EXTRACTION OF WAX FROM SORGHUM BRAN

by

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B. S., National Taiwan University, China, 1951

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A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

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INTRODUCTION

One of the functions of the Agricultural Experiment Station is the never ending search for means of better and fuller utilization of the agricultural products that are of particular interest in the state of Kansas. In line with this broad objective, the extraction of economically valuable lipid materials from the sorghum bran has been studied in several theses in the Departments of Chemical Engineering and Chemistry in recent years. Generally the emphasis has been placed upon either the chemical and physical properties of these lipides or the equipment design and performance for the solvent extraction operation. A brief review of the previous work is presented in the ensuing section.

All the soluble material that is extracted from the bran is thenceforth referred to as "miscella" and its weight expressed on a solvent-free basis. The fraction of the miscella that remains in the solid state at room temperature after the separation, is referred to as "wax"; the other fraction being the "oil". The objectives of the present investigation can be stated as follows:

1. To develop an economically feasible process for the separation of the wax and oil fractions in the miscella. Since the sorghum wax resembles the commercially valuable Carnauba wax (Bunger and Kummerow, 2) in many of its physical properties, the desired process must recover the wax fraction more completely and in purer form whereas the yield and quality of the oil fraction is only of secondary importance.

2. Also to see whether or not some new solvent, or mixture of solvents, could be found that would be superior to the one used previously, namely, Skellysolve-B, a commercial product consisting of mixed hexanes. The first

criterion is its selectivity; that is, not only must it be able to extract large amounts of miscella, but furthermore it must extract wax in preference to oil.

The analytical procedure used previously in the laboratory to determine the wax content of miscella was based on the precipitative crystallization principle using acetone as the precipitative solvent. For large scale separation, this method has some serious inherent difficulties: One, the refrigeration cost would be considerable. Two, the filtration of fine wax crystals would be slow. If this method could not be successfully developed for production purposes, then other alternatives must be investigated, such as:

Separation by differences in molecular size and shape--thermal diffusion.

Separation by differences in volatility--fractional distillation.

Separation by differences in spatial and molecular structure--urea-complex or thio urea-complex method.

Separation by differences in solubility--solvent extraxtion.

Thermal diffusion is inherently a slow process which has little possibility of developing into a production process on the industrial scale. Because of the thermal sensitivity of the materials, distillation would have to be performed under vacuum. Through literature research and exploratory experimentations, these two approaches were abandoned, at least tentatively. During the course of the present investigation, the urea-complex method was studied and a laboratory procedure evolved that appeared to be promising. Also an equipment flow sheet of this process was prepared to serve as a basis for the pre-construction cost estimation of an industrial plant. The laboratory procedures, experimental data and their evaluation are presented in detail in the latter part of the body of this report.

If a sufficiently selective solvent could be found, then it would be possible to recover wax from bran by a single step of solvent extraction. The selectivety of seven single solvents and two azeotropic mixtures has been studied in a series of extraction runs with a Pyrex Soxhlet extractor. The results are presented in the first part of the body of this thesis.

PREVIOUS WORK

A brief review of several previous theses carried out in the Chemical Engineering Department during the years from 1947 through 1951 is as follows:

Foveaux (3) investigated the various possible solvents for wax and oil extraction. After a comparison of properties he concluded that trichloroethylene would be a suitable solvent, with the major drawback being the high cost per gallon. He also built and operated a screw type conveyor for extraction of the whole grain. Wax was his main product.

French (4), following the recommendation of Kummerow (7) and Foveaux (3) that the wax extraction be carried out on the bran fraction only, obtained data on the equilibrium values of wax and solvent. The data thus gathered were on a batch process with extraction temperatures from 68 to 122° F. He also presented a method for transposing these data to the design of a continuous extraction unit.

Medlin (9) built and operated a pilot plant that used a basket type of conveyor and trichloroethylene for the extraction operation. He found, through a short series of runs at a temperature of 160° F. over small time intervals, that the main product was wax. The recommendation was made that work be initiated on the possibility of obtaining a commercial wax, without

further refining by the selection of optimum operating conditions.

Hub (5) carried on with Medlin's extraction unit making many minor changes in the construction of the unit. After several futile attempts to reproduce Medlin's results, Hub came to the conclusion that the basket type of extraction unit was not the one for the particular job at hand. He pointed out that because the unit was not enclosed in a vapor-tight housing, it was virtually impossible to maintain the extracting temperature high enough to do any good. With that he brought the entire project back to the small scale laboratory and conducted a series of extractions in an attempt to obtain valuable data which could be used in the design of some other more desirable type of extraction unit. Hub presented curves showing the effect of temperature, time of contact, solvent ratio, and moisture content of the bran on the amounts of wax and oil extracted. All of his data apply when using trichloroethylene as the solvent.

Kehm (6) carried out Hub's investigation by using Skellysolve-B as a solvent whereas Hub's investigation was confined to using trichloroethylene as the solvent. Kehm also presented breakdown curves of the miscella (total extractables) curves into its component curves, that of wax and oil respectively. He found that the bran previously used had not been properly milled and that the bulk of the weight could be attributed to grain fractions other than bran. He made a more thorough separation of the bran and ran extractions on each separated fraction. He found that when the bran is properly milled, wax is the predominant constituent and oil is a secondary constituent. Excellent results were obtained with the pure bran fraction. He also made a crude economic analysis of a proposed twenty-five ton Kennedy unit indicating that the extraction process should be an economical one.

The following is a brief review of some related work carried out previously elsewhere:

Kummerow (7) reported that the sorghum wax was removed from the hull by extracting the unground grain with Skellysolve-B and the oil removed from the germ and endosperm by extracting the ground grain with Skellysolve-F. This suggests that it might be possible to extract the wax and oil from sorghum bran by fractional solvent extraction, using such selective solvents as Skellysolve-B and Skellysolve-F, alternately.

Warth (16) indicated that carnauba wax is composed of the following substances:

(1) A hydrocarbon (m.p. 59° C.), probably heptacosane ($C_{27}H_{56}$).

(2) An alcohol ($C_{26}H_{52}OH$, m.p. 76° C.), probably ceryl alcohol, and not necessarily the n-alcohol, 1-hexacosanol.

(3) An alcohol ($C_{27}H_{55}OH$, m.p. 80-82.5° C.), which has been named carboceryl alcohol, an isomer of 1-heptacosanol.

(4) An alcohol ($C_{28}H_{57}OH$, m. p. 83.2° C.), identified as octacosanol.

(5) An alcohol ($C_{30}H_{61}OH$, m.p. 86.4-86.8° C.), which is probably triacontanol.

(6) An alcohol ($C_{32}H_{65}OH$, m.p. 89.4° C.), in greater proportion than the C_{30} alcohol, and isolated by Koonce and Brown in the proved state of 100% purity, probably 1-dotriacontanol.

(7) A dihydric alcohol [$C_{25}H_{50}(OH)_2$, m.p. 103.5-103.8° C.] convertible to the corresponding dibasic acid (m.p. 102.5° C.).

(8) Carnaubic acid ($C_{24}H_{48}O_2$, m.p. 72.5° C.), described as an isomer of lignoceric acid (m.p. 84.2° C.).

(9) An acid ($C_{27}H_{54}O_2$, m.p. 82.5° C.). The acid was that first discovered by Brodie in the free state, but is now conceded to be a

mixed dimer of the C_{26} and C_{28} n-aliphatic acids.

(10) Cerotic acid ($C_{26}H_{52}O_2$, m.p. 79° C.), which is almost entirely combined with myricyl alcohol to form the alkyl ester myricyl cerotate.

(11) An ω-lactone of 21-hydroxyl-1-uncosanic acid (m.p. 103.5° C.).

Since the melting point of sorghum wax is slightly lower than that of carnauba wax, the composition of sorghum wax may consist more of those lower melting substances than carnauba wax.

Schwarz (13) included an official list from the Brazilian Ministry of Agriculture which describes the specifications of various commercial types of carnauba wax. These types are designated as "flow type","first type", "medium type", "sandy type", and "fat type". The specifications include wax, moisture and impurity percentages, Iodine index and color description.

MATERIALS

The bran used in the entire work was obtained from Grain Products Company, Dodge City, Kansas, in May, 1954. Average moisture content: 10% by weight of bran dried under 26 inches Hg vacuum at 100° C for six hours.

Screen Analysis: (15 minutes shaking)	Weight %
below 20 mesh	11.06 ± 1.46
20 - 30 mesh	13.37 ± 1.87
30 - 40 mesh	25.42 ± 2.69
40 - 50 mesh	29.11 ± 2.01
50 - 70 mesh	15.83 ± 1.81
Above 70 mesh	5.21 ± 1.35
	100.00

The solvents used and their sources are listed below:

	Source	Grade	Boiling Point °C
Skellysolve-B	Skelly Oil Company Kansas City, Missouri	Technical	69
cetone	Chemistry Department	Technical	56
Methyl Ethyl Ketone	Missouri Solvent and Chemical Co., St. Louis, Missouri	Technical	80
Absolute Alcohol	Chemistry Department	Technical	78
Secondary Butyl Alcohol	Eastman Kodak Company Rochester, New York	Reagent	99.5
n-Butyl Ether	Eastman Kodak Company Rochester, New York	Reagent	142.4
Ethylene Dichloride	Chemistry Department	Technical	84
Methanol	Chemistry Department	Technical	67
Urea	Merck Company Rahway, New Jersey	Reagent	M.P. 132 - 133°C.

GLASS SOXHLET EXTRACTION AND ANALYSIS OF WAX AND OIL IN MISCELLA

Procedure of Using Soxhlet Extractor

A photograph of the Pyrex glass Soxhlet extractor is shown on Plate I. At the start of each run, about 30 grams of bran were carefully weighed and charged into the fresh extraction thimble. The bran was extracted with 250 ml of solvent for eight hours. After removing the hot plate, the thimble was lifted above the solvent level to allow all the excess solvent to drain back into the 300 ml flat bottom flask. Usually two or three minutes draining time was sufficient. Then the flask containing all the collected extract

was disconnected from the Soxhlet assembly and placed on a steam cone to recover the bulk of the solvent by distillation. Next the flask was transferred into a vacuum oven and maintained at 90°C for about eight minutes to drive off the last traces of solvent from the miscella. After cooling over calcium chloride for 30 minutes, the flask and its contents were weighed to determine the amount of miscella obtained.

Separation of Wax from Oil by the Acetone Method

In this part of the experimental work, the term wax refers to that portion of the miscella which remains solid in acetone at 6°C. Twenty-five ml of acetone were added to the molten miscella which was obtained from each Soxhlet extraction run. A swirling action was applied to the flask to insure sufficient mixing. Then another 25 ml. of acetone were added to wash down any miscella adhering to the inside surfaces of the flask. The flasks were stoppered and placed in a refrigerator at 6°C for at least 16 hours. Then the solvent containing the oil fraction was filtered from the wax through an asbestos-lined Gooch crucible into an evaporating dish. Two additional 10-ml. portions of cold (6°C) acetone were used to rinse the flask and wash the filter cake.

The above mentioned filtration was carried out by using a vacuum desiccator with the crucible mounted in the top of the desiccator and the evaporating dish inside the desiccator as shown in Plate 1. The crucible was filled with pure pre-cooled acetone before turning on the vacuum valve. As the vacuum valve was opened, the acetone-miscella mixture was slowly poured into the crucible while the pure acetone receded. The filtration proceeded faster when the crucible was not allowed to be sucked empty before

all the acetone-miscella mixture had been poured from the flask. Before washing, the wax cake should be allowed to air-dry first, otherwise the filtration through the wet cake would be so slow as to allow the crucible and wash acetone sufficient time to warm up to a temperature high enough to dissolve some of the wax. Then the crucible was placed in a vacuum drying oven at 90°C for about five minutes or until the wax began to melt around the edge of the cake. After cooling for 30 minutes over calcium chloride, the crucible and wax were weighed.

The bulk of acetone in the evaporating dish was evaporated over a steam cone; the residual acetone and moisture were removed from the flasks and evaporating dishes by heating in a vacuum drying oven for five minutes at 90°C. After cooling for 30 minutes over calcium chloride, the containers and contents were weighed. The wax content of a sample was determined from the combined weights of the wax in the flask and crucible, while the oil was found in the evaporating dish. The procedure of this method is summarized in the flow diagram in Fig. 1.

Summary of Results

Eight single solvents: skellysolve-B, acetone, methyl-ethyl ketone, absolute alcohol, secondary butyl alcohol, n-butyl ether, ethylene dichloride and methanol, have been tried for Soxhlet extraction. Acetone was used as solvent for the separation of the oil and wax fractions in the miscella. The following results were obtained:

The largest amount of miscella was obtained by using absolute alcohol as the extracting solvent and this gave also the highest weight ratio between wax and oil. During the extractions, however, suspension of wax-like material

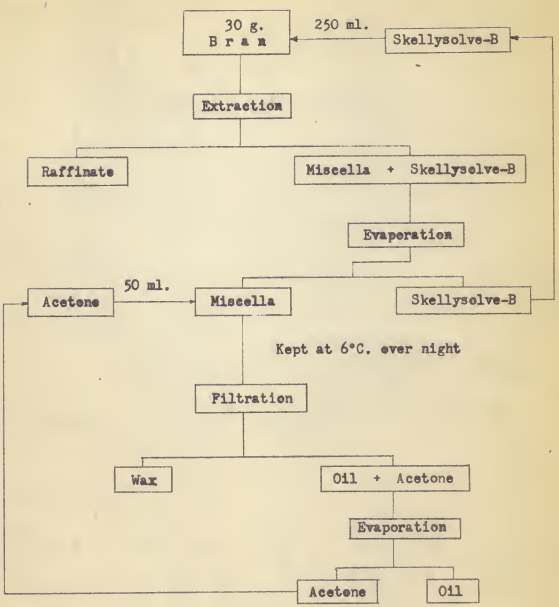


Fig. 1. Flow diagram of acetone method, bench scale.

EXPLANATION OF PLATE I

Soxhlet Extractor and Crude Separation Equipment

A. Vacuum desiccator

B. Asbestos-lined Gooch crucible

C. Evaporating dish

D. Two-way stopcock

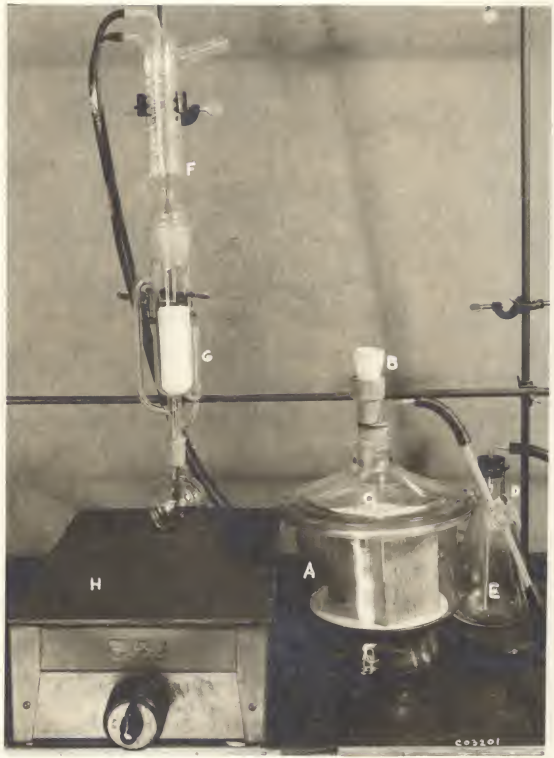
E. Trap

F. Condenser

G. Soxhlet extractor and thimble

H. Hot plate

PLATE I



came out of the solvent and obstructed the overflow tube in the Soxhlet so as to prevent the recycle of solvent. Bunger and Kummerow (2) indicate that this solid is probably a polymerization product of the wax and the alcohol.

Also two azeotropic mixtures have been used as the extracting solvent: ethylene dichloride-heptane-water (volume ration 2:2:1) and methyl-ethyl ketone-heptane-water (volume ration 2:2:1). Sixteen extracting runs were made with each mixture and no increase in the yield of miscella was detected over the single solvents. But after cooling to room temperature some wax-like solid material was seen to float at the water-organic interface of the mixed solvent. Also the bran in the extract thimble was partially disintegrated by the hot water. The weight ratio between the wax and oil fractions was also the same as that obtained by single solvents, but the color of both fractions was a little darker.

The experimental data seem to suggest the following correlation between the azeotrope mixture and single solvents:

$$W = N_a W_a + N_b W_b + - - - -$$

Where W = the weight of miscella extracted with mixed solvent.

$N_{a,b}$ = the mole fraction of solvent a,b, ---- respectively

$W_{a,b}$ = the weight of miscella extracted with pure solvent a, b, ---- respectively.

The melting point of the wax fractions was determined with the Fisher-Johns Melting Point Apparatus; the refractive index of the oil fraction was determined with the Abbe refractometer at 28° C. The readings are shown in Table 1 below. The higher melting points indicate better separations of wax from oil, and a narrow melting point range indicates the purity of the wax.

Table 1. Melting point of waxes and refractive index of oil fractions

Solvent Used	Melting point Range °C.	Refractive Index at 28° C.
Skellysolve-B	67 -74	1.4698
Acetone	73 - 76	1.4652
Methyl ethyl ketone	69 - 74	1.4661
Absolute alcohol	72 - 74	1.4652
Secondary butyl alcohol	72 - 76	1.4652
n-Butyl ether	61 - 65	1.4729
Ethylene di-chloride	82 - 84	1.4652
Methanol	71 - 75	1.4652
Methy ethyl ketone-heptane-water	63 - 69	1.4652
Ethylene dichlororide-heptane-water	64 - 68	1.4652

The color of the wax fraction from the Skellysolve-B extract was grayish green and the oil fraction was dark green. Both wax and oil from the absolute alcohol and methanol extracts were deep tan. The products from all other solvents were tan. It was also observed that in a few earlier extraction runs where the temperature of the hot plate was set too high, the color of the resulting fractions were darker.

Altogether 16 extractions were made with each solvent. The results are averaged and shown in Tabe 2. The complete data are included in the Appendix.

Table 2. Summary of the results of Soxhlet extractions and the separation of wax by the acetone method at 6° C.

Solvent	(wt. per wt. of dry Bran) x 100			Wt. ration Wax
	Miscella	Wax	Oil	Oil
Skellysolve-B	6.35 ± 0.29	2.76 ± 0.27	4.09 ± 0.32	0.719 ± 0.236
Acetone	8.58 ± 0.39	3.33 ± 0.20	5.31 ± 0.33	0.640 ± 0.186
Methyl ethyl Ketone	8.20 ± 0.28	2.83 ± 0.24	5.36 ± 0.21	0.532 ± 0.198
Absolute alcohol	12.93 ± 0.34	7.86 ± 0.35	5.01 ± 0.23	1.586 ± 0.291
Secondary butyl alcohol	10.17 ± 0.20	5.05 ± 0.22	5.12 ± 0.19	0.993 ± 0.120
n-Butyl ether	8.86 ± 0.33	2.51 ± 0.10	6.53 ± 0.39	0.396 ± 0.020
Ethylene dichloride	7.35 ± 0.30	2.40 ± 0.26	4.94 ± 0.48	0.493 ± 0.064
Methanol	12.56 ± 1.54	7.32 ± 0.18	5.24 ± 0.64	1.412 ± 0.276
Ethylene dichloride-heptane-water	7.08 ± 0.18	2.80 ± 0.43	4.28 ± 0.28	0.656 ± 0.061
Methyl ethyl ketone-heptane-water	7.00 ± 0.31	2.88 ± 0.32	4.13 ± 0.30	0.669 ± 0.59

PILOT PLANT EXTRACTION

In order to obtain a sufficient amount of miscella for the subsequent investigation of the separation of wax from oil, a large batchwise extraction was carried out with the Pfaudler distillation unit in the pilot plant. A photograph of this unit is shown on Plate II. It operates on the same principle as the bench scale, Pyrex glass Soxhlet extractor. Skellysolve-B was used as the extracting solvent in all the pilot plant runs.

In each batch, 20 pounds of bran contained in a nylon cloth bag were placed in the basket extraction chamber and seven gallons of Skelly-solve-B were charged into the steam-jacketed still pot. The solvent was first vaporized then condensed in the overhead, water-cooled condenser, then accumulated in the basket extraction chamber to come in contact with the bran. When the solvent level reached the top of the overflow pipe, it was automatically siphoned back into the still pot to start another cycle. At the end of about 15 such cycles, or about eight hours of operation, all the extract was drained into the still pot and the receiver was disconnected from the rest of the still through proper valve arrangement on the by-pass line. Then the solvent was distilled off as over-head and recovered and the solvent-free miscella was withdrawn from the bottom of the still pot. The miscella was then placed on a steam cone to drive off the residual traces of solvent.

Starting with 20 pounds of bran and seven gallons of solvent, a typical batch yielded 850 grams of 1.6 pounds of miscella. No attempt was made to recover that portion of the solvent which was retained by the bran. The average solvent loss was about 1 gallon per batch.

The miscella was dark green in color while in the molten state. Upon cooling to room temperature, it solidified into a light green paste. This paste was used as the starting material in the subsequent studies of various methods of wax-oil separation.

SEPARATION OF WAX AND OIL

Effect of Temperature in the Acetone Method

Previously, the precipitative crystallization of wax from oil with the

aid of acetone was all done at 6° C. To study the completeness of separation at a lower temperature, 52 separation runs were made using the same batch of miscella extracted in the pilot plant as the starting material. Twenty-six were carried out at -8° C. and another 26 runs at 6° C., otherwise following the identical procedures as described in a previous section. The results were averaged and are shown in Table 3. The complete data are included in the Appendix section. Note the increase in the amount of wax and its melting point at the lower refrigeration temperature.

Table 5. Temperature Effect in the Acetone Method.

Refrigeration Temperature	Wax, Wt. % of miscella	Oil, Wt. % of miscella	Wax to Oil ratio	M. P., °C.	Refractive Index at 28° C.
-8° C.	26.4 ± 2.8	73.6 ± 2.0	0.359	68 - 78	1.4672
+6° C.	16.8 ± 3.7	83.2 ± 3.7	0.200	67 - 74	1.4700

Urea Complex Method of Separation

Theory. Recently it has been found that urea can be made to form complexes with certain types of organic compounds. This new technique offers a method for the separation of compounds by size and shape rather than by other physical properties such as boiling point or solubility (Mange, 8). X-ray analyses show the urea complexes to be a hollow tubular-like structure composed of urea which encloses the organic component.

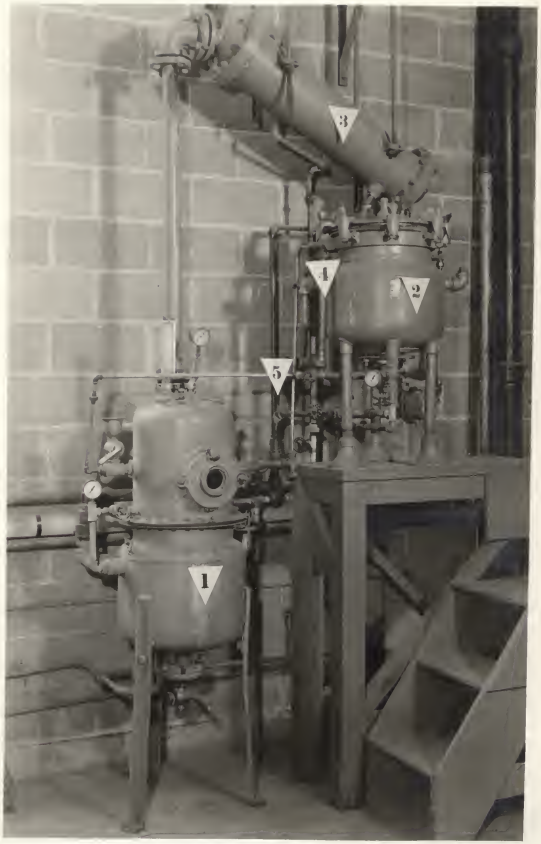
The structure of a typical urea adduct is illustrated by Plate III. The urea molecules form a triple interlocking helix arranged in the hexagonal system, thus forming long hollow tubes in which the molecules of the

EXPLANATION OF PLATE II

Pilot Plant Extractor

1. Still
2. Basket extraction chamber
3. Condenser
4. Overflow pipe
5. By pass pipe

PLATE II



internal components can be accommodated. The unit cell contains six molecules of urea spiralling over a length of 11.1 Å. The carbon, nitrogen, and oxygen atoms of the urea molecules are coplanar and each oxygen is hydrogen-bonded to four nitrogens, and each nitrogen to two oxygens. There are no bonds between the urea molecule and the component enclosed, and the only forces holding the two components together seem to be Van der Waal's forces (unless there is enclosed a molecule with a very polar group in which case there may be some hydrogen bonding). When the enclosed organic component is removed, then the hexagonal urea lattice rearranges to its more stable tetragonal form.

The cross section of the hexagonal urea crystal is shown in Fig. 1, Plate III. The inside diameter of the channel is approximately 5.5 Å. Based on the Van der Waal radii, the maximum diameter of an extended linear hydrocarbon is about 4.5 Å so it may be easily accomodated. If the cross section of an organic compound is greater than about 5.5 Å., it normally will not complex (e.g. isooctane).

In general, ease of formation and stability of urea complexes increase with increasing chain length. The maximum chain length reported to form a urea complex with hydrocarbons is C_{50} with esters C_{46}. These should not necessarily be considered as upper limits, however (Swern, 14). Certain branched chain compounds or even those containing cyclic structures will form urea complexes provided that there is a sufficiently long straight chain in the molecule and the branch or cycle is not too large.

The use of urea to form complexes with certain types of organic compounds has found application in the separation of free fatty acids, which readily form urea complexes from fats, tall oil, polymerized fatty acids,

and other noncomplex-forming substances. Also urea can be used to fractionate mixtures of fatty acids, esters, alcohols, and other derivatives. There are three main types of separations, namely, separations based on differences in chain length, in degree of saturation and in branching respectively. In separation based on differences in chain length, advantage is taken of the fact that the longer chain compounds form urea complexes preferentially. That is, if insufficient urea is employed to combine with all the components of a mixture the longer chain components will combine with the urea and precipitate as complexes. For the best results, the components to be separated should differ in chain length by at least four carbon atoms and preferably by six. When the chain length difference is six or more carbon atoms, other separation methods can be used, such as distillation or low temperature crystallization (-90° C. for example).

The principle in separations based on differences in unsaturation is that as a long chain fatty component becomes more unsaturated it shows greater deviation from the normal straight chain structure. Therefore, at a given chain length, saturated components of a mixture would be expected to form urea complexes preferentially to mono-unsaturated, mono-unsaturated preferentially to di-unsaturated, etc. Taking advantage of this difference in complex forming ability, purified saturated, oleic, linoleic, linolenic, and more highly unsaturated fatty acids, as well as their methyl-esters, have been isolated from natural sources. The method has also been applied to alcohols and nitriles. No temperature below about 0° C. is required in these separations, whereas the usual fatty acid or ester solvent purification techniques may require crystallization temperatures in the range of -50° to -90° C.

In studies on wool wax and other alcohols as well as other classes of compounds, the separation of straight chain or only slightly branched compounds from the more highly branched has been accomplished by perferential urea complex formation (11).

In general, waxes are considered as mixed esters of mono- and di-hydric alcohols with fatty acids, and oils are mixtures of the glycerides of various fatty acids. In view of the above theory, it was believed that the separation of the wax and oil in the miscella extracted from sorghum bran might be carried out by virtue of their difference in molecular structure. Accordingly, experimental procedures were developed and tested in the laboratory. These are discussed in the ensuing sections.

Experimental Procedure. Twenty-six separation runs were made with 1-gram batches of miscella. The laboratory procedure for each run is summarized as follows: Fifty grams of urea were dissolved in 300 ml. of hot (about 50° C.) methanol to prepare a saturated urea-methanol solution. Fifty ml. of this saturated solution were mixed with the carefully weighed sample of molten miscella. On standing the crystalline complex separated out shortly. After the mixture of miscella and urea-methanol solution reached room temperature, in order to complete the formation of the complex, the mixtures were kept in the refrigerator at 6° C. over night. The complex precipitated out and accumulated at the bottom of the flask. Then 250 ml. of hot water (60° C.) were added to the cold complex mixture and stirred. As the complex formation was destroyed the wax coalesced and floated on the surface of the liquid. The wax fraction was then filtered off with an asbesto-lined Gooch crucible mounted on a vaccumm desiccator. The filtrate was boiled to release the oil fraction from the aqueous solution

EXPLANATION OF PLATE III

Fig. 1. Lattice arrangement of hexagonal aduct of urea complex

Fig. 2. Cross section of urea complex aduct

a. n-paraffin

b. Benzene

c. 3-methylheptane

d. 2,2,4 Trimethylpentane

PLATE III

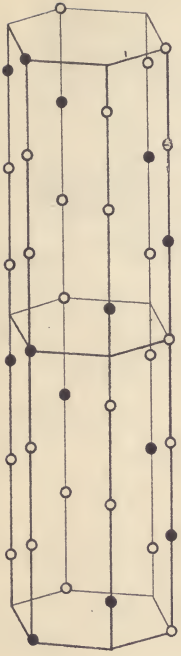


Fig. 1.

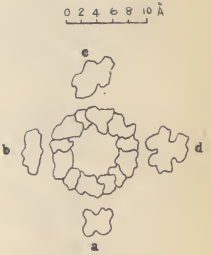


Fig. 2.

of urea and methanol. The oil fraction now floating on top of the solution was recovered by means of a separatory funnel. Fifty ml. of methanol was used to wash the funnel and added to the oil fraction. It was found necessary to add a small amount of either methanol, acetone, or absolute alcohol to the oil in order to drive off the last traces of entrained water. Otherwise violent bumping or sputtering occurred towards the latter part of the evaporation period. The aqueous solution separated from the hot filtrate was evaporated to dryness to recover urea.

To check material balances the weight of wax in the crucible was added to the weight of oil from the separatory funnel. If the combined weight did not approach the weight of the starting miscella closely, the wax was again washed with hot (60° C.) water to make certain that all urea was recovered. The wax was allowed to air dry for at least 24 hours before weighing.

The procedure is illustrated in the flow diagram of Fig. 2. Also two additional separation runs were made with approximately half-pound batch of miscella. The same procedure as indicated above was followed.

Methanol was chosen as the carrier solvent in this procedure because of the high solubility of urea in this alcohol. The solubility of urea in other solvents at 30° C. are given below for comparison:

Alcohol	Grams per 100 g. Alcohol
Methanol	27.7
Ethanol	7.2
n-Propanol	3.6
Isobutanol	2.3
Iso amyl alcohol	1.6

The solubility of urea in water at various temperatures was reported as follows (1):

Temp °C	Solubility grams per 100 g. water
0	66.7
10	85.2
20	108
30	135
40	167
50	203
60	251
70	310
80	400
90	525
100	733

These data suggested the use of hot water (60°C.) in this procedure to destroy the urea-complex after it has precipitated out.

Summary of Results. There was nearly a two-fold increase in the wax fraction yield when the urea complex method was used instead of the acetone method at -8°C. The wax fraction obtained by the urea complex method was light yellow in color and harder than that separated by the acetone method. The melting point increased to 74-81°C. as compared to the melting point of the wax obtained by the acetone method which varied between 68° and 78°C.

The detailed data of the 26 runs of 1-gram size batches are given in the Appendix. The average values are tabulated below:

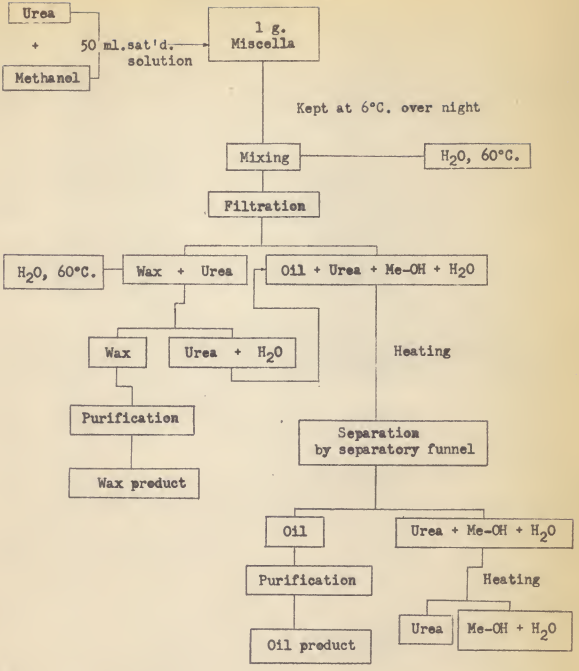


Fig. 2. Flow diagram of urea complex method, bench scale.

Wax, % of Miscella	58.36 ± 1.01
Oil, % of Miscella	41.64 ± 0.44
Melting point range	74-81°C.
Refractive Index at 28°C.	1.4661

These results were reproducible in larger batches wherein about one half pound of miscella was treated.

Wt. (gram)		% (based on total yield)
Wax fraction	150.2	58.2
Oil fraction	108.2	41.8
Total yield	258.4	100.0 %
Starting Miscella	269.9	
Wt. loss	11.5, or 4.28% of Miscella	

The temperature of the hot water used to destroy the complex was the most sensitive factor in the separation. The upper limit is the melting point of the wax fraction. On the other hand, if the temperature is too low, the dissociation of the wax fraction from the complex would not be complete and some urea would still remain in the wax product. This can be checked by a material balance in the last step in the procedure. The optimum temperature for dissociation was found to be 60°C. In the present procedure, methanol was diluted to about 9 percent mole fraction concentration by 60°C. hot water.

In the other large batch run with 223.3 gm. of miscella, the step of using 60°C. water to destroy the complex before filtration was omitted. Instead, the urea complex along with the enclosed wax was filtered off first and then washed with 60°C. water. The result was unsatisfactory. The filter cake turned into a viscous paste contaminated with large amounts of oil. It was concluded then that the treatment with 60°C. water before filtration was necessary not only for destroying the complex but also for the removal of oil contamination.

The crude wax product still needs to be recrystallized either with acetone or with alcohol in order to purify it. Because of this disadvantage, it appears that the urea method would be more applicable if the product to be recovered in the purer form were the oil fraction instead of the wax fraction. In such case, the addition of hot water to destroy the complex would not be necessary. The urea complex together with the enclosed wax could be filtered off to obtain a filtrate which contains mainly oil and methanol. Thus one would not have the large volume of dilute methanol-water solution to contend with.

During the final recovery of urea by evaporation, traces of oil were found floating on the surface of the methanol solution. This indicates that the oil fraction of miscella was not completely recovered. These small weight losses of the oil fraction also appear in the material balance of Table 4 in the Appendix.

COST ESTIMATION OF A WAX RECOVERY PLANT

An equipment flow sheet of the urea complex process for a plant capable of processing one ton of miscella per eight-hour shift has been prepared as shown on Plate IV, This preliminary design was made on the basis of the laboratory procedures and results reported in the preceding sections.

The size of the major pieces of equipment has been determined from the approximate material balance and heat balance calculations. From the equipment specifications the initial costs were estimated. Then the annual operating cost and fixed cost were computed. Finally the percent return on investment was computed to indicate the feasibility of this projected plant. The results and the various assumptions are summarized as follows

and the detailed calculations are included in the Appendix section.

The essential assumption involved in the calculations are as follows:

1. The methanol loss of the process is 5%
2. The urea loss of the process is 10%
3. Two percent of Skellysolve-B loss is assumed in the initial extraction step, and this cost is charged to the urea complex separation process as the cost of the starting raw material, namely miscella.

The summary of preliminary cost estimation of the wax are as follows:

1.	Size of the plant		1 ton of miscella per 8-hour shift
2.	Materials required		
	a. Methanol	13,200 gal./day	$ 9,240
	b. Urea	17,000 lb./day	850
	c. Water	74,000 gal./day	10
3.	Heat required 76,800,000 Btu/day By using waste steam assume the cost is negligible		
4.	Capital Cost		$235,690
5.	Yearly manufacturing cost		
	a. fixed cost		9,172
	b. direct operating cost		198,200
			$ 207,372
6.	Expected Yearly Sales		
	a. Wax	360,000 lbs./yr. 0.70	$ 252,000
	b. Oil	240,000 lbs./yr. 0.10	24,000
			$ 276,000
7.	Cost of the Wax		$ 0.51 / lb.
8.	Annual profit before tax		$ 68,628
9.	Annual return on investment before tax		29%

DISCUSSION

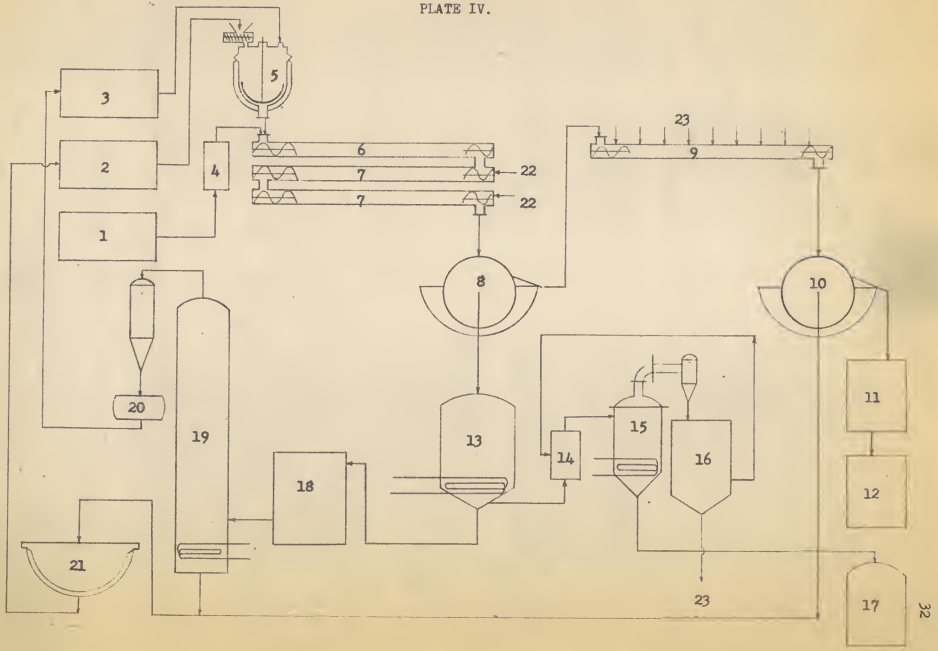
The temperature of the Soxhlet extraction is dependent on the boiling point of the solvent, the power input to the hot plate and the radiation from

EXPLANATION OF PLATE IV

Schematic Diagram of Separation of Sorghum Wax from Oil by the Urea Complex Method

1. Miscella storage tank
2. Urea storage tank
3. Methanol storage tank
4. Miscella preheater
5. Methanol-urea saturation tank
6. Crystalizer
7. Crystalizer—Hot water mixing section
8. Rotary vacuum filter
9. Wax washer
10. Rotary vacuum filter
11. Vacuum chamber dryer
12. Crude wax storage tank
13. Settling tank
14. Mixing tank, oil and entrainer solvent
15. Evaporator
16. Condensate receiving tank
17. Purified oil storage tank
18. Aqueous phase receiving tank
19. Methanol-water-urea fractiontion column
20. Methanol condensate tank
21. Evaporation kettle for urea recovery
22. Hot water
23. Water

PLATE IV.



the hot plate, the temperature and the rate of circulation of the cooling water in the condenser, etc. In the 160 extraction runs no special attempt was made to control the temperature other than to regulate the boiling and condensation at a steady rate. According to a report of the Southern Regional Research Laboratory (11) on their experience with the extraction of rice bran, it was possible to remove the oil first by cold hexane before removing the wax by hot hexane. Since the solubilities of sorghum oil and wax are not preferentially influenced by temperature (Hub, 5), any effect such as reported in the rice-bran case would probably be due to the variation in diffusion rates with temperature. This would suggest a need for future investigation of the effect of temperature on the diffusion rates of oil and wax, respectively.

In the urea complex method of separation, thiourea might also be used instead of urea. Thiourea also forms complexes with many branched chain and cyclo-aliphatic compounds but generally not with straight chain compounds, aromatics and terpenes. Furthermore, Swern (14) reported a number of compounds which would form complexes with thiourea exclusively and not with urea. For instance, if sorghum wax contains appreciable amounts of such cosanes as 3-ethyltetracosane, 2-cyclohexyleicosane and 1-cyclopentylheneicosane, then thiourea would be a more effective separation agent than urea.

The equipment flowsheet and plant cost estimation were prepared for the urea complex method mainly because of its high wax yield. Furthermore, there are also several operational difficulties that would render the acetone method less desirable as an industrial process. These disadvantages are:

1. In the acetone method, it is necessary to have low temperature for

crystallization. The refrigeration cost could be considerable.

2. The filtration of fine wax crystals would be difficult. The size of crystals formed depends on the cooling rate during crystallization. Thus the requirement on temperature control would be critical.

3. It would require 16 hours or so to complete the crystallization and settling. This would cause large material hold-up and large equipment volume in the process.

4. Acetone is highly volatile and inflamable, hence the necessity of special provisions in handling and safety precautions.

Sakurai (12) reported that in the formation of urea complexes with fatty acid and methyl-ester, respectively, in a methanol solution, the effect of agitation and temperature were not appreciable. Therefore, the refrigeration equipment and cost were not considered in the preparation of the flow sheet and the cost estimation. The other essential assumptions involved are:

1. The methanol loss of the process is 5%.
2. The urea loss of the process is 10%.
3. 2% Skellysolve-B loss is assumed in the initial extraction step, and this cost is charged to the urea complex separation process as the cost of the starting raw material, namely, miscella.

These estimations and specifications are by no means final or complete. A positive recommendation as to the feasibility of this process can not be made until further pilot plant tests and detailed design calculations have been performed. The preliminary flow sheet and specification should be helpful in the planning of such further studies in the future.

CONCLUSIONS

1. One hundred sixty extraction runs were made in the Pyrex Soxhlet Extractor with 8 single solvents and 2 azeotrope mixtures. Absolute alcohol was found to extract the largest amount of miscella from the bran and produce the highest wax to oil ratio in the miscella.

2. Fifty-two separation runs were made by the acetone method. By lowering the crystallization temperature from 6°C. to -8°C., the amount of crude wax separated from the miscella was increased by approximately 50 per cent.

3. A laboratory procedure for the separation by the urea-complex method was developed. By this method the crude wax yield doubled that which was obtained by the acetone method at -8°C.

4. Cost-wise the major problem in the urea-complex method is the necessity to concentrate large volumes of dilute methanol and urea solutions, respectively. However, these concentration steps can be carried out in the usual distillation and evaporation equipment. Therefore, technically these should not pose any problems in adopting the urea-complex process on an industrial scale.

5. An equipment flow sheet for the urea-complex process was prepared for a plant capable of processing one ton of miscella per 8-hour shift. Although there are indications that this process could be made feasible on an industrial scale, a positive recomendation can not be made until further pilot plant tests and detailed calculations have been performed.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to the Kansas State College Agricultural Experiment Station for the financial assistance which made this research possible, and to:

Professors Henry T. Ward, S. L. Wang, William H. Honstead and Raymond C. Hall of the Chemical Engineering Department for their invaluable advice and encouragement in carrying out this project.

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APPENDIX

Table 2. Data for the Soxhlet extraction and the separation of wax by the acetone method at 6° C.

Run No.	Wt. dry Bran (grams)	Wt. Wax (grams)	Wt. % Wax in dry Bran	Wt. Oil (grams)	Wt. % Oil in dry Bran	Wt. Miscella (grams)	Wt. % Miscella in dry Bran	Wt. Wax / Wt. Oil
				Solvent - Skellysolve B				
1	39.7212	1.0221	2.57	1.6311	4.11	2.6532	6.68	0.627
2	43.3303	1.1303	2.61	1.7316	4.00	2.8619	6.61	0.653
3	34.6507	1.1430	3.30	1.2098	3.49	2.3528	6.79	0.945
4	39.4418	1.8211	2.16	1.5043	3.81	3.3254	5.97	1.211
5	24.1616	0.5370	2.22	1.1091	4.59	1.6461	6.81	0.484
6	29.0901	0.8054	2.77	1.1999	4.12	2.0053	6.89	0.671
7	36.1803	1.0686	2.95	1.4331	3.96	2.5017	6.91	0.746
8	35.2721	1.0752	3.05	1.3292	3.77	2.4044	6.82	0.809
9	43.5306	1.6726	3.84	1.7750	4.08	3.4476	7.92	0.942
10	20.5812	0.4000	1.94	0.8546	4.15	1.2546	6.09	0.468
11	29.9831	0.7277	2.43	1.2376	4.13	1.9653	6.56	0.588
12	29.3405	0.7619	2.60	1.4002	4.77	2.1621	7.37	0.544
13	41.2602	1.0987	2.66	1.6058	3.89	2.7045	6.55	0.684
14	32.5606	1.1718	3.60	1.4295	4.39	2.6013	7.99	0.820
15	30.0821	0.7337	2.44	1.2876	4.28	2.0213	6.72	0.570
16	36.3009	1.0702	2.95	1.4351	3.95	2.5053	6.90	0.746
Average value			2.76 ± 0.27		4.09 ± 0.32		6.85 ± 0.29	0.719 ± 0.236

Table 2 (con't)

Run No.	Wt. dry Bran (grams)	Wt. Wax (grams)	Wt. % Wax in dry Bran	Wt. Oil (grams)	Wt. % Oil in dry Bran	Wt. Miscella (grams)	Wt. % Miscella in dry Bran	Wt. Wax / Wt. Oil
				Solvent - Acetone				
1	21.0046	0.7714	3.67	0.9645	4.59	1.7359	8.26	0.800
2	20.7930	0.6550	3.15	1.0590	5.09	1.7140	8.24	0.619
3	23.4526	0.8326	3.55	1.0859	4.63	1.9185	8.18	0.767
4	31.9984	1.1171	3.49	1.3528	4.23	2.4699	7.72	0.826
5	29.6228	0.9482	3.20	1.5719	5.31	2.5201	8.51	0.603
6	37.4728	1.3441	3.59	1.8474	4.93	3.1915	8.52	0.728
7	31.6844	1.3702	4.32	1.5841	5.00	2.9543	8.32	0.865
8	24.5321	0.7467	3.04	1.3702	5.84	2.1169	8.88	0.545
9	24.2332	0.6935	2.85	1.3253	5.47	2.0188	8.32	0.523
10	23.9665	0.7714	3.22	1.2928	5.39	2.0642	8.61	0.597
11	28.1901	0.9344	3.31	1.1493	6.21	2.6837	9.52	0.334
12	40.8421	1.4159	3.47	2.5612	6.27	3.9771	9.74	0.553
13	34.7708	1.1973	3.44	2.2649	6.51	3.4622	9.95	0.529
14	38.4611	1.2012	3.12	2.3654	6.15	3.5666	9.27	0.508
15	37.9231	1.0462	2.76	1.7730	4.68	2.8192	7.44	0.590
16	40.4908	1.2422	3.06	1.9100	4.72	3.1522	7.48	0.650
Average value			3.33 ± 0.20		5.31 ± 0.33		8.58 ± 0.39	0.640 ± 0.186

Table 2 (con't)

Run No.	Wt. dry Bran (grams)	Wt. Wax (grams)	Wt. % Wax in dry Bran	Wt. Oil (grams)	Wt. % Oil in dry Bran	Wt. Miscella (grams)	Wt. % Miscella in dry Bran	Wt. Wax / Wt. Oil
				Solvent - Methyl Ethyl Ketone				
1	20.1470	0.4271	2.12	1.0997	5.46	1.5263	7.58	0.388
2	20.6802	0.4414	2.13	1.1181	5.41	1.5595	7.54	0.395
3	20.5540	0.4749	2.31	1.1212	5.45	1.5961	7.76	0.424
4	20.5152	0.4174	2.03	1.0878	5.26	1.5052	7.29	0.384
5	18.9978	0.5553	2.93	1.0930	5.75	1.6488	8.68	0.509
6	19.0282	0.5379	2.83	1.0823	5.69	1.6202	8.52	0.497
7	19.5908	0.5784	2.95	1.1303	5.77	1.7087	8.72	0.512
8	19.5471	0.5898	3.02	1.1552	5.91	1.7450	8.93	0.511
9	20.4511	0.6927	3.39	1.0542	5.15	1.7469	8.54	0.657
10	22.6349	0.6569	2.90	1.2023	5.31	1.8592	8.21	0.546
11	23.8993	0.7771	3.25	1.0784	4.51	1.8555	7.76	0.721
12	22.0744	0.7283	3.30	1.2385	5.61	1.9668	8.91	0.588
13	26.3941	0.8393	3.18	1.2467	4.72	2.0860	7.90	0.673
14	19.2821	0.6435	3.34	1.0318	5.35	1.6753	8.69	0.624
15	23.5768	0.6407	2.72	1.2468	5.29	1.8875	8.01	0.514
16	22.0266	0.6417	2.91	1.1412	5.18	1.7829	8.09	0.562
Average value			2.83 ± 0.24		5.36 ± 0.21		8.20 ± 0.28	0.538 ± 0.198

Table 2 (cont)

Run No.	Wt. dry Bran (grams)	Wt. Wax (grams)	Wt. % Wax in dry Bran	Wt. Oil (grams)	Wt. % Oil in dry Bran	Wt. Miscella (grams)	Wt. % Miscella in dry Bran	Wt. Wax / Wt. Oil
				Solvent - Absolute Alcohol				
1	34.0127	2.8885	8.49	1.5373	4.52	4.4263	13.01	1.878
2	38.3922	2.8703	7.48	1.9782	5.15	4.8485	12.63	1.451
3	29.7845	1.8872	6.34	1.6492	5.54	3.5364	11.88	1.144
4	29.1621	2.1080	7.23	1.3839	4.75	3.4919	11.98	1.523
5	36.0807	2.9052	8.05	1.5429	4.28	4.4481	12.33	1.888
6	36.3504	2.9287	8.06	1.7289	4.76	4.6576	12.82	1.694
7	34.3303	2.8249	8.23	1.5009	4.37	4.3258	12.60	1.882
8	37.1411	2.8521	7.68	1.9689	5.30	4.8200	12.98	1.449
9	37.1623	2.8382	7.77	1.9759	5.32	4.8641	13.09	1.462
10	36.1258	2.9083	8.05	1.5489	4.29	4.572	12.34	1.878
11	37.4728	2.9003	7.74	1.9982	5.33	4.8985	13.07	1.451
12	31.6854	2.1203	6.69	1.6523	5.21	3.7726	12.90	1.283
13	18.9978	1.6111	8.48	1.0053	5.29	2.6164	13.77	1.603
14	19.0282	1.6235	8.53	1.0172	5.35	2.6407	13.88	1.596
15	19.5908	1.6601	8.47	1.0396	5.31	2.6997	13.78	1.597
16	19.5471	1.6623	8.50	1.0389	5.31	2.7012	13.81	1.600
Average value			7.86 ± 0.35		5.01 ± 0.23		12.93 ± 0.34	1.586 ± 0.291

Table 2 (cont)

Run No.	Wt. dry Bran (grams)	Wt. Wax (grams)	Wt. % Wax in dry Bran	Wt. Oil (grams)	Wt. % Oil in dry Bran	Wt. Miscella (grams)	Wt. % Miscella in dry Bran	Wt. Wax / Wt. Oil
				Solvent - n-Butyl Ether				
1	31.7074	0.7147	2.25	1.8903	5.96	2.6050	8.21	0.378
2	29.1635	0.7457	2.56	1.8664	6.40	2.6121	8.96	0.400
3	28.2294	0.7358	2.61	1.7708	6.27	2.5066	8.88	0.416
4	30.5530	0.7456	2.44	1.8443	6.04	2.5899	8.84	0.404
5	26.3941	0.6839	2.59	1.6892	6.40	2.3731	8.99	0.405
6	31.9984	0.8103	2.53	1.9882	6.21	2.7985	8.74	0.407
7	23.4529	0.6153	2.62	1.5408	6.57	2.1561	9.19	0.398
8	31.9628	0.8114	2.54	2.0091	6.29	2.8205	8.83	0.404
9	28.6916	0.7163	2.50	1.8023	6.28	2.5091	8.78	0.398
10	31.6344	0.7992	2.52	2.0005	6.31	2.7997	8.83	0.399
11	29.6228	0.7394	2.49	1.8905	6.38	2.6299	8.87	0.390
12	37.4728	0.9382	2.50	2.3321	6.36	3.3203	8.86	0.393
13	19.2821	0.4813	2.49	1.2468	6.47	1.7281	8.96	0.385
14	26.3941	0.6721	2.55	1.7359	6.58	2.4082	9.13	0.388
15	23.5768	0.5998	2.54	1.5428	6.52	2.1429	9.08	0.388
16	22.0266	0.5531	2.51	1.4231	6.46	1.9762	8.97	0.389
Average value			2.51 ± 0.10		6.35 ± 0.39		8.86 ± 0.33	0.396 ± 0.020

Table 2 (cont)

Run No.	Wt. dry Bran (grams)	Wt. Wax (grams)	Wt. % Wax in dry Bran	Wt. Oil (grams)	Wt. % Oil in dry Bran	Wt. Miscella (grams)	Wt. % Miscella in dry Bran	Wt. Wax / Wt. Oil
				Solvent - Ethylene dichloride				
1	31.8181	0.7403	2.33	1.5340	4.82	2.2743	7.15	0.486
2	33.4426	0.9216	2.76	1.6561	4.95	2.5777	7.71	0.558
3	31.4681	0.7878	2.50	1.5091	4.80	2.2967	7.30	0.521
4	34.3891	0.7871	2.29	1.7673	5.14	2.5554	7.43	0.446
5	24.3889	0.5795	2.38	1.1039	3.21	1.6834	5.59	0.741
6	27.7656	0.6227	2.24	1.4328	5.16	2.0555	7.40	0.434
7	27.8438	0.6273	2.25	1.4342	5.15	2.0615	7.40	0.437
8	23.5073	0.4363	1.86	1.2848	5.47	1.7211	7.33	0.340
9	20.4511	0.5128	2.51	1.0054	4.92	1.5182	7.43	0.510
10	22.6349	0.5693	2.52	1.1329	5.01	1.7022	7.53	0.503
11	23.8993	0.5795	2.42	1.2863	5.38	1.8658	7.80	0.450
12	22.0744	0.5552	2.52	1.1111	5.03	1.6663	7.55	0.501
13	31.6844	0.7893	2.49	1.5862	5.01	2.3755	7.50	0.497
14	29.6229	0.7328	2.47	1.4921	5.04	2.2249	7.51	0.490
15	37.4728	0.8315	2.22	1.8931	5.05	2.7246	7.27	0.440
16	29.1621	0.7821	2.68	1.4498	4.97	2.2319	7.65	0.539
Average value			2.40 ± 0.26		4.94 ± 0.48		7.35 ± 0.30	0.493 ± 0.064

Table 2 (cont)

Run No.	Wt. dry Bran (grams)	Wt. Wax (grams)	Wt. % Wax in dry Bran	Wt. Oil (grams)	Wt. % Oil in dry Bran	Wt. Miscella (grams)	Wt. % Miscella in dry Bran	Wt. Wax / Wt. Oil
				Solvent - Methanol				
1	39.6829	2.9312	7.39	2.2704	5.72	5.2016	13.11	1.292
2	34.2884	2.5231	7.36	1.6871	4.92	4.2102	12.28	1.496
3	38.2388	2.8132	7.36	1.8908	4.97	4.7040	12.30	1.490
4	34.5476	2.5372	7.34	1.7305	5.01	4.2697	12.35	1.465
5	25.0476	1.8456	7.34	1.2752	5.09	3.1208	12.43	1.442
6	30.1053	2.2103	7.34	1.4025	4.66	3.6128	12.00	1.575
7	28.3062	2.0821	7.36	1.3507	4.77	3.4328	12.13	1.543
8	29.2031	2.1659	7.42	1.3372	4.58	3.5031	12.00	1.620
9	28.6849	2.1003	7.33	1.4000	4.88	3.5003	12.21	1.502
10	30.7198	2.3007	7.50	2.0287	6.60	4.3294	14.10	1.136
11	32.2559	2.3968	7.43	1.4753	4.57	3.8721	12.00	1.626
12	32.7986	2.2869	6.97	1.7002	5.18	3.9871	12.15	1.346
13	33.2872	2.4428	7.34	1.8780	5.64	4.3208	12.98	1.301
14	31.2986	2.2480	7.18	1.8413	5.88	4.0893	13.06	1.221
15	33.3297	2.4093	7.24	1.8690	5.60	4.2783	12.84	1.293
16	29.8238	2.1538	7.22	1.7290	5.80	3.8828	13.02	1.245
Average value			7.32 ± 0.18		5.24 ± 0.64		12.56 ± 1.54	1.412 ± 0.276

Table 2 (cont)

Run No.	Wt. dry Bran (grams)	Wt. Wax (grams)	Wt. % Wax in dry Bran	Wt. Oil (grams)	Wt. % Oil in dry Bran	Wt. Miscella (grams)	Wt. % Miscella in dry Bran	Wt. Wax / Wt. Oil
			Solvent - Methyl Ethyl Ketone-Heptane-Water Volume ratio 2:2:1					
1	31.9321	0.8933	2.80	1.2995	4.07	2.1928	6.87	0.687
2	32.6394	0.9281	2.84	1.3330	4.08	2.2611	6.92	0.696
3	28.6532	0.8210	2.87	1.1421	3.99	1.9631	6.86	0.709
5	35.6321	1.0023	2.69	1.4721	4.13	2.4743	6.82	0.681
6	29.3821	0.8459	2.88	1.3003	4.43	2.1412	7.31	0.651
7	38.4354	1.2301	3.20	1.5673	4.08	2.7974	7.28	0.785
8	26.2821	0.7653	2.91	1.1523	4.38	1.9176	7.29	0.664
9	29.6321	0.8561	2.89	1.2121	4.09	2.0682	6.98	0.706
10	28.6211	0.8321	2.91	1.1432	3.99	1.9753	6.90	0.728
11	29.6321	0.8569	2.89	1.1831	3.99	2.0400	6.88	0.724
12	28.3621	0.8123	2.86	1.1639	4.10	1.9762	6.96	0.698
13	30.3829	0.8821	2.90	1.2231	4.03	2.1052	6.93	0.721
14	32.8324	0.9308	2.84	1.4128	4.30	2.3436	7.14	0.659
15	28.6327	0.8150	2.85	1.1421	3.99	1.9571	6.84	0.714
16	29.8321	0.8321	2.79	1.2930	4.33	2.1251	7.12	0.644
Average value			2.88 ± 0.32		4.13 ± 0.30		7.00 ± 0.31	11.186 0.669 ± 0.059

Table 2 (concl)

Run No.	Wt. dry Bran (grams)	Wt. Wax (grams)	Wt. % Wax in dry Bran	Wt. Oil (grams)	Wt. % Oil in dry Bran	Wt. Miscella (grams)	Wt. % Miscella in dry Bran	Wt. Wax / Wt. Oil
				Solvent - Ethylene dichloride-Heptane-Water Volume ratio 2:2:1				
1	32.9143	0.9503	2.89	1.3382	4.07	1.3382	6.96	0.710
2	30.6204	0.8524	2.78	1.3180	4.30	1.3180	7.08	0.647
3	34.9488	1.0091	2.86	1.4423	4.13	1.4423	6.99	0.700
4	28.7489	0.8235	2.88	1.1713	4.07	1.9998	6.95	0.707
5	29.9931	0.8974	2.99	1.2521	4.17	2.1495	7.16	0.717
6	34.1766	0.9409	2.75	1.4625	4.28	2.4034	7.03	0.643
7	26.9324	0.6406	2.38	1.2190	4.53	1.8596	6.91	0.526
8	35.3146	1.0589	3.00	1.4904	4.22	2.5493	7.22	0.710
9	31.1168	0.8948	2.88	1.3028	4.19	2.1976	7.07	0.688
10	29.0536	0.8152	2.81	1.2913	4.44	2.1065	7.25	0.631
11	24.7026	0.7036	2.85	1.0658	4.31	1.7694	7.16	0.660
12	38.4354	1.0582	2.75	1.6294	4.24	2.6376	6.99	0.649
13	30.2432	0.8506	2.81	1.3125	4.34	2.1631	7.15	0.648
14	26.2832	0.6231	2.37	1.2003	4.56	1.8234	6.93	0.519
15	27.8623	0.7998	2.87	1.2241	4.39	2.1239	7.26	0.653
16	29.5868	0.8674	2.93	1.2592	4.26	2.1266	7.19	0.689
Average value			2.80 ± 0.43		4.28 ± 0.28		7.08 ± 0.18	0.656 ± 0.061

Table 3. Data for the separation of wax and oil by the acetone method.

Run No.	Wt. Miscella (grams)	Wt. Wax (grams)	Wt. % Wax in Miscella	Wt. Oil (grams)	Wt. % Oil in Miscella	Material balance Wt. of Wax + Wt. of Oil
			Temperature: 6° C.			
1	1.1144	0.1817	16.6	0.9139	83.4	1.0956
2	1.1928	0.1737	15.3	0.9875	84.7	1.1162
3	1.0651	0.1740	17.1	0.8426	82.9	1.0166
4	1.2710	0.2551	21.1	0.9497	78.9	1.2048
5	1.0289	0.1740	17.3	0.8293	82.7	1.0033
6	1.1164	0.1869	17.2	0.8991	82.8	1.0860
7	1.2098	0.1796	15.6	0.9726	84.4	1.1522
8	1.0432	0.1436	14.1	0.8759	85.9	1.0195
9	1.0042	0.1372	14.0	0.8489	86.0	0.9861
10	1.1662	0.2250	19.4	0.8902	80.6	1.1152
11	1.1718	0.2373	20.5	0.9172	79.5	1.1545
12	1.1225	0.2083	19.1	0.8828	80.9	1.0911
13	1.0156	0.1632	16.5	0.8307	83.5	0.9939
14	1.0136	0.1633	16.1	0.8492	83.9	1.0125
15	1.0281	0.1721	16.7	0.8588	83.3	1.0309
16	1.0583	0.1728	16.3	0.8865	83.7	1.0593
17	1.0293	0.1699	16.5	0.8522	83.5	1.0321
18	1.0862	0.1830	16.8	0.9061	83.2	1.0891
19	1.0963	0.1829	16.6	1.0174	83.4	1.1003
20	0.9231	0.1562	16.1	0.7737	83.9	0.9300

Table 3 (cont)

Run No.	Wt. Miscella (grams)	Wt. Wax (grams)	Wt. % Wax in Miscella	Wt. Oil (grams)	Wt. % Oil in Miscella	Material balance Wt. of Wax + Wt. of Oil
21	0.9921	0.1598	16.1	0.7345	83.9	0.9943
22	0.9627	0.1572	16.2	0.8111	83.8	0.9683
23	1.2912	0.2130	16.5	1.0766	83.5	1.2896
24	1.1203	0.1853	16.5	0.9470	83.5	1.1223
25	1.2454	0.2018	16.1	1.0464	83.9	1.2482
26	0.9998	0.1593	15.9	0.8186	84.1	0.9979
Average value			16.8 ± 3.7		83.2 ± 3.7	

Table 3 (cont)

Run No.	Wt. Miscella (grams)	Wt. Wax (grams)	Wt. % Wax in Miscella	Wt. Oil (grams)	Wt. % Oil in Miscella	Material balance Wt. of Wax + Wt. of Oil
			Temperature: 8° C.			
1	1.0554	0.3153	31.5	0.6872	68.5	1.0030
2	1.0174	0.2645	26.5	0.7326	73.6	0.9971
3	1.0525	0.2818	26.7	0.7728	73.3	1.0546
4	1.1166	0.2605	23.6	0.8444	76.4	1.1049
5	0.9979	0.2596	26.0	0.7375	74.0	0.9971
6	1.0200	0.2624	25.4	0.7718	74.6	1.0342
7	1.0381	0.2550	25.4	0.7897	75.6	1.0447
8	1.0240	0.2953	28.9	0.7363	71.9	1.0216
9	0.9833	0.2496	25.1	0.7444	74.9	0.9940
10	1.0542	0.2606	24.6	0.7971	75.4	1.0575
11	1.0532	0.2703	25.5	0.7845	74.5	1.0548
12	1.0429	0.2691	26.0	0.7742	74.0	1.0433
13	1.1231	0.2933	26.6	0.8260	73.4	1.1253
14	1.1321	0.2969	26.3	0.8330	73.7	1.1299
15	1.0329	0.2741	26.5	0.7602	73.5	1.0343
16	1.0533	0.2789	26.4	0.7772	73.6	1.0561
17	1.0021	0.2648	26.3	0.7423	73.7	1.0071
18	1.0388	0.2738	26.4	0.7631	73.6	1.0369
19	1.0621	0.2821	26.5	0.7830	73.5	1.0651
20	1.1235	0.2960	26.4	0.8264	73.6	1.1204

Table 3 (concl)

Run No.	Wt. Miscella (grams)	Wt. Wax (grams)	Wt. % Wax in Miscella	Wt. Oil (grams)	Wt. % Oil in Miscella	Material balance Wt. of Wax + Wt. of Oil
21	1.1421	0.3012	26.4	0.8401	76.6	1.1413
22	1.0213	0.2731	26.8	0.7466	73.2	1.0197
23	1.0242	0.2730	26.7	0.7509	73.3	1.0239
24	0.9958	0.2629	26.5	0.7297	73.5	0.9926
25	1.2136	0.3213	26.4	0.8835	73.6	1.2148
26	1.1187	0.3097	27.7	0.8101	72.3	1.1198
Average value			26.4 ± 2.8		73.6 ± 2.0	

Table 4. Data for the separation of wax and oil by the urea complex method.

Run No.	Wt. Miscella (grams)	Wt. Wax (grams)	Wax, % Miscella	Wt. Oil (grams)	Oil, % Miscella	Wt. of Oil + Wt. of Wax	% Miscella Unrecovered
1	1.1012	0.5902	58.54	0.4196	41.46	1.0098	-8.3
2	1.0986	0.6057	57.91	0.4402	42.09	1.0459	-4.8
3	1.1243	0.5921	58.65	0.4183	41.35	1.0104	-10.1
4	1.0583	0.5883	58.77	0.4124	41.23	1.0007	-5.4
5	1.1628	0.6193	58.27	0.4443	41.72	1.0636	-8.5
6	1.0672	0.5959	58.23	0.4283	41.77	1.0242	-4.0
7	1.0529	0.5931	58.28	0.4241	41.72	1.0172	-3.4
8	1.0723	0.5854	57.10	0.4578	42.90	1.0432	-2.7
9	1.0861	0.6311	58.68	0.4453	41.32	1.0764	-1.0
10	1.1203	0.5842	58.07	0.4225	41.93	1.0067	-10.1
11	1.0032	0.6153	58.18	0.4431	41.82	1.0584	+5.5
12	1.1283	0.6003	57.99	0.4359	42.01	1.0362	-8.2
13	1.0736	0.6291	59.63	0.4265	40.37	1.0555	-2.1
14	1.0021	0.5789	58.46	0.4159	41.54	0.9948	-0.7
15	1.1026	0.6621	58.49	0.4712	41.51	1.1333	+2.9
16	1.1231	0.6109	57.64	0.4497	42.34	1.0606	-5.6
17	1.0021	0.6054	59.37	0.4218	40.63	1.0272	+2.5
18	1.1281	0.6408	58.12	0.4621	41.88	1.1029	-2.2
19	1.1621	0.6723	58.22	0.4827	41.78	1.1550	-0.6
20	1.1291	0.6081	58.15	0.4381	41.85	1.1182	-1.0

Table 4 (concl)

Run No.	Wt. Miscella (grams)	Wt. Wax (grams)	Wax, % Miscella	Wt. Oil (grams)	Oil, % Miscella	Wt. of Oil + Wt. of Wax	% Miscella Unrecovered
21	1.0928	0.6429	58.23	0.4609	41.77	1.1038	+1.0
22	1.1234	0.6421	58.16	0.4625	41.84	1.1046	-1.7
23	1.1230	0.6239	58.57	0.4424	41.43	1.0663	-5.1
24	1.0736	0.6127	58.91	0.4207	41.09	1.0334	-4.2
25	1.0862	0.6038	58.51	0.4302	41.49	1.0340	-4.8
26	1.0128	0.5803	58.24	0.4179	41.76	0.9982	-1.4
Average value			58.36 ± 1.01		41.64 ± 0.44		

COST ESTIMATION FOR UREA COMPLEX PROCESS

Approximate Material Balance

1. Methanol-urea saturation tan (Equipment No. 5)*

   a. Ureau — 2,000 lb. x (50/6) = 17,000 lb./day
   = 2,125 lb./hr.

   b. Methanol — 1 m^3 x (300/6) = 50 m^3/day
   = 13,200 gal./day
   = 1,650 gal./hr.

2. Crystalizer (Equipment No. 6)*

   a. Miscella — 2,000 lb./day
   = 250 lb./hr.

   b. Methanol — 1,650 gal./hr.

   c. Ureau — = 2,125 lb./hr.

3. Crystalizer, Hot water mixing section (Equipment No. 7)*

   140° F. (60° C.) water — 66,000 gal./day
   = 8,250 gal./hr.

4. Rotary vacuum filter (Equipment No. 8)*

	To Equipment No. 13	To Equipment No. 9
a. Hot water	8,250 gal./hr.	
b. Methanol	1,650 gal./hr.	
c. Urea	2,125 lb./hr.	
d. Oil fraction 2,000x(0.4) =	800 lb./day	
=	100 lb.hr	
e. Wax fraction	---	150 lb./hr.
	9,900 gal./hr.	150 lb./hr.
	100 lb./hr.	

*Refers to the equipment number on the flow sheet, p. 32.

5. Urea washing-off section (Equipment No. 9)*

Water	8,000 gal./day = 1,000 gal./hr.

6. Rotary vacuum filter (Equipment No. 10)*

	To Equipment No. 21	To Equipment No. 11
a. Filtrate	1,000 gal./hr.	
b. Wax fraction		150 lb./hr.

7. Vacuum dryer (Equipment No. 11)*

Wax	150 lb./hr.

8. Settling Tank (Equipment No. 13)*

	To Equipment No. 18	To Equipment No. 15
a. Water	8,250 gal./hr.	
b. Methanol	1,650 gal./hr.	
c. Urea	2,125 lb./hr.	
d. Oil fraction		100 lb./hr.
	9,900 gal./hr. 2,125 lb./hr.	100 lbs./hr.

9. Evaporator (Equipment No. 15)*

a. Oil fraction	100 lb./hr.
b. Solvent	100 gal./hr.

10. Methanol-water-urea fractionation column (Equipment No. 19)*

a. Water	8,250 gal./hr.
b. Methanol	1,650 gal./hr.
c. Urea	2,125 lb./hr.

Mole fraction of methanol on urea free basis:

$$\frac{\frac{1650}{32}}{\frac{1650}{32} + \frac{8250}{18}} = 0.10$$

Mole fraction of water: $1 - 0.10 = 0.90$

*Refers to the equipment number on the flow sheet, p. 32.

11. Evaporation Kettle for Urea recovery (No. 21)*

a. Water 9,250 gal./hr.

b. Urea 2,125 lb./hr.

Approximate Heat Balance

Assume that heat capacity of water and methanol are equal to 18 Btu. per 1 lb.-mole per °F. and the temperature of city water is 68° F.

1. Crystalizer, Hot water mixing section (Equipment No. 7)*
   Heat required to raise city water to 140° F.:
   Water 8,250 gal./hr. = 69.300 lb./hr. = 3,850 lb.-mole/hr.
   3,850 x 18 x (140-68 = 5,539,600 Btu/hr.

2. Settling tank (Equipment No. 13)*

   Assume that the temperature drop of the solution during the process is

   40o F. from the 140° F. hot water:
   Methanol 1,650 gal./hr. = 13,860 lb./hr. = 433 lb.-mole/hr.
   433 x 18 x (212-100) = 872,908 Btu/hr.

3. Evaporator (Equipment No. 15)*

   Assume that temperature of the oil fraction at the inlet of the unit is at 180° F. and the boiling point of purifying solvent is 180° F. and the volume ration of oil and the solvent is one to four.
   Temperature of the oil and solvent mixture is:

   100 gal. x 180 = 18,000
   +) 400 gal. x 68 = 27,200
   500 gal. 45,200

   Average temperature = 45,200 ÷ 500 = 90° F.

   Assume that the average molecular weight of the mixture is 50

   $\frac{500 \times (8.4)}{50} \times .18 \times (180-90) = 136,080$ Btu/hr.

4. Methanol-water-urea fractionation column (Equipment No. 19)*

   Water 9,250 gal./hr. = 4,856 lb.-mole/hr.
   Methanol 433 lb.-mole/hr.
   (4,856 + 433) x 18 x)200-180) = 190,404 Btu/hr.

*Refers to the equipment number on the flow sheet, p.

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5. Evaporator for Urea recovery (Equipment No. 21)*

Neglect the boiling point elevation of the urea-water mixture
4,856 x 18 x (212-180) = 2,797,056 Btu/hr.

Total heat required:
5,589,600 + 872,908 + 136,080 + 190,404 + 2,797,056
=9,586,048 Btu/hr.
=9,600,000 Btu/hr.

Since 1 Boiler H.P. = 33,475 Btu/hr.
Therefore $\frac{9,600,000}{33,476}$ = 287 Boiler Horsepower required

*Refers to the equipment number on the flow sheet, p. 32.

Table No. 5. Specifications of equipment and their costs.

Items	Quantity	Unit Price	Amount
Methanol-urea Saturation tank Enameled lined, steam jacketted with 5 H.P. agitator, Capacity = 2,000 gal.	1	$2,000	$2,000
Crystalizer and washing off section Galvanized screw conveyer with tight cover 6" dia. x 20' with 1/4 H.P. motor Capacity = 315 cu. ft./hr. r.p.m. 160	4	2.40	960
Rotary vacuum filter 5 1/4' dia. x 8', 139 sq.ft., steel, 39 ton/hr., with 1 1/2 H.P. motor	1	4,500	4,500
Rotary vacuum filter 3' dia. x 2', 18 sq. ft., cast-iron drum, 5.4 ton/hr. with 1/2 H. P. motor	1	1,200	1,200
Evaporator Steam jacketted, capacity = 725 gal. with condenser and premixer	1	1,000	1,000
Settling tank Steel, cylindrical, capacity = 30,000 gal. with 100 sq. ft. heating coil and condenser	1	3,000	3,000
Aequeous phase receiving tank Steel, cylindrical tank, Capacity = 30,000 gal.	2	3,000	6,000
Methanol-urea-water fractionation column Capacity = 1,000 gal. alcohol/hr. 12 theoretical plates	1	47,000	47,000
Evaporation kettle for urea recovery Capacity = 1,000 gal.	10	1,200	12,000
Oil storage tank Capacity = 1,000 gal.	1	1,000	1,000
Vacuum chamber dryer Shell size 39' x 39'	1	1,800	1,800
Total			$30,460

These figures are "delivered cost", as reported by Vilbrandt (15).

Table 6. Estimation of capital requirements.

Item	Cost
Machinery and Equipment	$ 80,460
Installation cost (43% of the delivered cost of equipment) (17), including the cost of foundation, support, insulation, erection and necessary piping	34,600
Land and Building	50,000
Seven days raw material stock (10)	
Methanol $0.70 / gal.	64,680
Urea $0.05 / lb.	5,950
Total	$ 235,690

Yearly manufacturing cost.

a. Machinery and equipment depreciation (17).

Items	A Initial Cost	B Average life, Year	$\frac{A - \underline{A}}{B}$ / B Depreciation/yr.
1. Methanol-urea saturation tank	$ 2,000	15	$ 124
2. Crystalizer and washing off section	960	15	59
3. Rotary vacuum filter	4,500	15	280
4. Rotary vacuum filter	1,200	15	68
5. Evaporator	1,000	20	48
6. Settling tank	3,000	20	143
7. Aequeous phase receiving tank	6,000	30	193
8. Methanol-urea-water fractionation column	47,000	20	2,240
9. Evaporation Kettle for urea recovery	12,000	25	448
10. Oil storage tank	1,000	30	33
11. Vacuum chamber dryer	1,800	20	86
Total			$ 3,722

b. Cost of miscella (Assume 2% Skellysolve-B loss)	$ 13,200
c. Raw Mater'al Loss (300-working days base) 1. Methanol 13,200 x 0.05 = 660 gal./day 600 x 0.7 = 462 dollars/day (10) 462 x 300 = 138,600 dollars/year	138,600
2. Urea loss (Assume 10% loss)	25,500
d. Insurance and tax (17) 2% of capital invested	4,700
e. Depreciation of Building and maintenance fee (assume 5% of initial cost)	1,750
f. Water and Power	4,500
g. Labor and Supervision (Assume 3 workers, at $2.00/hour 3 x 300 x 8 x 2 = 14,400	14,400
h. Others	1,000
Total	$207,372

Amount of yearly sale

Crude Wax:	1,200 lb./day 1,200 x 0.7 = 840 dollars/day (10) 840 x 300 = 252,000 dollars/year	252,000
Oil:	800 lb./day 800 x 0.1 = 80 dollars/day (10) 80 x 300 = 24,000 dollars/year	24,000
Total		$276,000

Cost of the wax = $\frac{\text{Annual Manufacturing Cost - Sales values of byproduct}}{\text{No. of Pound of wax produced}}$

$$= \frac{183,372}{1,200 \times 300} \times 100 = 51 \text{ cents/lb. of wax}$$

Annual Profit before tax = Net sales-Manufacturing Cost = 276,000-207,372 = 68.628 dollars/year

Annual Return on Investment = $\frac{\text{Annual Profit}}{\text{Capital Investment}} = \frac{68,628}{236,690} \times 100 = 29\%$

Note: The expressions of annual profit and annual return on investment were obtained from Chemical Engineering Cost Estimation by Robert S. Aries and Robert D. Newton.

EXTRACTION OF WAX FROM SORGHUM BRAN

by

HSIEN-WEN HSU

B. S., National Taiwan University, China, 1951

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1955

One of the functions of the Agricultural Experiment Station is the never ending search for means of better and fuller utilization of the agricultural products that are of special interest in the state of Kansas. In line with this broad objective, the recovery of wax from the sorghum bran has been studied in several theses in the Departments of Chemical Engineering and Chemistry in recent years. The present work has been concerned primarily with the second phase of the recovery process, that is, the separation of wax from the miscella which was extracted from sorghum bran with Skellysolve-B.

The temperature effect of the precipitative crystallization method of separation using acetone as the solvent was studied. It was found that by lowering the crystallization temperature from 6°C. to -8°C., the crude wax yield could be increased by approximately 50 per cent.

A laboratory procedure of separation was developed applying the urea-complex technique. It was found that this method would give a nearly two-fold increase in the crude wax yield over the acetone method at -8°C. The amount of the wax and oil fractions recoverable by the various methods, reported as weight per cent of the starting miscella, are summarized as follows:

Method of Separation	Wax Fraction	Oil Fraction
Acetone at 6° C.	16.8 ± 3.7%	83.2 ± 3.7%
Acetone at -8° C.	26.4 ± 2.8%	73.6 ± 2.0%
Urea-Complex	58.36 ± 1.01%	41.64 ± 0.44%

Cost-wise the major problem in the urea-complex method is the necessity to concentrate large volumes of dilute solutions of methanol and urea, respectively. These concentration steps can be carried out with the standard

distillation and evaporation equipment, therefore, technically, it should not introduce any difficulties were this method to be adopted for plant operation. An equipment flow sheet for the urea-complex method could be made feasible on an industrial scale, a positive recommendation can not be made until further pilot plant tests and detailed design calculations have been performed.

The secondary objective of this investigation was to seek another solvent, or solvents, that is superior to Skellysolve-B in that it could extract larger amounts of miscella from the bran and it could also increase the wax to oil ratio in the miscella. Seven additional solvents and two azeotrope mixtures were studied in altogether 16[illegible] extraction runs with the Pyrex Soxhlet. The single solvents studied include the following: acetone, methyl ethyl ketone, absolute alcohol, secondary butyl alcohol, n-butyl ether, ethylene dichloride, and methanol. The azeotrope mixtures were ethylene dichloride-heptane-water and methyl ethyl ketone-heptane-water. Also a series of runs were made with Skellysolve-B for comparison. It was found that the absolute alcohol gave the highest yield of miscella as well as the highest wax-oil ratio in the miscella.

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