oil. Brooklyn, New York, Private Communication, October, 1942.

27. Hawley, L. F., Numberical Relation between Cells and Treatments in Extraction Processes, Ind. Eng. Chem., 12, 493-496, (1920).

28. Heitmann, H., Apparatus for the Continuous Extraction of Material, U. S. Patent 2,043,409, June 9, 1936.

29. Hildebrandt, K. H., The Continuous Extraction of Seeds and the Equipment for its Accomplishment. Fette u. Seifen 46, 350-352, (1939).

30. Horvath, A. A., The Soybean Industry, p. 42-58. Chemical Publishing Co. of New York, (1938).

31. Hutchins, W. D., Acorn Oil. Oil and Soap, 14, 148, (1937).

32. Hunter, T. G. and Nash, A. W., Liquid-Liquid Extraction Systems, Ind. Eng. Chem., 27, 836-845, (1935).

33. Jamieson, G. S., Vegetable Fats and Oils, 2nd Edition, p. 19-22. Reinhold Publishing Corp., New York, (1943).

34. Kinney, G. F., Leaching Calculations, Ind. and Eng. Chem., 34, 1102, (1942).

35. Kinney, G. F., Per cent Oil in Sprouted Acorns, Brooklyn, New York, Private Communication, March, 1942.

36. Lamprey, L., The Story of Cookery, p. 146. Frederick Stokes, New York, (1940).

37. Lange, N. A., Handbook of Chemistry, p. 482. Handbook Publishers Inc., Sandusky, Ohio, (1934).

38. Lange, N. A., Handbook of Chemistry, p. 1048-1049. Handbook Publishers' Inc., Sandusky, Ohio, (1939).

39. Levine, A. A., Sweeney, O. R., and Kircher, Jr., C. E., Apparatus for Extraction, U. S. Patent 2,264,390, Dec. 2, 1941.

40. Limonov, P. and Kalugin, Ya., Production of Alcohol from Acorns. Brodilnaya Prom. 10, No. 4, 18-20, (1933). Original not seen. Chem. Abst. 28, 7415, (1934).

41. McBride, C. W., Chemical Engineering Advances in Soybean Processing, Chem. and Met., 47, 614-618, (1940).

42. McDonald, D., Solvent Extraction of Oil from Oleaginous Material, U. S. Patent 2,198,413, April 23, 1940.

43. McKinney, R. S., Problems in the Field of Tung Oil Extraction. Oil, Paint and Drug Reporter, 140, 5, 33, 34, (1941).

44. McKinney, R. S., Rose, W. G., and Kennedy, A. B., Continuous Process for Solvent Extraction of Tung Oil, Ind. and Eng. Chem., 36, No. 3, 138-140, (1944).

45. Monarca, C. J. and Lynn, E. V., Acorns of Quercus rubra, J. Am. Pharm. Assoc., 26, 493-495, (1937).

46. Muraoka, H. J., Electric Treatment of Horse Chestnuts and Acorns. Electrochemical Association, Japan, 3, 289-292, (1935). Original not seen. Chem. Abst. 30, 3268, (1936).

47. Newberry, J. S., Food and Fiber Plants of the North American Indians. Popular Science Monthly, 32, 38, (1887-1888).

48. O'Brien, W. J. and Brett, R. C., Apparatus for Solvent Extraction, U. S. Patent 2,074,988, March 23, 1937.

49. Olcott, H. S., Solvent Extraction of Cottonseed Oil, Ind. and Eng. Chem., 33, 611-615, (1941).

50. Pattee, E. C., Continuous Solvent Extraction Apparatus, U. S. Patent 2,187,890, January 23, 1940.

51. Perry, G. S., Keys to the Oaks of the Tennessee Valley. TVA Bulletin, March 15, 1941.

52. Perry, A., Acorns in Georgia. Brooklyn, New York, Private Communication, August, 1942.

53. Porcher, F. P., Resources of the Southern Fields and Forests, p. 620-621. Walker, Evans and Cogswell, Charleston, South Carolina, (1839).

54. ibid., p. 614.

55. Prentice, E. P., Hunger and History, p. 87-93, 110, Harper and Bros., New York, (1939).

56. Puntambekar, S. V. and Krishna, S., Indian Acorn Oils. J. Indian Chem. Soc. 11, No. 10, 721-726, (1934). Original not seen. Chem. Abst. 29, 2007, (1935).

57. Puntambekar, S. V. and Varma, B. S., Utilization of Indian Acorns. Indian Forester 60, 722-725, (1934). Original not seen. Chem. Abst. 31, 4148, (1937).

58. Ravenscroft, E. A., Extraction of Solids with Liquids, Ind. Eng. Chem., 28, 851-855, (1936).

59. Remlinger, P. and Charrier, H., The Ballota or "gland doux" in Human Nutrition in Morocco. Rev. hyg. med. prevent 13, 919-925, (1931). Original not seen. Chem. Abst. 26, 5355, (1932).

60. Roberts, E. N., Recovery of Solvents from Oil, U. S. Patent 2,081,844, May 25, 1937.

61. Rosenthal, H. and Trevithick, H. P., Low-Boiling Hydrocarbons as Oil-Extraction Media. Oil and Soap, 11, 133, (1934). Chem. Abst. 28, 5267, (1934).

62. Schmid, A., The Extractor, Based on the Hansa-Muhle System, Its Construction and Manner of Operation. Fette u. Seifen 46, 464-465, (1939).

63. Schonfeld, H., Chemie und Technologie der Fette und Fettproduckte. Vol. I. Chemie und Gewinnung der Fette, p. 591-665, and p. 667-681. Julius Springer, Wein, 1936.

64. Soyer, A., Panthropheon, p. 23-24. Simphin and Marshall, London, (1853).

65. Sugisaki, Seisaku, Alcoholic Fermentation of Acorn, Quercus glanca Thumb. I. Saccharification by Acid. J. Agr. Chem. Soc., Japan, 15, 1173-1178, (1939). Original not seen. Chem. Abst. 34, 3430, (1940).

66. Sugisaki, Seisaku, Alcoholic Fermentation of Acorn. II. Amylo Process. J. Agr. Chem. Soc., Japan, 16, 281-287, (1940). Original not seen. Chem. Abst. 34, 6007, (1940).

67. U. S. Tariff Commission, Fats, Oils and Oil-Bearing Materials in the United States. Washington, D. C., (1941).

68. Vahlteich, H. W., Custom-Built Fats, Chem. and Eng. News, 21, 1238-1242, (1943).

69. Verrill, A. H., Foods America Gave the World, p. 178, 239. L. C. Page and Co., Boston, (1937).

70. Wainio, W. W. and Forbes, E. B., Chemical Composition of Forest Fruits and Nuts from Pennsylvania. J. Agr. Research, 62, 627-635, (1941).

71. Webster, T. and Mrs. Parkes, American Family Encyclopedia, Paragraphs 2686, 4277. J. C. Derbey, New York, (1854).

72. Winton, A. L. and Winton, K. B., Structure and Composition of Foods, p. 300. John Wiley and Sons, New York, (1932).

73. Wittka, F., Acorn Oil. Fette u. Seifen 44, 464-465, (1937). Original not seen. Chem. Abst. 32, 1128, (1938).

74. Wittka, F., Reported in Handbuch der Lebensmittelchemie. Vol. IV. Fette und Seifen, p. 469. Julius Springer, Berlin, (1939).

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