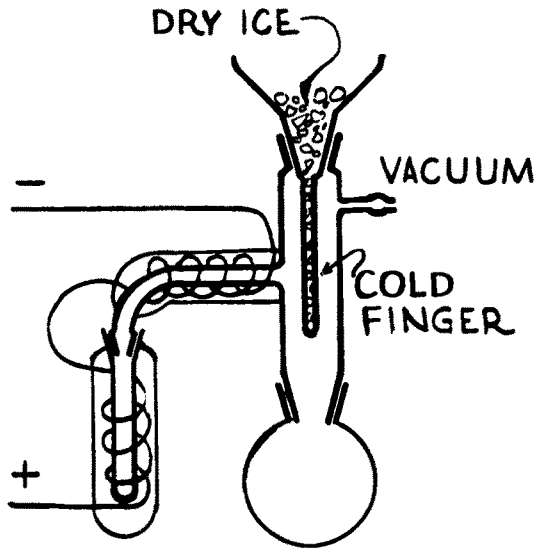



FIG. 1. Micro-sublimation apparatus. The impure benzoic acid (in ether) is placed in the left chamber. After evaporation of the ether, the benzoic acid is sublimed onto the cold finger. It is then shaken down into the round-bottom flask.

45-min. period. This reaction with isoamyl nitrite should be carried out in semi-darkness. After an additional 15-min. reaction period, the solution is made basic with 12 ml. of 3N NaOH. The solution is cooled to 0°C., and 2.0 g. p-toluenesulfonyl chloride are added in small portions over a 20-min. period. The solution is warmed to 50°C. and stirred for 2 hrs. The mixture is diluted with 300 ml. of water, transferred to a separatory funnel, and extracted with several portions of pentane.

The aqueous layer is warmed and then cooled slowly. The large particles of sodium heptadecanoate which precipitate are removed by filtration to yield 15–30 mg. The aqueous filtrate is acidified and extracted with several portions of diethyl ether (peroxide-free), and the extracts are transferred to a sublimation apparatus (Figure 1). After evaporation of the diethyl ether, the benzoic acid is sublimed at 78° to 80°C. and 200 mm. Hg pressure. The benzoic acid may be counted directly for beta radioactivity, or it may be converted to barium carbonate (4, 5). If the acid is counted directly, 8 to 10 mg. are uniformly spread over the surface of a copper planchet, air-dried for 36 to 48 hrs., and the specific activity determined.

The pentane solution is evaporated to dryness, and the remaining heptadecanonitrile is hydrolyzed by refluxing with 10 ml. of 15% KOH in n-propanol for 24 hrs. Hexane is slowly added to the solution until the precipitation of sodium heptadecanoate is complete. The solid is filtered out and recrystallized several times from hexane in a dry ice bath. This product is combined with that obtained previously from the aqueous layer. The combined salt is acidified and extracted with pentane. The free fatty acid is recrystallized twice from pentane in a dry ice bath.

This completes the degradation of the first carbon. The degradation procedure is repeated, using the heptadecanoic acid, and degradations may be continued until an insufficient amount of acid is obtained. Yields of at least 70–75% fatty acid and benzoic acid may be expected. Consequently a minimum starting quantity of 1 g. of fatty acid is required in order to degrade three carbon atoms. The procedure permits the removal of at least six carbon atoms from stearic acid.

REFERENCES

1. Adams, R., Voorhees, V., and Shriner, R. L., "Organic Syntheses, Coll. Vol. I," Wiley and Sons, New York, pages 463–470 (1941).
2. Brown, J. B., and Orians, B. M., Arch. Biochem., *9*, 201–219 (1946).
3. Dauben, W. G., Hoerger, E., and Petersen, J. W., J. Am. Chem. Soc., *75*, 2347–2351 (1953).
4. Doering, W. E., Taylor, T. I., and Schoenewalt, E. F., J. Am. Chem. Soc., *70*, 455–457 (1948).
5. Entenman, C., Lerner, S. R., Chaikoff, I. L., and Dauben, W. G., Proc. Soc. Exper. Biol. Med., *70*, 364–368 (1949).
6. Gibble, W. P., Ph.D. Thesis, University of Arizona (1955).
7. Markley, K. S., "Fatty Acids," Interscience Publishers Inc., New York (1947).
8. Mikeska, L. A., Smith, C. F., and Lieber, E. J., J. Org. Chem., *2*, 499–505 (1938).
9. Millican, R. C., and Brown, J. B., J. Biol. Chem., *154*, 432–450 (1944).

[Received June 13, 1955]

# Selective Acidolysis, a Method for the Segregation of Drying and Semi-Drying Oils[1]

H. J. LANSON,[2] Alkyd Products Engineering, General Electric Company, Schenectady, New York

IN RECENT YEARS the glyceride structure of oils and fats has attracted considerable attention. From a consideration of the properties and uses of many oils it becomes obvious that products with improved technical applications can be obtained by the elimination or extraction of certain constituents (1). Thus drying oils contain a number of different fatty acid groups of varying degrees of unsaturation, and their value largely depends upon the proportion in which acids having two or more unsaturated groups are present. By removing the more saturated constituents, the performance of the oil as a film-former can be improved. This might be done either by fractionating the mixture of fatty acids obtained by hydrolysis and reesterifying, or by segregating the glycerides themselves into fractions of different degrees of unsaturation. Both of these methods have been investigated and have resulted in a better understanding of the number and types of glycerides present in drying and semi-drying oils as well as of valuable technical products.

In effecting separations of the oil glycerides, the efficiency of any process is limited by the mixed glyceride structure of the oil. Thus sardine oil, which contains about 25–27% saturated fatty acids, contains only about 0.5% of fully saturated glycerides. The remaining saturated acids are distributed on glyceride molecules also containing unsaturated acids. However with sardine oil a partial separation of the

[1] Presented at the 28th annual fall meeting, American Oil Chemists' Society, Minneapolis, Minn., Oct. 11–13, 1954.

[2] Present address: The P. D. George Company, St. Louis, Mo.

more saturated glycerides can be effected by "cold-pressing," in which the oil is slowly cooled to temperatures in the range of 0°–5°C., and filtering off the crystallized glycerides (2). The iodine value of the resultant oil is increased about 10 units, and the oil still contains a high proportion of saturated acids. While winterizing or cold-pressing improves the drying and film properties of sardine oil, the resultant dried films are still soft and somewhat tacky. The process of winterizing is of no value in the segregation of vegetable drying oils since few, if any, of the constituent glycerides have more than one saturated fatty acid.

The only method which is being used commercially today for the segregation of drying oils is that involving selective solvent extraction. Two distinct methods have been developed in recent years for refining and segregating drying oils. The furfural extraction process developed by the Pittsburgh Plate Glass Company has been used on and off to produce a soybean oil extract fraction having an iodine value 10–15 units higher than the starting oil. This process has been described in detail by Freeman and Gloyer (3). More recently the Solexol process has been developed by Hixon and the M. W. Kellogg Company (4). This process uses liquid propane at a slightly elevated temperature and under pressure. It is currently being used on fish oil to produce a 5% dark fraction having an iodine value of 235, and an 80% light-colored fraction with an I.V. of 220 and a 15% fraction having an I.V. of 140. The Solexol process is quite flexible and, by varying the conditions of operation, further separations can be obtained.

Although with glyceride oils the degree of separation is limited by the natural distribution of the fatty acids on the glycerides, the fractionation of the free fatty acids is limited only by the efficiency of the fractionation method. The tremendous growth in use of alkyd resins and the advent of new polyols have increased the demand for fatty acids. In addition, the increased use of various derivatives of fatty acids has demanded a greater degree of specificity and purity. Considerable progress has been made in separation methods, particularly, fractional crystallization from solvents and fractional distillation. By the former method the more saturated fatty acids are crystallized out and filtered off (5). Thus soybean fatty acids with an I.V. of 125 can be raised to an I.V. of 155 and cottonseed acids from 105 I.V. to 130. In fact, the acids thus obtained from regular cottonseed acids when esterified with polyfunctional alcohols give drying properties equal to that obtained with soybean acids.

Whereas fractionation by distillation of a fatty acid mixture cannot be effected upon the basis of differences in unsaturation alone, the fact that the saturated acids of cottonseed oil and soybean oil consist mostly of palmitic acid permits the separation of $C_{16}$ and lower acids from the mixed fatty acids of these oils. Cottonseed fatty acids, which contain about 25% palmitic acid, are particularly amenable to improvement by fractional distillation (6). By removal of the $C_{16}$ saturated acid, the iodine value can be increased from 110 to 130. Thus we frequently find that the so-called soybean fatty acids of commerce today are obtained from mixed soap-stocks, portions of which have been derived from the refining of cottonseed oil.

Since stearic, oleic, and linoleic acids cannot be separated by distillation, several investigators have attempted to effect a separation based on the fact that the polymerizing capacity in a drying oil is largely based on the polyunsaturated acids. Bradley (7) has described a method in which the mixed acids or esters are heated to the point of polymerization of the reactive components, and the resulting monomers and dimers are separated by distillation. This method has the disadvantage of requiring the splitting or methanolysis of the glyceride. Most of all, with slow-polymerizing oils, such as soybean oil, the polymerization times are exceedingly long.

IN A PAPER presented in 1946 Lanson and Spoerri (8) described the results of thermally copolymerizing soybean methyl esters with the reactive conjugated methyl esters from tung oil. The separation of polymerized ester from unpolymerized ester was made in a modified alembic flask (9), which offers a convenient method of separation.

TABLE I

| Charge | Time of polymerization @ 300°C. | Weight of polymeric residue | % Polymeric residue on total charge | I.V. of distillate esters |
|---|---|---|---|---|
| 125 g. S.M.E. | 3 hours | 10.3 g. | 8.3% | 125.1 |
| 41 g. Me St.<br>82 g. S.M.E. | 3 hours | 3.6 g. | 2.9% | ..... |
| 41 g. T.M.E.<br>82 g. S.M.E. | 3 hours | 42.0 g. | 34.2% | 107.0 |
| 41 g. T.M.E.<br>82 g. Me St. | 3 hours | 16.8 g. | 13.6% | ..... |
| 125 g. T.M.E. | 3 hours | 87.1 g. | 69.7% | ..... |
| 125 g. S.M.E. | 6 hours | 26.9 g. | 21.5% | 112.8 |
| 41 g. T.M.E.<br>82 g. S.M.E. | 6 hours | 53.5 g. | 43.5% | 94.9 |

S.M.E.—Soybean methyl esters.
T.M.E.—Tung methyl esters.
Me St. —Methyl stearate.

The results obtained are shown in Table I. It is seen that the polymerization of the soybean methyl esters in a 2:1 dilution with methyl stearate gave a polymeric residue of 2.9%. The polymerization of tung methyl esters in 1:2 dilution with methyl stearate gave a polymeric residue of 13.6%. If no interaction between the soybean methyl esters and tung methyl esters occurred on polymerizing a 2:1 mixture, a polymeric residue of 16.5% would be obtained. Actually 34.2% was obtained. Several years later Paschke and Wheeler (10) extended and improved on this work by using relatively pure fatty acids in their investigation of copolymerization. Their results are

TABLE II

Polymerizations @ 290° (50-50 Mixtures) 12 Hours of Normal and Conjugated Linoleate Mixtures

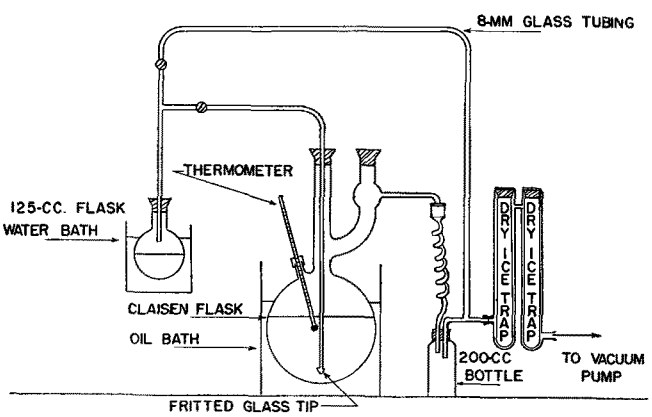
| Components | % D + T | D/T | $n_d^{20}$ of dimer |
|---|---|---|---|
| N + St | 4.6 | 10.0 | 1.4760 |
| C + St | 33.9 | 3.4 | 1.4744 |
| C + N | 66.7 | 4.5 | 1.4760 |
| N alone | 25.3 | 14.1 | 1.4762 |
| C alone | 80.9 | 2.9 | 1.4753 |

Paschke & Wheeler, J. Am. Oil Chemists' Soc., *26*, 281 (1949).

shown in Table II, where St designates methyl stearate. If there was no reaction between normal and conjugated linoleate, each component would act as a diluent of the other, and one might expect 33.9 and 4.6, or 38.5% of polymer in the non-conjugated-conjugated mixture. Actually 66.7% was found, which would indicate 66.7 minus 38.5, or 28.2% of the polymer, which could be due to the N + C ⟶ D reaction. This 28.2% represents 42.3% of the total polymer. As Paschke and Wheeler have pointed out, this probably represents a minimum since any N + C reaction decreases the concentration of N and of C and would decrease the amount of their polymerization by themselves.

On turning back to Table I, it is seen that the presence of the conjugated tung oil esters greatly increases the proportion of non-conjugated polyunsaturated methyl esters which become polymerized. The distillate esters from the straight soybean methyl esters polymerized for 3 hrs. had an iodine value of 125.1 while those after a 6-hr. period had an I.V. of 112.8. The distillate esters obtained after copolymerization with tung methyl esters for the same times had iodine values of 107.0 and 94.9, respectively, proving, as might be expected, that the more highly unsaturated esters preferentially enter into the copolymerizations.

By heating tung oil fatty acids with soybean oil, polymerization of the conjugated acids with the polyunsaturated acids in the soybean oil occurs, together with acid interchange leading to an equilibrium mixture. Extraction experiments have shown that the extracted acids are practically free of conjugation. By employing conditions favoring fatty acid distillation, acidolysis occurs and the less unsaturated acids come off. The acids which come off are essentially non-conjugated and definitely lower in unsaturation than the average unsaturation of the starting oils. Figure 1 represents the laboratory set-up for




SET UP FOR ACIDOLYSIS

FIG. 1

conducting this reaction, which for lack of a better name, might be termed "selective acidolysis."

## Acidolysis Procedure

The modified 2-l. Claisen flask shown in Figure 1 was charged with 800 g. of alkali-refined soybean oil, 200 g. of conjugated linseed fatty acids (Conjulin), and 2.4 g. of anthraquinone. The reaction mixture was heated to 300° and held at this temperature for 3 hrs. with a slow stream of nitrogen bubbling through the oil-acid mixture. The temperature was then lowered to 200°C., and the steam generator was attached to the gas inlet tube. Vacuum was slowly applied to the system. The rate of steam passage was controlled by a stopcock and by the temperature of the water-bath in which the steam generator was immersed. The pot temperature was slowly raised to 275°C. and held for 5½ hrs. The data obtained are shown in Table III.

TABLE III

| | |
|---|---|
| Charge— | 800 g. alkali refined soybean oil (I.V. 141.5)<br>200 g. conjugated linseed fatty acids 2.4 g. anthraquinone<br>Polymerization—3 hrs. at 300°C.<br>Steam distillation 5½ hrs. at 275°–280°C. |
| Distillate acids—188 g. | |
| I.V. (Wijs) | 99.7 |
| A.N. | 202.0 |
| % Saturated acid (Earle-Milner) | 23.1% |
| % Saturated acids in original soybean oil | 13.4% |
| Residual Oil | |
| Color | 5 Gardner |
| Viscosity | $Z_4$–$Z_5$ |
| A.V. | 4.3 |
| $n_D^{25}$ | 1.4875 |
| Gel time @ 310°C. | 17½ min. |
| (Commercial $Z_5$ linseed oil gave a gel time of 41 min.) | |

The film properties of the modified oil were compared with a commercial Z5 bodied linseed oil.

Both oils were thinned to 60% solids, with mineral spirits and 0.5% lead and 0.05% cobalt as naphthenates added on weight of the oil. After ageing overnight, flow-downs were made on glass and the drying characteristics were determined. The modified soybean oil set to a firm film in 4 hrs. while the linseed oil required 5–5¼ hrs. to reach the same degree of dryness.

The comparative water resistance was determined by immersing the 48-hr. films in water at room temperature for 24 hrs. The linseed film whitened to a considerable degree while the modified soybean oil film developed only a slight haze which disappeared within 10 min. after removal from the water.

Similarly, milkweed seed oil, a semi-drying oil, was up-graded as shown in Table IV.

TABLE IV

| | |
|---|---|
| Charge— | 750 g. alkali refined milkweed seed oil (I.V. 122.3)<br>250 g. conjugated linseed fatty acids<br>2.4 g. anthraquinone |
| | Polymerization—3 hrs. at 300°C.<br>Steam distillation—4½ hrs. at 280°C. |
| Distillate acids—240 g. | |
| I.V. | 101.5 |
| $n_D^{25}$ | 1.4655 |
| Residual oil: | |
| Viscosity | X-Y |
| A.V. | 2.0 |
| Dry time (0.5% Pb–0.05% Co) | 6½ hours |
| "X" linseed oil dry time | 5½ hours |

Fish oil, which contains a very high proportion of saturated and mono-unsaturated acids, can be considerably improved in drying and film properties by treatment with dehydrated castor oil fatty acids as shown in Table V.

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 |

REFERENCES

1. Potts, R. H., Oil & Soap, *18*, 199–202 (1941).
2. Brocklesby, H. N., "The Chemistry and Technology of Marine Animal Oils," Fisheries Research Board of Canada, Ottawa, 1941.
3. Freeman, S. E., U. S. Patent 2,200,391 (1940) to Pittsburgh Plate Glass Company; Gloyer, S. W., Ind. Eng. Chem., *40*, 228 (1948).
4. Passino, H. J., Ind. Eng. Chem., *41*, 280 (1949).
5. Kistler, R. E., Muckerheide, V. J., Myers, L. D., J. Am. Oil Chemists' Soc., *23*, 146 (1946).
6. Potts, R. H., U. S. Patent 2,450,611, U. S. Patent 2,450,612, to Armour and Company.
7. Bradley, T. F., and Johnson, W. B., Ind. Eng. Chem., *32*, 802 (1940).
8. Lanson, H. J., and Spoerri, P. E., Paint, Oil & Chem. Rev., *110*, March 20 (1947).
9. Cowan, J. C. *et al.*, Ind. Eng. Chem., Anal. Ed., *16*, 90 (1944).
10. Paschke, R. F., and Wheeler, D. H., J. Am. Oil Chemists' Soc., *26*, 281 (1949).

[Received June 24, 1955]

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

W. H. KING, L. T. WOLFORD, F. H. THURBER, and A. M. ALTSCHUL, Southern Regional Research Laboratory,[1] New Orleans, and A. B. WATTS, C. W. POPE, and JEAN CONLY, Louisiana State University, Baton Rouge

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.

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

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