TABLE V

| | |
|---|---|
| Charge— | 850 g. alkali refined fish oil (I.V. 189.4)<br>150 g. dehydrated castor oil fatty acids |
| Polymerization | 1 hr. at 275°C. |
| Steam distillation | 6 hrs. at 275°C. |
| Distillate acids—138 g. | |
| A.N. | 202 |
| I.V. | 79.7 |
| % Saturated acids (Earle-Milner) | 38.1% |
| (%Saturated acids in original oil | 23.4%) |
| Residual oil | |
| Viscosity | $Z_3$ |
| Color | 8–9 Gardner |
| A.V. | 2.8 |

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# Effect of pH During the Cooking of Cottonseed on the Properties of Meals and Oils

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IN EARLIER PAPERS results were presented, demonstrating that variations in time, temperature, and moisture in the cooking of cottonseed greatly influenced the chemical properties of the extracted oil and both the chemical properties and nutritive values of the meals (4, 7). In a screw press plant, meals prepared from cottonseed meats cooked at a low temperature and a low moisture content were far superior to those cooked at a high temperature and high moisture content. In these papers it was also pointed out that different processing procedures are required for cottonseed than for other oil seeds because cottonseed contains pigment glands. The chief component of these glands is gossypol, which makes up from 30 to 50% of the weight of the glands and about 0.4 to 1.7% of the weight of the dry meats. Gossypol and perhaps other unidentified pigments associated with it interfere with the growth of swine and poultry and are responsible for color reversion in cottonseed oils (11). Based on these results, it would appear that the objective in processing cottonseed should be to produce a good oil and at the same time either to remove or inactivate gossypol without lowering the nutritive value of the protein by excessive heating or any other means.

One approach is to use successive solvent extractions to produce superior meals and oil. Solvents suitable for extracting gossypol from cottonseed were investigated, and butanone was selected (3, 8). Experimental lots of meal were prepared with a very low gossypol content by first extracting the oil with hexane, followed by the extraction of gossypol with butanone. The protein efficiency of this meal (grams gain in weight per gram of protein consumed) determined from chick-feeding studies was exceptionally high. For that reason the meal is being used as a standard in determining the nutritive value of other cottonseed meals. It is assigned an arbitrary index value of 100, and other meals are rated above or below this figure. On this scale commercial meals that have been evaluated rate from as low as 30 to as high as 90.

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The extraction of gossypol with butanone was time-consuming and probably would not be commercially feasible unless valuable products could be made from it to defray at least a part of the extraction costs.

Another approach involves attempts to inactivate rather than to remove gossypol without using high temperature cooking or other procedures which would lower nutritive values. In the experiments reported in this paper the effect upon meal and oil of variations in moisture during the cooking procedure and of addition of acid and alkali were determined.

## Materials, Methods, and Equipment

Three lots of cottonseed were used in the experiments: one lot from the 1951 crop raised in the vicinity of Greenwood, Miss.; another from the 1952 crop from the Hill County, Tex., area, and the third from the 1953 crop from the same area.

After some preliminary trials in which high and low moistures with and without stirring were used, it was found that vigorous stirring was essential. For that reason a planetary type of mechanical mixing machine with a 3-speed stirrer, manufactured by the Hobart Manufacturing Company,[2] was used as a cooker. The bowl was fitted with ribs to increase agitation and with a thermocouple well for temperature control. A gas burner served as the main source of heat, and warm air, supplied by fans with heating coils attached, aided in the rapid removal of moisture. With this type of cooker it was found that the experiments could be divided into two groups, *i.e.*, those in which the moisture was below about 22% and those in which it was above this amount. At moisture contents above 22% the flakes become plastic, and the pigment glands are broken by the moisture and beating action produced by the stirrer. (The flakes were produced by carefully rolling the meats in a pair of pilot plant smooth rolls to a thickness of 0.01 in. If not comminuted to at least this extent, difficulty in obtaining a homogeneous plastic mass resulted in incomplete gland breakage.) Below 22% moisture the flakes do not become plastic, and it is difficult to break the pigment glands without high

temperature cooking or the use of extremely high shearing forces, such as those obtained in a screw press. Both of these procedures damage the protein to some extent, as shown by a decrease in soluble nitrogen content.

The pH of the material in the cooker was varied at intervals from 4 to 9.5 by the addition of either orthophosphoric acid or sodium hydroxide dissolved in the added water. A glass-calomel electrode system was used in determining pH values, and all readings were made on finished meal slurries prepared by agitating 10 g. of meal and 100 ml. of water for 2 min. with a Waring Blendor.[2] After several different cooks had been made, it was found that the pH of the finished meal and the percentages of acid or base could be plotted and curves constructed as shown in Figure 1. From these curves the amount of acid

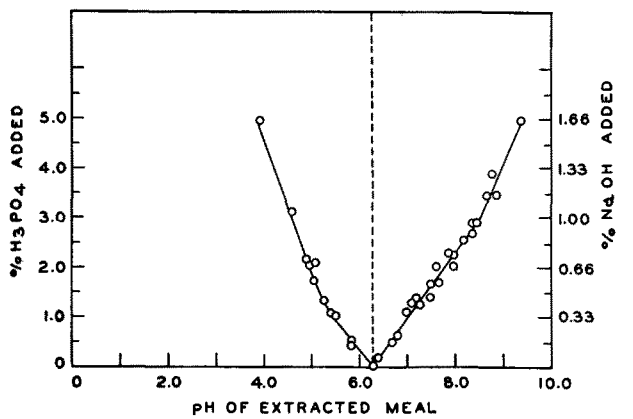


FIG. 1. Effect of addition of $H_3PO_4$ or NaOH before cooking on pH of extracted meal.

or sodium hydroxide required to produce meals of any required pH can be determined. The curves were essentially identical for seeds containing a moderate amount of free fatty acid obtained from two different localities but may not be accurate for all types of seed.

A run at pH 8.2 typical of the procedures used at all pH levels is described below. Thirty-five hundred grams of flakes (7.0% moisture) containing a sufficient amount of hulls to produce approximately 50% protein meal were stirred with 1,500 ml. of water containing 25 g. of sodium hydroxide (35% total moisture). The temperature rose to 110°F. during a prestirring period of 30 min. with application of a current of warm air. It was then raised to 170° in 10 min. and to 212° in an additional 20 min. Total time of cooking was 30 min. (Figure 2 shows typical temperature-moisture-time relationships. The purpose of this type of cook is to remove the moisture evaporatively at low temperatures as rapidly as possible after it has served its purpose in breaking the glands and as a reaction medium between the chemical agents and the components of the cottonseed. Higher temperatures than were used have a detrimental effect on the protein quality of the meal.) The stirrer was operated at high speed in the early stages of the preparation to insure breakage of the pigment glands and

[2] Company and trade names have been used only for the purpose of identifying equipment or materials actually used in conducting the work, and such use does not imply endorsement or recommendation by the U. S. Department of Agriculture over other firms or similar products not mentioned.

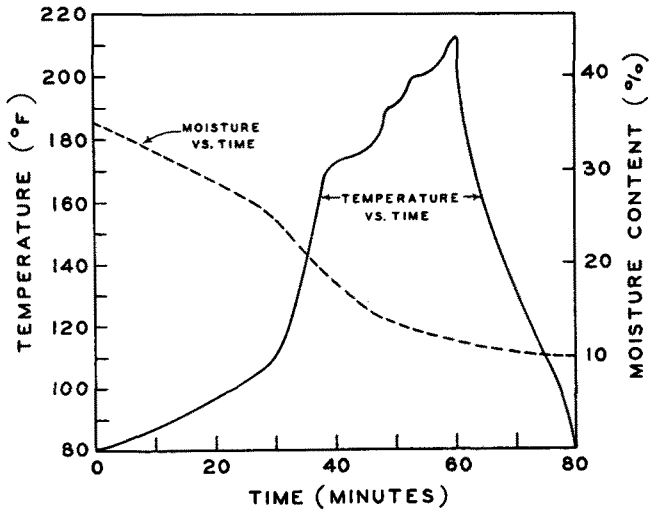


FIG. 2. Relationship between moisture content and temperature during cooking.

in later stages was reduced to medium or low speed. After about 10 min. oil begins to separate, and in about 20 min. the moisture content is reduced to a point at which the plastic mass becomes granular. At the close of the heating period the moisture content varies from about 7 to 10%. The cooked flakes were cooled and extracted with hexane in a laboratory-type solvent extraction apparatus.

Moisture, oil, total nitrogen, and free gossypol were determined by official methods of the American Oil Chemists' Society (1); total gossypol by methods proposed by Pons *et al.* (9); nitrogen solubility in 0.02 *N* sodium hydroxide by the procedure of Lyman *et al.* (6); and oils were refined by official methods Ca-9a-52 of the American Oil Chemists' Society. The refined oils were bleached in accordance with official method Cc-8a-52 and oil color determined by use of the photometric method Cc-13c-50 of the American Oil Chemists' Society (1). Nutritive values were obtained from chick-feeding studies conducted at Louisiana State University. In making these evaluations, day-old chicks are placed on a depletion diet for 10 days and then supplied with the diet to be evaluated (protein level 12%, 6% from a standard corn meal, and 6% from cottonseed meal) for an additional 14 days. Except for minor modifications the method used was that of Heiman *et al.* (5). Grams gain in weight per gram of protein consumed, or protein efficiencies are determined and compared with the protein efficiencies obtained in feeding a standard meal (2, 5).

## Results

In the low temperature cooks of the type described the amount of gossypol extracted with the oil varies with pH. In acid cooks there may be as much as 1% of gossypol in the oil, and the amount decreases with increase in pH. At about pH 8 there are only traces of gossypol remaining in the oil. Conversely, bound gossypol in the meal increases with increase in pH. Gossypol is soluble in alkaline solutions, and when the pigment glands break, the gossypol is evidently taken up in the alkaline solution and then becomes bound to other components of the meal, leaving the oil essentially free from gossypol and a meal with a high bound gossypol and low free gossypol content. In the meals that have been prepared the free gossy-

pol of the alkaline cooked meals varies from about 0.02 to 0.05% and the acid cooks from about 0.03 to 0.08%. Total gossypol content varied from a low of 0.4% for the acid cooks to 1.2% for the alkali cooks.

The soluble-nitrogen content of raw cottonseed meats varies from 87 to 99% (10). Typical soluble nitrogen values for the experimental meals are shown in Figure 3. The base line 80 in Figure 3 represents

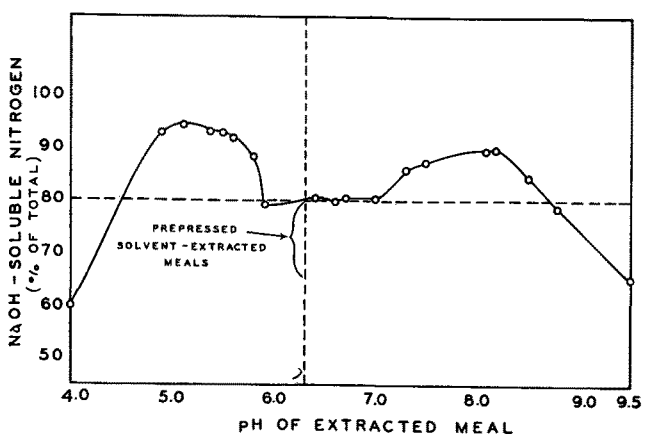


FIG. 3. Influence of pH during cooking on soluble nitrogen content of cottonseed meal.

the amount of soluble-nitrogen in butanone-extracted meal, and the circles show values of a series of meals made up at pH levels varying from 4 to 9. It is interesting to note that most of these points with the exception of those of the very high and very low pH meals are higher than the standard meal. The solubilities of the meals prepared at pH 5.1 and pH 8.2 are exceptionally high. It may be that some hydrolysis takes place at these points that produces an increase in nitrogen solubility. The range of values for a series of prepress-solvent-extracted meals are shown below the base line. They range in value from about 65 to 80 and range in pH from 6.0 to 6.3 (10).

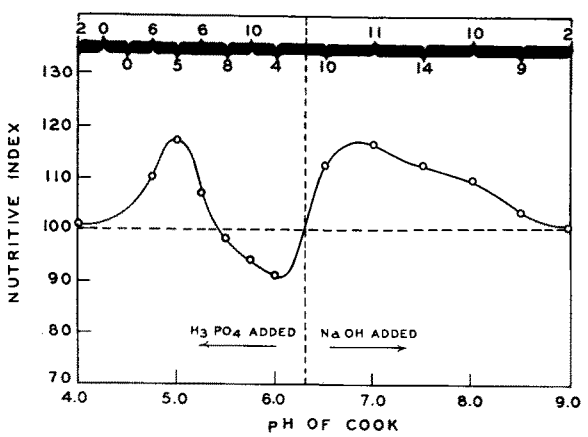


FIG. 4. Influence of pH during cooking on nutritive value of cottonseed meal.

Variation in nutritive value with pH of the meals is shown in Figures 4, 5, and 6. The circles are averages of the number of values obtained at each of the indicated ranges shown at the top of the figures. There were some variations in some of the individual results used to obtain the average values for the different pH levels.

Figure 4 illustrates graphically the effect of cooking at the pH levels indicated, and Figures 5 and 6

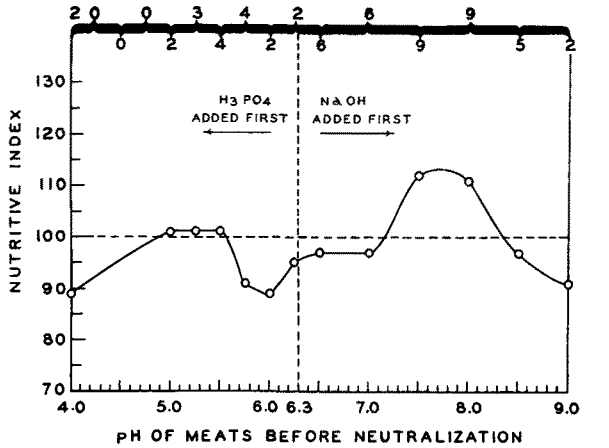


FIG. 5. Nutritive value of cottonseed meals prepared by stirring raw cottonseed meats at room temperature and at varying pH levels followed by neutralization before cooking.

illustrate the effect on nutritive value of adjusting the pH to approximately 5.6 before and after cooking. In the cooks represented in Figure 5 the flaked meats were stirred at room temperature (80–110°F.) for approximately 15 min. at high moisture levels and at the pH levels indicated, followed by the addition of phosphoric acid or sodium hydroxide to obtain a pH of approximately 5.6, stirring for an additional 15 min., and cooking as previously described. Figure 6 illustrates the effect of cooking at the pH

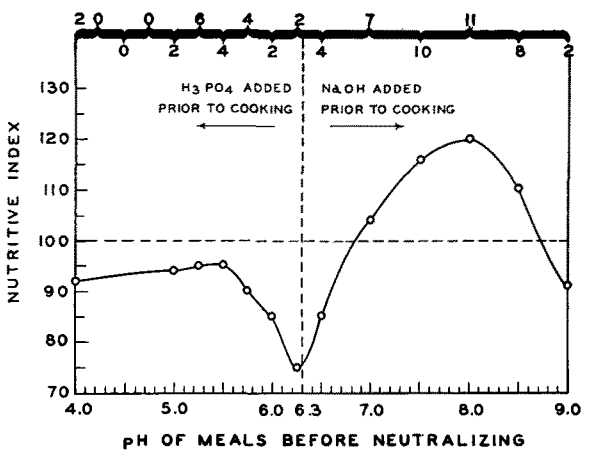


FIG. 6. Nutritive value of cottonseed meals cooked at varying pH levels followed by neutralization after oil extraction.

levels indicated, followed by extraction of the oil and neutralization of the extracted meal to approximately pH 5.6 with either $H_3PO_4$ or NaOH.

Nutritive values obtained with the meals produced were unexpected in that many of the meals were higher in nutritive value than the butanone-extracted meal, which was assigned a value of 100.

In Figure 4 the averages show high nutritive levels at a pH of about 4.5 to 5.5, a dip near the neutral point, and another high level at about pH 6.5 to 8.5.

TABLE I

Effect of pH in Cooking Cottonseed Meats on Properties of the Extracted Oil

| Sample No. | Type of cooking | pH of cook | Gos. in oil, % | % FFA | Refining[c] procedure | NaOH added | | % Refining loss | Refined color[d] | Bleached color[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Bé | Gms. (dry) per 100 gms. oil | | | |
| 1 | Acid cooked (B.S.)[a] | 5.1 | 1.0 | 1.6 | Hydraulic | 12 | 0.85 | 4.9 | 8.2 | 2.7 |
| 2 | Acid cooked (B.S.) | 5.1 | 1.0 | 1.6 | Expeller | 20 | 0.91 | 4.0 | 7.3 | 2.5 |
| 3 | Acid cooked (B.S.) | 5.1 | 1.0 | 1.6 | Slow break | 16 | 1.44 | 4.7 | 5.0 | 1.0 |
| 4 | Acid cooked (A.S.)[b] | 5.1 | 1.0 | 1.7 | Slow break | 16 | 1.44 | 5.6 | 7.0 | 2.9 |
| 5 | Alkali cooked (B.S.) | 8.2 | 0.013 | 0.3 | Slow break | 12 | 0.60 | 9.4 | 4.0 | 0.9 |
| 6 | Alkali cooked (B.S.) | 8.2 | 0.013 | 0.3 | Slow break | 12 | 0.30 | 4.5 | 6.0 | 1.2 |
| 7 | Alkali cooked (B.S.) | 8.2 | 0.013 | 0.3 | Slow break | 12 | 0.32 | 4.5 | 5.8 | 0.8 |
| 8 | Alkali cooked (B.S.) | 8.2 | 0.013 | 0.3 | Centrifuge | 12 | 0.30 | 3.7 | 3.9 | 1.1 |
| 9 | Alkali cooked (A.S.) | 8.2 | 0.013 | 0.3 | Slow break | 12 | 0.50 | 7.7 | 5.0 | 1.1 |
| 10 | Water cooked (B.S.) | 6.3 | 0.80 | 1.1 | Slow break | 14 | 0.60 | 6.2 | 7.1 | 2.6 |
| 11 | Water cooked (A.S.) | 6.3 | 0.80 | 1.0 | Slow break | 14 | 0.59 | 5.5 | 10.0 | 3.9 |

[a] B.S. = before storage. [b] A.S. = after storage for 30 days at 100°F. [c] Official Methods of American Oil Chemists' Society (1). [d] Spectrophotometric Red.

The type of cooking illustrated in Figures 5 and 6 lowers the nutritive values on the acid side and shifts the points of highest nutritive value to higher pH levels. These preliminary results indicate that variations in pH during cooking at high moisture levels, can have a pronounced influence on the chemical composition and nutritive values of cottonseed meals.

## Oil Recovery and Oil Quality

While this study was chiefly concerned with the establishment of the quality of the meal under varying processing conditions, the yield and quality of the oil are also of importance. At the high moisture levels used in these tests (30 to 40%) some of the oil separates during the early stages of cooking and is lost due to spillage from the open cooker. For this reason accurate data on oil yields could not be obtained with the equipment available. Some interesting results were obtained on the quality of the oils produced from the high moisture cooks.

In an earlier paper (11) it was pointed out that color reversion in cottonseed oils is a serious problem in some areas and that color reversion does not occur in oils from which gossypol and related pigments have been removed. In these studies oils from the acid cooks were high in gossypol, those from the neutral cooks somewhat lower, and those from the alkali cooks were essentially free from gossypol. Oils of these three types were refined and bleached immediately after extraction, and identical samples were stored for 30 days at 100°F., then refined and bleached.

As may be seen from the results in Table I, those oils which contained gossypol tended to revert in color and were more difficult to refine after storage. When the maximum amount of lye recommended for oils from the alkali cooks (0.6 g. per 100 g. oil) was used, an unexpectedly high refining loss (9.4%) and a color of 0.9 were obtained. When half this amount of lye was used (No. 6), the loss was reduced to 4.5% and the color was 1.2. That is, 0.3 g. of lye gave about the same results as 1.44 g. of lye with the acid cook. The foots from the acid-cooked oils were hard and contained less than 3% of neutral oil. Those from the alkali cooks were granular and soft and contained over 30% of neutral oil. Hard foots and consequently a lower refining loss were obtained when the oils were refined by a centrifugal method (No. 8) supplied by the DeLaval Separator Company.[2] The method was designed to give results which correlate closely with those obtained in commercial operations. These results suggest that oils with a low refining loss and a low bleached color can be obtained by the high moisture alkaline cooking procedure.

## Conclusions

The cooking of cottonseed meats in the laboratory at varying pH levels, low temperatures, and high moistures resulted in improvement in the quality of both the meals and oils. The meals were high in soluble nitrogen, and at optimum pH levels their nutritive value as measured by the growth rates of chickens in short-term tests was superior to that of a butanone-extracted meal. Oils from meats cooked at low pH levels were high in gossypol and were subject to color reversion during storage while those from meats cooked at high pH levels had a low refining loss, were low in gossypol, and were not subject to color reversion during storage. Both types of oils could be refined satisfactorily immediately after extraction.

Parallelism between the curves showing the relationship between pH and nitrogen solubility and pH and nutritive value was marked.

## Acknowledgment

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