Farmer and Moore found good agreement between the yields of dehydro-polymers produced from cyclohexene and those calculated from the amount of peroxide used. In our case we should expect that each peroxide molecule is capable of converting two linoleate chains into free radicals so as to form one dehydro-dimer molecule, but it is not possible to check the stoichiometry of the total reaction unless the polymers are quantitatively resolved into dimer, trimer, etc. With the small quantities of linoleate used and the relatively large distillation losses it was impossible to check the stoichiometry except that it is calculated from the $E^{1\%}_{1\,cm.}$ values in Table II that the total product would contain 37% (*i.e.* 155/420x100/1) of dimer (if the latter only were formed) whereas complete expenditure of the peroxide to give dimer only would result in a 55% dimer content. Similarly complete expenditure of the peroxide could give a maximum of 41.5% of trimer as the only species. These figures are reasonable since the reaction is not complete in 10 hours.

Methyl Stearate. Using the same reaction conditions and peroxide/fatty ester molar ratio as in the preparation of linoleate dehydro-dimer, methyl stearate gives dehydro-polymers containing only a little dimer. Although the points of attack in the stearate molecule remain to be determined, it is clear from this experiment that linking can occur where olefinic double-bond activation is absent. Thus it is probable in the case of linoleate that linking occurs between positions which are, and are not, activated by the proximity of olefinic double bonds. The small percentage of dimer isolated from the stearate product may reflect the superior ease of attack (6) of tertiary α-methylidyne groups (—CHR—) as compared with secondary methylene groups ($-CH_2-$) so that the initially formed dimer is more readily attacked than the unchanged stearate. The case of stearate differs from that of linoleate where the dimer/higher polymers ratio is substantially higher.

The small amount of unsaturation present in the stearate polymers is analogous to that found in the dehydro-polymers of cyclohexane (6).

Carbon and hydrogen percentages of the dimer and higher polymers indicate that very little, if any, incorporation of tert.-butoxy radicals takes place in agreement with the fact that tert.-butyl alcohol is the main product from the peroxide.

Summary

a) Reaction of methyl linoleate with di-tert.-butyl peroxide yields tert.-butyl alcohol and dehydro-polymers of methyl linoleate as the main products.

b) The dehydro-dimers and higher dehydro-polymers of methyl linoleate contain conjugated diene unsaturation, thus indicating the involvement of the pentadiene system $-CH{=}CH-CH_2-CH{=}CH-$ in the reaction.

c) Methyl stearate yields dehydro-polymers on reaction with di-tert.-butyl peroxide, thus indicating that reaction can occur at points in the fatty acid chains not activated by the proximity of olefinic double bonds.

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The Solvent Extraction of Cottonseed

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COTTONSEED is a unique oil seed. It is more complex and is subject to more variation than any other oil seed. It is not strange, then, that the problems of solvent extracting this oil seed are greater and more numerous than for any other oil seed. Any other seed has one preferred method of handling. There are three distinct, commercially-proven methods of extracting cottonseed. Although exact comparative data are not available, it seems desirable to make a preliminary examination of the advantages and disadvantages of these three basic methods.

The most widely applied method of extracting cottonseed is to pre-press the cottonseed meats in a mechanical screw press or expeller, then to extract the pre-pressed and the prepared cake. Figure 1 shows a flow chart for this method. The cottonseed is first cleaned, de-linted, hulled, and the meats separated from a substantial part of the hulls. These meats are then put through a crushing roll, familiar to the cottonseed industry, and cooked. Dry meats will be humidified in the cooker or possibly even before the crushing rolls. Cooking will require from 30 to 60 minutes, and the cooked meats will be discharged at a moisture of from 5 to 8% and a temperature of 220 to 235°F. A majority of the oil is then pressed out in a continuous mechanical screw press.

The oil in the pre-pressed cake will vary in current practice from 9% oil up to 15%. The cake will be broken up in a cracking roll or cake granulator and

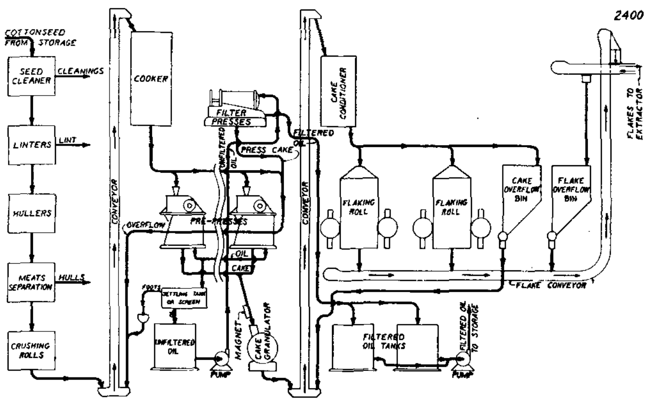

FIG. 1

conveyed to a conditioner where it will be humidified, usually from 9 to 11% moisture, and tempered to a discharge temperature of 130 to 170°F. The conditioned cake is then flaked and sent to the extractor. In actual practice the cake granulator and cake conditioner are sometimes eliminated. There have also been quite successful operations in which flaking rolls are by-passed and cake sent directly from the presses to the extractor. There have been proposals to grind and size the cake before extraction instead of conditioning and flaking. The chief advantages of this process, which is the one most widely used in the industry at the present time, is that it is easier to control. Variations in the seed quality are fairly well smoothed out in the pre-pressing operation. This method also gives the lowest residual oil in flakes. This method can also be used fairly satisfactorily in any type of extractor. There are about a dozen plants operating on this system at present and about six more that will be ready to operate on the new crop of seed. Extraction systems that appear to handle prepared pre-pressed cake satisfactorily include Anderson, French, Allis-Chalmers, Blaw-Knox, Hildebrand, and Kennedy.

An incidental benefit from the application of this process is the improved capacities which have been found possible by using pre-pressing set-ups. The mechanical screw presses or expellers are speeded up for pre-pressing and handle the meats from up to and above 100 tons of cottonseed per day. It was found that this pre-pressing set-up had great merits in increasing operating efficiency on a complete pressing basis, and these discoveries are being developed by further plant tests.

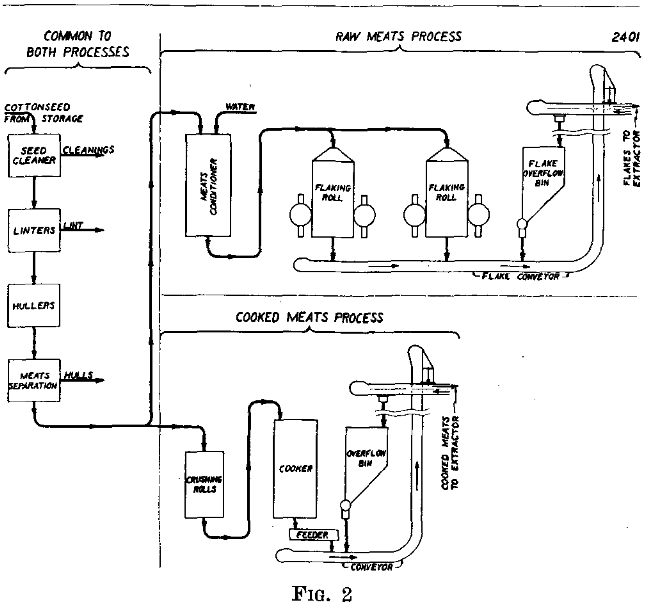

FIG. 2

Figure 2 shows the direct extraction of cottonseed by both the raw meats and cooked meats process. The raw meats process takes the meats from the huller room after the cleaning, de-linting, and hulling and conditions them in a cooker-dryer type of a unit or a steam tube dryer. The conditioning consists in heating the meats to 120 to 150°F. and raising the moisture to approximately 10½ plus or minus 1%. These meats are then flaked quite thin, to around .005 to .006, and sent to the extractor.

This method has an extensive full plant application, particularly by Buckeye Cotton Oil Company, which has two operating plants and a third under construction. Another large capacity plant has been put into production by Plains-Cooperative Oil Mill in Lubbock, Texas, and very good results are being obtained. The greatest appeal is the possibility of improved oil quality.

This method has been satisfactorily applied only with the basket type of extractor. Percolation of solvent and miscella through a relative thin layer of flakes seems to be necessary for this process. Total immersion of flakes in solvent is not satisfactory.

The greatest uncertainty with this process is the meal quality. It is possible to bring out a very light-colored meal only by allowing a high free gossypol content to remain in the meal. By increasing the intensity of toasting, it is possible to reduce the free gossypol at the expense of producing a somewhat darker meal. The Buckeye Cotton Oil Company has a patented process involved in the extraction of raw cottonseed flakes which produces a meal low in free gossypol but still very light in color. It is claimed that this process also produces meal with superior nutritional qualities.

The same flow chart shows the cooked meats process which utilizes the existing crushing rolls and cookers of an existing hydraulic press mill. By installing a feeder in the place of the former, the meats are sent directly to the extractor. Some cooling of the meats is found to be desirable. This process has had a number of plant scale trials by various processors but is not presently being used to great extent. Two large capacity mills will be ready to run this fall on this process. One is a basket type extractor, and the other is the vacuum filter extractor being developed by the Southern Regional Laboratory.

The greatest advantages are that it has the lowest first cost to an existing hydraulic mill and will also have the lowest operating costs. The products produced will be equal to hydraulic products.

Figure 3 shows a chart of the comparative costs of these three methods. The cooked meats plant cost is taken as a basis. It is seen that, for a processor with an existing hydraulic mill, a pre-press and extraction plant might cost about 10% more. A plant to extract raw cottonseed flakes would cost approximately 6% more. As for operating costs, both the pre-pressing extraction plant and the extraction of raw flakes would cost approximately 14% more than would a cooked meats extraction plant. The difference in operating cost is chiefly caused by the fact that it would presumably take one operator in the press room if

COTTONSEED EXTRACTION

COMPARATIVE COSTS — 200 TON CAPACITY

	PRE-PRESS AND EXTRACT	EXTRACT RAW FLAKES	EXTRACT COOKED MEATS
INSTALLED COST	10% MORE *	6% MORE	BASIS
OPERATING COSTS	14% MORE	14% MORE	BASIS
PRODUCTS VALUE	1% MORE	SAME	BASIS

* 12% LESS IF SCREW PRESSES OR EXPELLERS ARE ALREADY INSTALLED

FIG. 3

mechanical presses and flaking rolls are being operated. For the extraction of cooked cottonseed no preparation operator would be required.

The steam usage of process No. 2 and No. 3 is greater than for No. 1, and the electrical power is greater for No. 1. A greater solvent loss is figured for processes No. 2 and No. 3. As for product value, for the purposes of this comparison we have assumed that the pre-press and extraction process would yield about 1% greater value. In some cases this might more than offset the difference in operating costs. The 1% edge for the pre-press process has been allotted on the basis of yields only and does not allow any credit for better quality of products which would probably favor the raw extraction process.

You will also note that if a mill has mechanical screw presses or expellers installed now, the initial cost for an extractor to combine with the presses would be less than the basic cost. Note that 12% less means a total reduction of 22 to 25% below the cost when the presses are included. It should be understood that these figures are only approximate and are worked up based on information that is currently available.

Figure 4 shows a chart comparing the product quality from these three methods of extraction. It would seem that for oil color the pressed oil should be somewhat better as to color and refining loss than hydraulic oil, and the extracted portion of the residual oil left in cake will be somewhat poorer. The average will be somewhere close to hydraulic oil. On the extraction of raw flakes there is some evidence that the oil quality may be better. In the extraction of cooked cottonseed meats quality will be very nearly the same as for hydraulic pressing. Note (1) that oil quality is not certain or established for off-quality seed might very well apply to this complete chart or to this complete talk, for that matter. Cottonseed is so complex that years of research will be required to get all the answers.

COTTONSEED EXTRACTION

COMPARATIVE PRODUCT QUALITY

	PRE-PRESS AND EXTRACT	EXTRACT RAW FLAKES	EXTRACT COOKED MEATS
1. OIL COLOR-PRESS	BETTER	—	—
EXTRACT	POORER	BETTER (1)	SAME (1)
2 REFINING LOSS-PRESS	BETTER	—	—
EXTRACT	POORER	BETTER(1)	SAME (1)
3. MEAL COLOR	DARKER	VARIABLE (2)	BRIGHTER
4. MEAL NUTRITION	SAME (3)	SAME (3)	SAME (3)
5. MEAL TOXICITY	BETTER (4)	POORER (4)	SAME (4)

(1) NOT CERTAIN OR ESTABLISHED FOR OFF QUALITY SEED.
(2) BRIGHT COLOR WITH HIGH TOXICITY; DARK COLOR WITH LOW TOXICITY. BUCKEYE PATENTED PROCESS GETS BOTH DESIRABLE FEATURES.
(3) NOT WELL ESTABLISHED.
(4) AS SHOWN BY FREE GOSSYPOL CONTENT.

FIG. 4

For meal color the tendency is to have a somewhat darker meal in the pre-press and extraction operation, simply because the meal is kept hot longer and has to be heated again after extraction in the removal of residual solvent. In the extraction of raw flakes it is possible to bring out a very bright colored meal high in gossypol or dark meal low in gossypol. The meal nutrition has been listed as the same for all three processes, but some available evidence favors direct extracted meal. The meal toxicity as shown by the free gossypol content is better in the case of the pre-press and extract, poorer for the raw flakes in general, and approximately the same for the cooked cottonseed extraction.

It might be concluded from this discussion that the best processing method will vary according to the particular situation of an individual processor. A plant that has presses or expellers now can almost certainly be best served by maintaining a pre-pressing step ahead of the extractor. The extraction equipment required is much smaller than required for direct extraction. Plants that have cookers and hydraulic presses might well consider the possibility of direct extraction.

The secondary oil seed crop will affect the choice of process. If soybeans are to be crushed, the raw meats process on cottonseed becomes relatively more attractive because the same equipment and flow can be used for both seeds. If peanuts are a secondary crop, the pre-press and extraction combination will be most attractive since pre-presses are essential in the extraction of peanuts. This talk has been designed to summarize the present status of the commercial application of solvent extraction to cottonseed. Progress is constantly being made, and new information as it becomes available, is being added to the complete picture. Sufficient information is available now to indicate that all three commercially practiced methods will continue in use and have new installations made for at least a great number of years.

Summary

There are three commercially proven methods of solvent-extracting cottonseed. They are: pre-press and extract, extract raw cottonseed flakes, and extract cooked cottonseed meats. Each of these methods of processing has advantages and disadvantages compared to the others. A comparison of installation costs, operating costs, extraction efficiency, and product quality has been made. The conclusion is drawn that the best method of extraction for an individual mill depends upon what equipment is available.

Plants which have existing mechanical screw presses or expellers available should probably stick to the pre-pressing and extraction method. Mills with cookers and hydraulic presses should consider the direct extraction of cooked or raw cottonseed. If a mill wishes to process soybeans as a secondary crop, the extraction of raw cottonseed flakes is relatively more advantageous than for mills who have no intention of processing soybean. If peanuts are a secondary crop, the pre-press-extraction combination is best.

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