Cottonseed Oil Extraction With Normal Hexane and Methylpentanes

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THE development of "tailor-made" solvents for the extraction of vegetable oils has been the goal of an extensive research program at Phillips Petroleum Company. In an earlier paper (1) it was established that various pure hydrocarbons extracted cottonseed oils with varying efficiencies. These data indicated that 3-methylpentane, and to a lesser extent 2-methylpentane, were the most efficient of the hexane hydrocarbons tested.

Commercial production of a solvent containing a high concentration of either of these components, at a cost sufficiently low to allow it to be employed in commercial extraction plants, is not possible at the present time. However a highly concentrated mixture of methylpentanes could be produced at a reasonable premium over the cost of producing n-hexane. Therefore commercial quantities of these methylpentanes were produced and the laboratory evaluation studies described herein, plus a limited number of plant scale tests, were conducted to determine the effectiveness of this solvent for the extraction of cottonseed oil.

A continuous countercurrent laboratory extractor, similar to the one developed at the Northern Regional Research Laboratory, Peoria, Ill. (2), was constructed and employed in these studies. This extractor contained all of the essential elements of a commercial extraction plant, thereby providing data which would be directly applicable to plant operation.

Extraction of cottonseeds with Phillips Commercial n-Hexane and Phillips Commercial Methylpentanes was compared in the aforementioned extractor. Both cooked and raw seeds were employed since both types of seeds are extracted commercially.

Experimental

Apparatus and Equipment. A schematic representation of the laboratory continuous countercurrent extractor is depicted in Figure 1. The extractor contains the major components of almost any commercial extraction plant; i.e., extraction unit, meal drier, decanter, conveyor, filter, and solvent stripper. Although the extractor was similar in overall design to that employed at the Northern Regional Research Laboratory, certain modifications are worthy of mention.

The extractor and drier are constructed of stainless steel tubing instead of glass to minimize the hazard of handling relatively large volumes of volatile hydrocarbons in the laboratory. The extracted flakes are discharged by gravity from rolls at the drive end of the belt conveyor instead of the removing of the flakes by twisting the belt. The idle side of the belt passes under the extractor instead of above. The miscella from the extractor passes directly through the filter and into the stripping section. A vapor bypass between the oil separator and oil accumulator increases the capacity of the stripper and gives better control of the recycle oil. The flake feed tube controls the flakes fed to the extractor automatically. More or less flakes are fed by adjusting the tube further from or closer to the conveyor. The decanter provides for a simple separation of solvent and water. The wet solvent is then dried over solid desiccant (anhydrous calcium sulfate) before the solvent is returned to the extractor. This prevents the build-up of water in the return solvent, which had been noted during operation of the unit prior to installation of the drier. Indicating desiccant in the drier insures that sufficient active desiccant is present.

A 16-quart pressure cooker (Presto) was employed to cook the seed for one group of extractions. This was a standard cooker with no modification. All other cooked seeds were processed in a one-gallon stainless steel, steam jacketed kettle. The kettle was closed and contained an anchor stirrer which allowed the contents to be mixed during the cooking period.

A flaker was improvised from an oat roller, manufactured by Farnum Products, Omaha, Nebraska. It was necessary to replace the two original corrugated rolls with smooth rolls in order to produce flakes.

Test Materials. The solvents employed in these extractions and their composition were as follows:

Phillips Commercial n-Hexane: boiling range 150-156°F.; average composition, 70% n-hexane, 19% methylcyclopentane, 6% 3-methylpentane, and 5% other hexane hydrocarbons.

Phillips Commercial Methylpentanes: boiling range 135-147°F.; composition, 60% 2-methylpentane, 26% 3-methylpentane, 5% n-hexane, 6% diisopropyl, and 3% other hexane hydrocarbons.

Three shipments of cottonseeds were employed: two from the Delta Products Company, Wilson, Arkansas, and one from Helena Cotton Oil Company, Helena Arkansas. The seeds from both sources had been dehulled commercially before being shipped. A large number of "fines" were produced in transit, so it was necessary to remove the "fines" before the seeds were processed. Therefore the seeds were sieved and all material which passed through a 24-mesh screen was discarded. The material retained was used to charge either the cookers or the flaker depending on whether cooked or raw seeds were to be processed.

Procedure and Analyses. Successful extraction of oil seeds can be obtained only after adequate seed preparation. In the cottonseed industry the hulls are first removed from the seeds, and the dehulled seeds are subsequently rolled into thin flakes from which the oil can be extracted by the solvent. It is desirable to produce the thinnest flakes possible, which will still retain sufficient mechanical strength to withstand extraction.

Seeds which were too dry to flake were sprayed with water until the desired moisture was obtained. The flaking rolls were set to produce the thinnest flakes possible without undue expression of oil on the rolls.

The seeds employed in Runs H-3 and H-4 were cooked in the pressure cooker. The seeds were cooked at 10 pounds of steam pressure for 20 minutes, cooled, and flaked. The cooling was necessary for the formation of flakes relatively free of "fines." All other

TABLE I

Extraction Data from Experimental Extraction of Cottonseed

Run No.	Solvent	Cooking Treatment	Residence Time	Flake Thickness	Moisture in Flakes	Extraction Temperature	Oil Content of Flakes	Oil Yield	Oil Content of Meal
			Minutes	*Inches*	%	°*F.*	%	%	%
D-1	n-Hexane	None	46	0.013	9.8	122	35.5	34.5	2.3
D-2	n-Hexane	None	46	0.015	9.8	122	35.6	32.0	3.2
D-3	n-Hexane	None	45	0.016	10.2	122	35.6	32.7	2.7
D-4	Methylpentanes	None	41	0.016	10.1	122	35.6	32.3	2.3
D-5	Methylpentanes	None	42	0.016	9.8	122	35.6	34.3	2.2
H-1	n-Hexane	None	48	0.016	9.3	133	36.3	32.9	2.6
H-2	Methylpentanes	None	45	0.016	9.3	131	36.3	32.2	2.4
H-3	n-Hexane	Pressure Cooker	45	0.021	9.6	127	36.0	32.6	5.7
H-4	Methylpentanes	Pressure Cooker	46	0.019	9.0	124	36.9	32.7	4.1
2D-1	Methylpentanes	None	43	0.017	6.4	135	35.4	32.9	2.3
2D-2	n-Hexane	Jacketed Kettle	47	0.014	8.7	132	35.1	31.9	3.2
2D-3	Methylpentanes	Jacketed Kettle	46	0.014	8.7	135	35.1	33.9	2.6
2D-4	n-Hexane	Jacketed Kettle	42	0.017	11.1	134	34.3	28.0	4.8
2D-5	Methylpentanes	Jacketed Kettle	44	0.017	11.0	135	34.1	29.4	3.6

cooked seeds were processed in the closed stainless steel kettle, which was heated by a steam jacket held at 30 psig. steam pressure during the initial heating stage. When the seeds had nearly reached the desired temperature, the steam was throttled to prevent further temperature rise. This method of temperature control was crude, and considerable fluctuation was encountered. During the cooking operation the seeds were continually agitated by the stirrer.

In order to obtain true data as to the operation of the unit, it was necessary that equilibrium be established throughout the extractor before a sampling period was commenced. Preliminary studies had indicated that two, and preferably three portions, each equal to the quantity required to fill the extraction unit, be passed through the extractor before equilibrium could be attained. Therefore three portions of flakes were passed through the extractor before any data for a given run were recorded. These data included weights of the solvent and flakes charged, weight of the spent flakes or meal, and the quantities of solvent and oil recovered during the test period. The extracted meal and the product oils were recovered and evaluated. The temperature readings of the extractor and drier during the entire operation were recorded.

The following analyses recommended by the American Oil Chemists' Society were employed: moisture and volatile matter in cottonseed flakes and meal (Ba 2-38); oil content of the flakes and meal (Ba 3-38); and free fatty acids (Ca 5-40). In addition, refining loss (Ca 9a-41) was modified to use only a 100-gram sample and to separate the oil from the soapstock by centrifuging the mixture. The Official Bleach Test (Cc 8a-46) was also modified to use 25-gram sample. The colors of refined and bleached oils were determined by obtaining the percentage of light transmission in a 25-mm. cell at 550 mμ with a Beckman Spectrophotometer.

Experimental Data. The operation of the extractor was generally satisfactory although extreme precision in control of the flake and solvent charges was not attained, Manual control of the temperature of the extraction unit and drier resulted in some fluctuation. Fluctuations in rates and temperatures encountered in a given run were not considered significant since they were no greater than the variations generally found in the composition of a given sample of natural product like cottonseed.

A total of 14 extractions was considered in this group of experiments, six with cooked seeds and eight with raw seeds. In the following tables run numbers of tests using the seeds from Delta Products Company are prefixed by D; and those using seeds from Helena Cotton Oil Company are prefixed by H.

The conditions under which these extractions were conducted were within the limits previously established as being satisfactory for the extraction of cottonseed flakes. No significant difference in operation was apparent when operation was switched from raw seeds to cooked seeds. The extraction data from this group of runs are presented in Table I. All values were calculated to a moisture-free basis so that data could be compared directly.

The relative extraction efficiency of the solvents is best obtained by considering individual runs which

TABLE II

Evaluation of the Quality of Methylpentanes and Normal Hexane Extracted Cottonseed Oils

Run No.	Solvent	Seed Preparation Cooking Treatment	Free Fatty Acid Wt. %	Refining Loss Wt. %	Color % Transmission	
					Refined	Bleached
D-1	n-Hexane	None	6.0	21.2	....	....
D-2	n-Hexane	None	4.5	16.5	....	....
D-3	n-Hexane	None	4.0	14 2	....	....
D-4	Methylpentanes	None	6.6	18.7	....	....
D-5	Methylpentanes	None	7.2	21.3	....	....
H-1	n-Hexane	None	2.2	9.6	91.1	96.6
H-2	Methylpentanes	None	2.6	7.5	93.5	97.3
H-3	n-Hexane	Pressure Cooker	1.0	8.0	83.6	93.2
H-4	Methylpentanes	Pressure Cooker	1.4	5.8	82.0	93.8
2D-1	Methylpentanes	None	1.9	7.0	76.7	91.6
2D-2	n-Hexane	Jacketed Kettle	2.2	9.8	73.0	91.6
2D-3	Methylpentanes	Jacketed Kettle	1.9	7.1	86.0	96.6
2D-4	n-Hexane	Jacketed Kettle	2.2	10.2	69.0	86.0
2D-5	Methylpentanes	Jacketed Kettle	2.2	9.2	82.7	93.8

employed comparable extraction conditions. The oil content of extracted meal is considered the criterion in determining the extraction efficiency of these data since this factor is usually employed in plant operation. In all cases methylpentanes reduced the oil content of the meal to a lower value than n-hexane. The improvement varied from 0.2% in Runs H-1 and H-2, under conditions which slightly favored n-hexane, to 1.6% in Runs H-3 and H-4 under conditions which slightly favored methylpentanes. The improvement from the use of methylpentanes averaged 0.6% with raw seed and 1.1% with cooked seed.

The oil evaluation data presented in Table II include the determinations of the free fatty acid contents, refining losses of the crude oils, and relative color determinations of both refined and bleached oils. With a single exception (H-3 with H-4) all oils extracted by methylpentanes refined to a lighter color than oils extracted from corresponding seeds by n-hexane. The oils extracted by methylpentanes, without exception, bleached to a lighter color than those extracted by n-hexane.

Cooking in the pressure cooker apparently deleteriously affected the color while cooking in the jacketed kettle seemingly improved the color.

The free fatty acid content of the seeds varied considerably from run to run making a direct comparison of the relative refining losses somewhat difficult. Figure 2 is a correlation of the free fatty acid content *versus* the refining loss for oils from both cooked and raw cottonseeds. This correlation indicates that, for a given solvent, a definite relationship exists between the free fatty acid content and the refining loss. It is evident that refining losses increase more rapidly as oils with higher free fatty acid contents are refined.

An improvement in refining loss of 2 to 4% is indicative of the superiority of methylpentanes over n-hexane.

Discussion

The extraction data obtained in the laboratory countercurrent extractor, with the exception of solvent losses, generally parallel data reported for commercial extraction plants. Results from operation of the laboratory extractor provide an excellent index to plant operation.

A reasonable check between the oil recovered, the oil residue in the meal, and the original oil content of flakes is noted in Table I. The oil residue is considered the most significant value of the group. The original oil content (and the oil yield) will vary greatly from seed to seed while, under a given set of extraction conditions, the seeds are more likely to be extracted to a significant and reproducible oil residue.

The solvent losses between extraction plants are so inconsistent that the results from extractions such as those that were conducted in these tests would, at best, be only applicable to a single plant. In addition, solvent losses obtained in these tests were sufficiently erratic to prevent conclusive correlation of these data.

The lighter color noted in the oils from seeds which were cooked in the jacketed kettle is probably due to the absence of water during cooking. It is probable that the deleterious effect of direct steam on the color

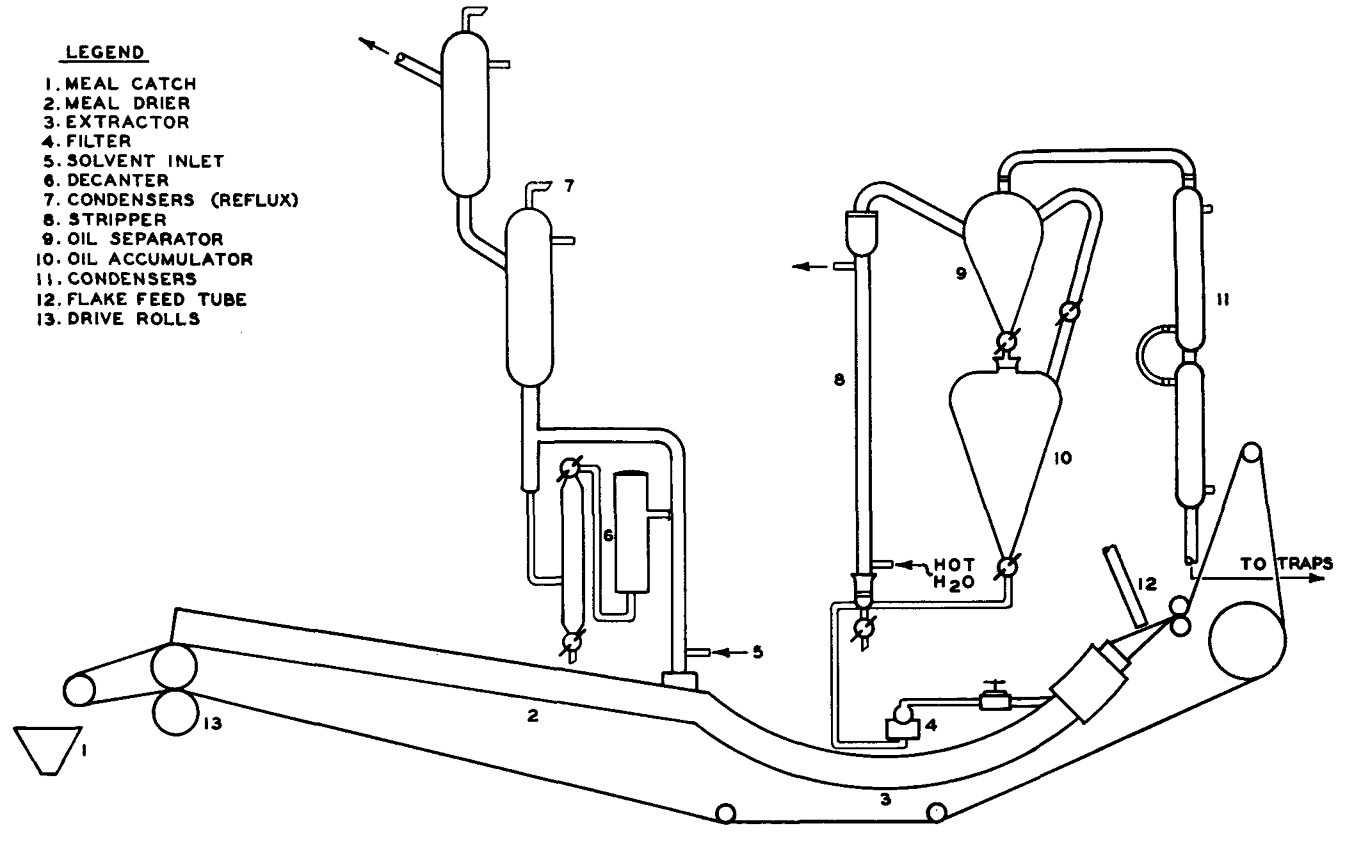

FIG. 1. Continuous countercurrent extractor.

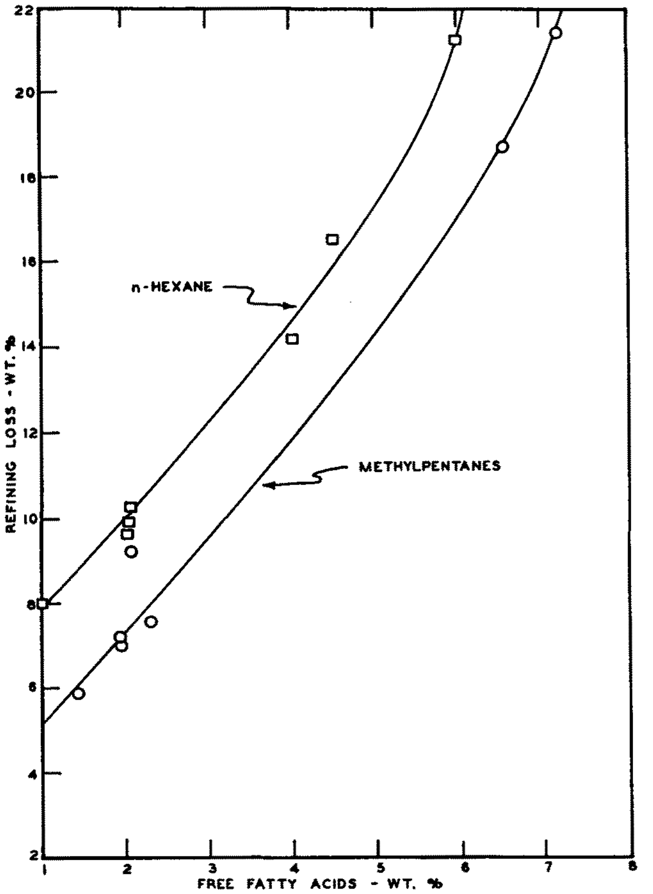

FIG. 2. Effect of free fatty acids on the refining losses of cottonseed oils extracted by n-hexane and methylpentanes.

of the oil is due to rupture of the color glands since the rupture of the glands by water and other polar solvents has been well established (3). The color of the refined oil from different shipments of seeds varies greatly. This is established by a comparison of runs H-2 and 2 D-1 (Table II), both with raw seeds employing methylpentanes as the solvent.

The results of laboratory extractions were confirmed by experimental runs in a 200-ton per day commercial extraction plant. In one commercial plant run, for a duration of 20 hours, methylpentanes extracted prime cottonseeds to 0.3% less residual oil than that extracted by n-hexane for a period of comparable operation. Also the oil extracted by n-hexane sustained an average refining loss of 6.5% while the oil extracted by methylpentanes sustained a refining loss of only 4.0%, a reduction of 2.5%. The oil extracted by methylpentanes refined to 4.7 Lovibond red color and bleached to 0.8; the oil extracted by n-hexane refined to 4.9 and bleached to 1.7 Lovibond red color.

Another test in the same commercial plant was conducted with 10 to 30% field damaged seeds for a duration of 38 days. Methylpentanes extracted these seeds to 0.2% (average based on 54 samples) less residual oil content than n-hexane. A 1.0 to 1.8% reduction in refining loss was noted in the methylpentanes extracted oil.

Analyses of oil samples made in the Phillips' laboratories were in good agreement with duplicate samples analyzed by an independent referee laboratory.

Conclusions

From the data obtained with the laboratory extractor and with commercial equipment, substitution of methylpentanes for normal hexane as a solvent for the extraction of cottonseed oil appears desirable. Use of methylpentanes should result in an increase in the oil recovered from the seeds, a decrease in the oil lost during subsequent refining, and an improvement in the color of both refined and bleached oils. The increased oil yield and decreased refining loss both directly increase the income which a plant can obtain for products from processing a given amount of seeds. Although no direct premium is offered for light colored oil, the color improvement may prove valuable when it is necessary to process poor grade seed which would normally yield oil that would be penalized for being "off-color." Much of these poor-grade seeds could be processed by methylpentanes and oils sufficiently light to pass color specifications produced.

In a "tight" plant with sufficient condenser capacity and low temperature cooling water, little, if any, increase in solvent losses would result from the substitution of methylpentanes for n-hexane. However considerable increase in solvent losses might occur in plants with inefficient equipment for solvent recovery.

Certain other advantages would also emanate from the use of methylpentanes:

1. The lower boiling point of methylpentanes coupled with a lower latent heat of vaporization should result in a decrease in steam costs.
2. The lower boiling point of methylpentanes should allow the solvent to be completely stripped from the oil at lower temperatures, resulting in even a greater improvement in the color of the oil, since it is well established that heating the crude oil tends to fix the color, making subsequent bleaching much more difficult.
3. The odor of methylpentanes is much more penetrating than n-hexane so that many leaks about a plant may be discovered by the odor of escaping solvent. Thus dangerous concentrations of solvent in the atmosphere can be more easily detected.

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