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# The Rate of Development of Acidity in Stored Tung Seeds and Kernels

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THE tung tree (*Aleurites fordii* Hemsl.) produces a fruit about 2 inches in diameter, which normally has 4 or 5 seeds. The entire fruit is covered by a spongy hull about a quarter of an inch thick. The seeds weigh 3 or 4 grams each and are composed of a kernel enclosed in a brittle shell about a sixteenth of an inch thick. The kernels contain about 65% oil and constitute about a third of the weight of the fruit. As part of the over-all processing operation incident to the expressing of the oil, tung fruit is hulled either at the mill or in the grove. Nearly all of the hull is removed, but varying amounts of shell remain on the seeds.

One of the specifications on which tung oil is bought and sold is the acid value, which is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of the oil. Actually it is approximately twice the percentage of free fatty acids expressed as oleic acid. The maximum acid value permitted by tung oil specifications (2) is 8.0, but if an oil of low acid value is desired, the acid value should not exceed 3.0. Development of free fatty acid usually occurs in the oil in the fruit or seeds before they are processed. Care needs to be exercised in storing tung fruit or seeds to avoid development of free fatty acids in the oil by hydrolysis of the triglycerides.

It has been shown that if commercially hulled nuts are dried to 10% moisture or less, they can be stored for several months without the development of appreciable free fatty acids in the oil (4, 5, 6). In that work the materials were stored in contact with the atmosphere. Hence the temperature fluctuated continuously, and the moisture content of the samples varied with the changing relative humidity of the air.

Commercially hulled nuts consist of a mixture of intact seeds and kernels with broken seeds and kernels. The authors have found on more than one occasion that the free fatty acids developed in commercially hulled nuts occurred mostly in the nuts that were broken. This investigation was undertaken to determine the rate of development of free fatty acids in whole seeds, whole kernels, and chopped kernels under controlled conditions of temperature and moisture. The chopped kernels were included to demonstrate that free fatty acids developed much faster in broken or ground nuts. Whole clean kernels are a product that does not occur in tung mills but were included in this investigation to determine if free fatty acid developed as fast in whole kernels as it did in chopped kernels.

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### Methods and Materials

The highest level of moisture was so chosen as to equal the equilibrium moisture content of the material at 85% relative humidity or higher (3). At this relative humidity molds grow readily, and these might have an important effect on the development of free fatty acids in the oil. The lowest level of moisture investigated was well below the equilibrium moisture content corresponding to relative humidities where most molds do not grow rapidly. The third moisture level was taken intermediately between these two.

Because tung fruit and/or seed are stored in large bins or piles where the conditions within the pile or bin approach those of a sealed rather than a ventilated storage facility, all samples were sealed in No. 2 tin cans prior to storage.

Seeds produced by commercial hulling were used in the experiments described here. All of the seeds with broken shells were removed by hand, and the remaining intact ones were spread out on the floor and allowed to air-dry at room temperature. A portion of the latter was shelled by hand, and a part of the shelled kernels were chopped in a cutting-type mill fitted with a 0.25-inch screen. This procedure gave samples of three different materials, namely, whole seed, whole kernels, and chopped kernels. Since all the seeds were air-dried in a heated building, they were used without further drying in determining the effect of the lowest content of moisture. For the investigations of the effect of maximum and intermediate content of moisture 200-gram portions of each material were placed in cans, and the amount of water required to bring the sample to the desired moisture content was added. Then the cans were sealed.

Samples of each material were stored in incubators maintained at 25°, 31°, and 38°C. The last-mentioned temperature was used because lipase is most active at this temperature and is inactivated above it in the presence of moisture (7). These temperatures cover the range that would be encountered up to drying or milling except where spontaneous heating has occurred in storage.

The free fatty acid content of the oil in the original whole seeds, whole kernels, and chopped kernels was determined at the start of the experiment and at intervals during the period of storage. At each sampling one container of each material corresponding to each moisture content and storage temperature was opened. The method of the American Oil Chemists'

Society for cottonseed (1) was used for determining the free fatty acid of the oil except that the material was twice ground in an electric food grinder. The moisture was determined by drying for 2.5 hours in a vacuum oven at 101°C.

## Data and Discussion

The free fatty acid content of the oil in terms of acid values for each material stored under the different conditions is given in Tables I, II, and III. The moisture content was determined on the material in each can as it was opened, but the value reported at the top of the column is the average for all samples shown in a given column.

TABLE I

Acid Value of Oil in Stored Seeds

| Weeks stored | Stored at 25°C. | | | Stored at 31°C. | | | Stored at 38°C. | | |
|---|---|---|---|---|---|---|---|---|---|
| | % Moisture | | | % Moisture | | | % Moisture | | |
| | 16.9 | 12.1 | 7.2 | 16.9 | 12.1 | 7.2 | 16.9 | 12.1 | 7.2 |
| 0 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| 1 | 1.1 | 2.2 | 1.2 | 0.6 | 1.3 | 0.3 | 1.0 | 1.3 | 0.4 |
| 2 | 0.9 | 1.3 | 0.6 | 0.7 | 0.6 | 1.8 | 1.2 | 0.8 | 1.5 |
| 4 | 1.0 | 0.5 | 0.5 | 1.3 | 0.5 | 0.7 | 4.0 | 1.4 | 2.5 |
| 8 | 2.1 | 1.4 | 0.7 | 4.2 | 4.2 | 0.9 | 4.4 | 2.9 | 1.0 |
| 13 | 4.2 | 1.6 | 0.6 | 5.2 | 7.3 | 0.6 | 4.7 | 7.2 | 3.0 |

TABLE II

Acid Value of Oil in Stored Kernels

| Weeks stored | Stored at 25°C. | | | Stored at 31°C. | | | Stored at 38°C. | | |
|---|---|---|---|---|---|---|---|---|---|
| | % Moisture | | | % Moisture | | | % Moisture | | |
| | 12.3 | 5.8 | 4.1 | 12.3 | 5.8 | 4.1 | 12.3 | 5.8 | 4.1 |
| 0 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| 1 | 0.6 | 0.5 | 0.7 | 0.8 | 0.4 | 0.3 | 0.6 | 0.8 | 0.3 |
| 2 | 0.9 | 0.6 | .... | 0.8 | 0.5 | .... | 1.1 | 0.7 | .... |
| 4 | 1.1 | 0.4 | 0.3 | 1.9 | 0.4 | 0.5 | 1.9 | 0.7 | 0.4 |
| 8 | 1.8 | 0.7 | 0.7 | 2.5 | 1.0 | 0.8 | 4.2 | 1.0 | 0.5 |
| 12 | 3.2 | 0.8 | 0.6 | 5.6 | 0.9 | 0.4 | 5.4 | 1.5 | 0.6 |
| 17 | .... | .... | 0.4 | .... | .... | 0.8 | .... | .... | 0.9 |

TABLE III

Acid Value of Oil in Stored Ground Kernels

| Days stored | Stored at 25°C. | | | Stored at 31°C. | | | Stored at 38°C. | | |
|---|---|---|---|---|---|---|---|---|---|
| | % Moisture | | | % Moisture | | | % Moisture | | |
| | 12.1 | 6.8 | 5.4 | 12.1 | 6.8 | 5.4 | 12.1 | 6.8 | 5.4 |
| 0 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| 3 | .... | 1.5 | 1.4 | .... | 1.9 | 1.7 | .... | 3.0 | 2.4 |
| 4 | 5.2 | .... | .... | 5.8 | .... | .... | 8.0 | .... | .... |
| 7 | .... | 2.2 | .... | .... | 3.1 | .... | .... | 4.8 | .... |
| 8 | 9.2 | .... | .... | 10.2 | .... | .... | 14.4 | .... | .... |
| 10 | .... | .... | 2.0 | .... | .... | 2.5 | .... | .... | 4.6 |
| 12 | .... | 2.8 | .... | .... | 4.2 | .... | .... | 7.2 | .... |
| 13 | 12.4 | .... | .... | 15.9 | .... | .... | 20.0 | .... | .... |
| 22 | .... | .... | 2.5 | .... | .... | 4.3 | .... | .... | 6.0 |
| 26 | .... | 4.6 | .... | .... | 6.6 | .... | .... | 13.7 | .... |
| 27 | 20.4 | .... | .... | 27.5 | .... | .... | 34.6 | .... | .... |
| 49 | .... | .... | 5.0 | .... | .... | 7.7 | .... | .... | 13.0 |
| 53 | .... | 7.8 | .... | .... | 13.1 | .... | .... | 19.1 | .... |
| 54 | 36.4 | .... | .... | 46.6 | .... | .... | 52.5 | .... | .... |
| 86 | .... | .... | 6.7 | .... | .... | 11.3 | .... | .... | 17.0 |

An inspection of Tables I-III shows that within the limits used free fatty acids develop more rapidly with increasing temperature of storage and moisture content of the material. These factors may however be small compared to the effect of chopping kernels as shown in Table III.

At all the temperatures (25°, 31°, and 38°C.) used, whole seeds with moisture contents of 7% and 12% were stored up to 4 weeks, and seeds with a moisture content of 17% up to 2 weeks without development of free fatty acids equivalent to an acid value of more than 2.0. Under none of the storage conditions did the oil in any sample of seed develop free fatty acids equivalent to an acid value in excess of 8.0, the maximum permitted by tung oil specifications (2).

Unbroken kernels stored under similar conditions developed less free fatty acids than did the whole seeds. Kernels containing 4% and 6% moisture were stored up to 12 weeks at temperatures as high as 38°C. without developing free fatty acids in the oil equivalent to acid values above 1.5. In 12 weeks under the same conditions the oil in kernels containing 12% moisture developed free fatty acids equivalent to acid values of 3.2 to 5.6.

Even the chopped kernels containing 5% and 7% moisture were stored for as long as 3 weeks at temperatures up to 38°C. without the development of free fatty acids in excess of an acid value of 8.0. The oil in chopped kernels containing 12% moisture developed free fatty acids equivalent to acid values above 8.0 in less than a week's time.

Whole tung fruit would be expected to behave very much as the whole seeds under the same temperature and relative humidities because in both materials the kernel is protected by the shell. However, at a given relative humidity, the moisture content of the whole fruit would be appreciably higher than that of the whole seeds because the hull of the fruit is more hygroscopic than the shell. Although the ratio between moisture content of seed and fruit varies widely, seeds containing 12% moisture would correspond to whole fruit containing about 17% moisture, while the seeds containing 17% moisture would correspond to fruit containing about 25% moisture.

In the tung belt of the Southeastern States tung fruit can remain on the ground throughout a wet winter without developing free fatty acids in the oil. The average winter temperatures in the tung belt vary from about 10° to 16°C. (50° to 60°F.). High moisture content of the fruit by itself is not therefore responsible for development of free fatty acids. This work has shown that intact seeds and kernels of moderately high moisture content can be stored for as much as 12 weeks at temperatures up to 38°C. without developing free fatty acids equivalent to acid values in excess of 8.0. On the other hand, free fatty acids developed rapidly in chopped kernels. In commercial hulling many of the kernels are broken, thus creating a condition favorable to development of free fatty acids, provided moisture content and temperature are also favorable.

The data reported here indicate that excessive acid values observed in freshly produced tung oil probably have resulted from unfavorable conditions of handling hulled seeds between hulling and pressing. Excessively high acid values may also arise as a result of spontaneous heating of the fruit in storage although no investigations have been made to substantiate this assumption.

## Summary

Whole tung seeds, whole kernels, and chopped kernels of high, medium, and low moisture contents were sealed in tin cans and stored in incubators maintained at 25°, 31°, and 38°C. At intervals samples were removed and the acid value of the oil determined.

The different temperatures used had slight effect on the rate of development of free fatty acids in the oil of the whole seeds and kernels, but the higher temperatures greatly increased the rate of development of free acid in the chopped kernels.

Whole seeds containing 7% and 12% moisture were stored for 4 weeks and seeds containing 17% moisture were stored for 2 weeks, during which periods the oils developed free fatty acids equivalent to acid values of 2.0 or less. Under none of the conditions used did the acid values of the oils exceed 8.0 after storage for 13 weeks.

Whole kernels developed even less free fatty acids than seeds stored under similar conditions. Kernels containing 4% and 6% moisture were stored for 12 weeks during which period the acid value of the oil never exceeded 1.5. Even in kernels containing 12% moisture the acid value of the oil did not exceed 6.0 at the end of 12 weeks.

Chopped kernels with moisture contents of 5% and 7% could be stored for 12 days without developing an acid value in the oil of more than 8.0. However chopped kernels with a moisture content of 12% developed an acid value in the oil in excess of 8.0 in less than a week.

Whole seeds with as much as 15% moisture could probably be stored for several weeks without developing an objectionable amount of free fatty acids. Since commercial hulled "nuts" practically always contain some broken kernels, to avoid development of free fatty acids in storage they should be dried to 10% or less moisture before storage.

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# Pilot-Plant Application of Filtration-Extraction to Rice Bran[1]

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APPLICATION to rice bran of a simplified solvent process, filtration-extraction, which was developed originally for cottonseed (1), tends to overcome several of the technological difficulties that have hampered the solvent extraction of rice bran. Many of these difficulties have been investigated at this laboratory and the results reported, including work on the storage of rough rice bran (6) and on the composition and processing of rice bran (5, 8) and rice bran oil (2, 4, 7, 9, 11, 13).

The previous work indicated that most of the functional processing difficulties arise from the large amount of fine material in the bran. For example, in the percolation type of extractors, fines result in channeling; a high concentration of fines in the miscella presents clarification problems; and fines in the marc (solvent-damp extracted bran) tend to clog the vapor system during desolventization.

The general process as applied to rice bran consists of cooking the bran, cooling, slurrying with miscella (oil-hexane mixture), filtering, counter-currently washing the cake three times on a rotary, horizontal vacuum filter (1), and conventional recovery of oil and meal products. Cooking is responsible for practically eliminating the fines problem by agglomeration to form larger particles and for altering the physical characteristics of the particles so that the resistance to compression is appreciably increased, which, in turn, increases the filtration rate and minimizes the possibility of channeling. Cooking also inhibits any further rise of free fatty acids of the oil in the bran by substantially inactivating the lipolytic enzyme action (6).

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The purpose of this paper is to report data obtained from pilot-plant-scale filtration-extraction runs, conducted following tests using small-scale batch equipment (12) which had indicated process advantages for rice bran similar to those found for cottonseed; such as rapid filtration rates, low fines content in the miscella, good oil extractability, high capacity, low solvent-to-meal ratio, low solvent content in the marc, and a good quality of oil and meal products.

## Process and Equipment

Figure 1 is a flow diagram of the filtration-extraction process. Figures 2, 3, and 4 show the equipment —cooker and filter with auxiliary equipment—used in the two major operations of the process.

The cooker is a standard 5-high unit, such as is used in processing cottonseed. It consists of five steam-jacketed kettles, placed one above the other. The four lower kettles are joined by means of valved connections to a common vent stack, which is equipped with an exhaust blower. Moisture and temperature of the bran in the top kettle are adjusted and controlled by the addition of steam and water, and by steam jacket pressure. As the bran drops from the top to the four lower kettles, moisture removal, or drying, is controlled by the vent system and jacket temperatures.

The bran discharged from the cooker is shaken through a ¼-inch mesh screen to break the large lumps before spreading on trays to cool.

The cooked, cooled bran is charged continuously to one end of a paddle-type of mixing conveyor, 1 foot in diameter by 12 feet long. To the bran is added the second of the four filtrates (see flow diagram) to form a slurry which has a retention time of 15 to 20 minutes in the mixing conveyor. During this time the cooked bran and miscella are gently but thoroughly mixed and conveyed to the discharge end of the conveyor.