CORRELATION OF pH AND QUALITY OF SHUCKED SOUTHERN OYSTERS[1/]

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ABSTRACT

From the experiments the spoilage pattern of refrigerated Southern oyster meats was found to be similar, in general, to that reported in other locations. This spoilage is fermentative in nature, characterized by a gradual and continuous decrease in pH and the development of a sour odor. The drop in pH is not necessarily correlated with the sour odor. A seasonal variation in pH, initially and at intervals during subsequent storage at 41° F. (5° C.), has been observed, with the values being lowest during the summer and highest during the winter.

Spoilage patterns and pH changes have been followed also in oyster liquor held under various conditions as compared to oyster meats, in the adductor muscles as compared to the soft tissues, in washed and unwashed oysters, and in homogenized oysters.

INTRODUCTION

The possible usefulness of pH measurements as a reliable objective means of judging freshness in shucked oysters has been suggested in several previous studies. Hunter and Linden (1923) found a relationship between the odor and appearance of Atlantic coast oysters (Crassostrea virginica) and the pH of their liquor. They concluded that oysters passed from good to stale in a zone represented by pH values of about 6.1 to 5.6. From a pH of 5.3 to 4.9 they passed from stale to sour or putrid, and below 5.0 the oysters were described as being in an advanced stage of putrefaction.

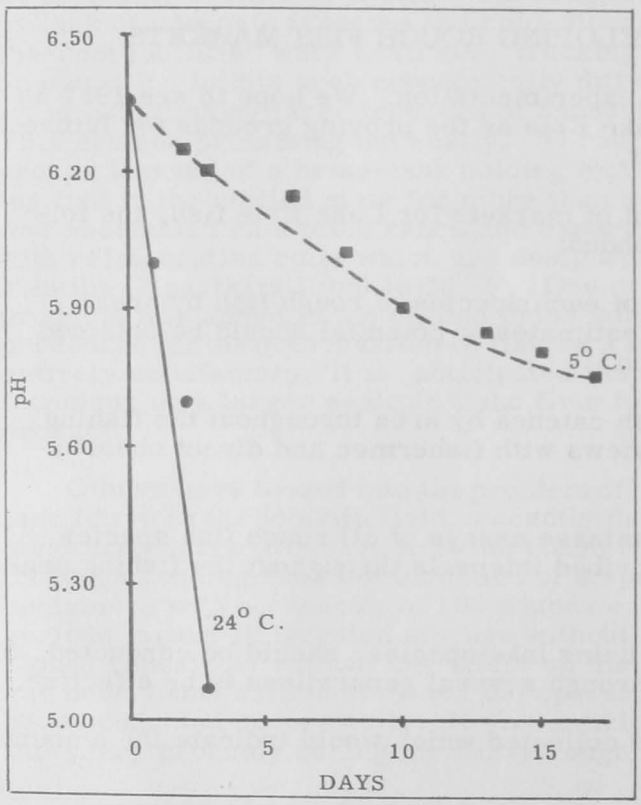

Fig. 1 - pH of shucked oysters held at 41° F. (5° C.) and 75° F. (24° C.) for 15 days.

In addition to pH values obtained with ground oyster meats as well as oyster liquor, Baldwin, Puncochar, and Pottinger (1941) measured changes in water-soluble nitrogen, alcohol-soluble nitrogen, and total titratable acids during storage of Eastern oysters. From the standpoint of ease, rapidity, and reliability of results, pH values seemed to them to be the most promising of these measurements as an indicator of oyster freshness. They found that the pH of the liquor was initially higher than that of the oyster meats, but both values tended to be equal near the end of a storage period of about a week or ten days. According to their results, they described oysters at a pH of 6.2 to 5.9 as being in a good condition, at pH 5.8 in an "off" condition, at pH 5.7 to 5.5 in musty condition, and at 5.2 and below as sour or putrid.

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Piskur (1947) concluded that pH measurements may possibly serve as an objective index of the quality of commercially-shucked Pacific oysters (Ostrea gigas). In more recent work, Pottinger (1948, 1951), using Eastern oysters, found that the pH continued to decrease during storage in crushed ice, with the oysters becoming progressively more sour and changing markedly in appearance. The time required for an off-odor to develop after the liquor reached a pH of 6.0 or 5.9 varied between three and six days.

In none of the aforementioned studies was any mention made of the mechanisms which might be responsible for the souring, nor were the products which were formed identified. Presumably, acids are formed from the breakdown of glycogen known to be distributed throughout the oyster. It is not known whether this breakdown is due to bacterial action or to glycolytic enzymes within the oyster tissue.

Humphry (1944, 1950), in a basic study of glycolysis in the oyster adductor muscle, demonstrated a relatively slow production of lactic and pyruvic acids in tissue homogenates. He concluded that glycolytic activity in the oyster muscle proceeds at a much slower rate than in mammalian muscle, where all available glycogen is converted into lactic acid within a few hours under anaerobic conditions which develop within the tissue following slaughter. Apparently, no work is available on glycolytic systems in other oyster tissues, although Hatanaka (1941) found that most of the glycogen is in the soft tissues. Bargeton (1941) reported that connective tissue was richest in glycogen.

The present study, conducted from February 1, 1955, to February 1, 1956, was directed toward the correlation of pH and organoleptic changes in the Southern oyster (Crassostrea virginica) under various storage conditions and investigation of the mechanism involved in souring as a basis for appropriate control measures.

EXPERIMENTAL

MATERIAL AND METHODS: All oysters used in this study were of the species Crassostrea virginica, tonged from Cat Point Reef near Apalachicola, Fla. Some were tonged directly and others were purchased either in the shell or freshly-shucked from a commercial packing house in Apalachicola, Fla. The pH of all oysters was measured initially in from 1 to 4 hours after shucking and washing.

All pH measurements were made with a Beckman model H^2 pH meter using the slurries of 35- to 50-gram (3-4 oysters) random samples of oysters which were blended in a Waring blendor for about two minutes. The odor and appearance of the oysters and liquor were noted at the time pH values were determined. Odor was rated organoleptically by the authors.

RESULTS: Oysters Held at Refrigerator and Room Temperature: Shucked oysters were stored in pint metal friction-top cans at 41° F. (5° C.). To determine the rate at which spoilage would occur in unrefrigerated oysters, some were held at room temperature, 75° F. (24° C.). The pH, odor, and appearance were determined at intervals.

During refrigerator storage, the pH decreased gradually and continuously as the oysters and surrounding free liquor became less fresh in odor and appearance. Odor was noted to pass from fresh to stale, then musty. As the pH decreased, the off-odor became progressively more sour and finally became very sharply sour. At this time the oysters were less firm and were slightly darker and muddy in color. The surrounding free liquor was turbid with many gas bubbles rising to the surface.

When oysters were held at room temperature, the drop in pH was greatly accelerated and accompanied by equally rapid development of sour odor, flabbiness, and gas formation. Spoilage was qualitatively similar to that of refrigerated sam-

ples, but the rate was much more rapid. Figure 1 illustrates the difference in the rate of souring between refrigerated and unrefrigerated samples from one lot of oysters tested during the month of February.

An interesting observation was that shucked oysters stored at 41° F. (5° C.) in glass beakers or in metal cans with loose-fitting aluminum foil covers developed very little or no sour odor, although the pH decreased at the same rate as that of oysters from the same lots in containers with tight-fitting covers.

Seasonal Variations: During the period from February through June it was noted that the mean initial pH for oysters from the monthly sampling decreased slightly during each succeeding month. The range of this decrease was from 6.38 in February to 6.02 in June. This difference represents a real seasonal variation in pH of the oysters. It could not be attributed to increased ambient temperatures during holding and shucking periods, since the low initial pH in June was obtained on oysters that our laboratory workers tonged, placed immediately in iced containers, then shucked and analyzed the same day.

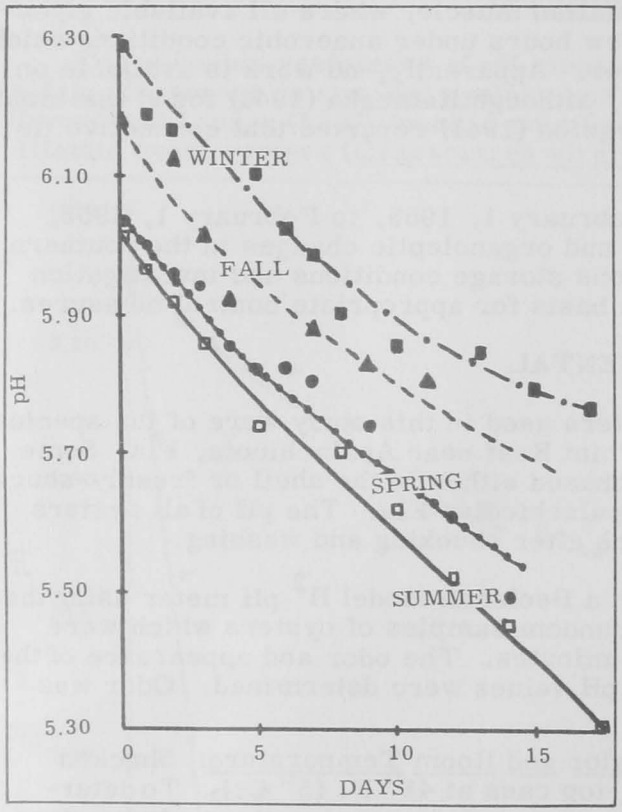

Fig. 2 - Seasonal variations in pH of shucked oysters stored at 41° F. (5° C.) for 15 days.

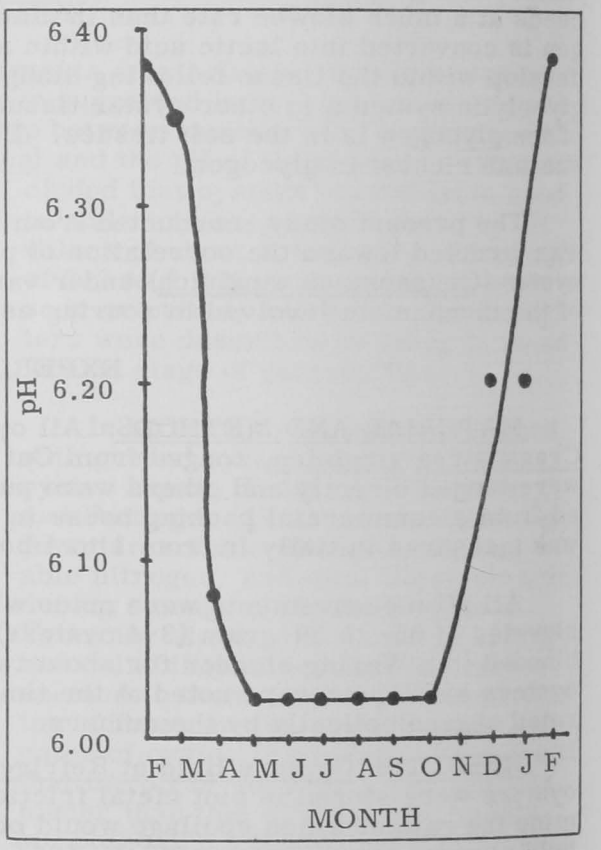

Fig. 3 - Initial pH of shucked oysters by months.

Throughout the spawning period, which in this area extends from April through October, not only did the initial pH remain low (6.02), but also pH values at subsequent storage periods were correspondingly lower. Although the pH initially and at all storage times was lower in the summer than in the winter oysters, the sour odor did not appear at an earlier storage time in the summer. In all oysters, slight off-odors began to be detected after 6 to 9 days of storage. After 12 to 16 days of storage they were generally designated sour. Direct odor comparisons of oysters from different seasons could not, of course, be made, but it was the authors' impression that sour odor showed up slightly earlier and became more intense in winter than in summer oysters, although the pH of the winter oysters was higher at all times. Changes in pH are shown in figures 2 and 3.

Oyster Liquor: If the drop in pH of oysters during refrigerated storage is caused by the action of glycolytic enzyme systems within the oyster tissue rather than by bacterial action, it might be expected that liquor, removed from all contact with the oyster meats immediately after shucking, might show little or no drop in pH on subsequent storage. On the other hand, a drop in pH of oyster liquor which remains in contact with the oyster meats might be expected since acids formed by glycolysis in the oysters could pass out into the liquor. Accordingly, pH changes were followed in (1) the shucking liquor stored separately from the oyster meats, (2) in the "contact" liquor (exuded by the oysters after washing and allowed to remain in contact with the oysters), and (3) in the oyster meats. The shucking liquor was drained from laboratory-shucked oysters, allowed to settle for 5 to 10 minutes to eliminate particles of shell and grit, then decanted and stored at 41° F. (5° C.) in glass beakers covered with aluminum foil. The washed oysters were also stored in glass beakers at the same temperature, and the liquor which was exuded was allowed to remain in contact with the oysters until time for pH determinations.

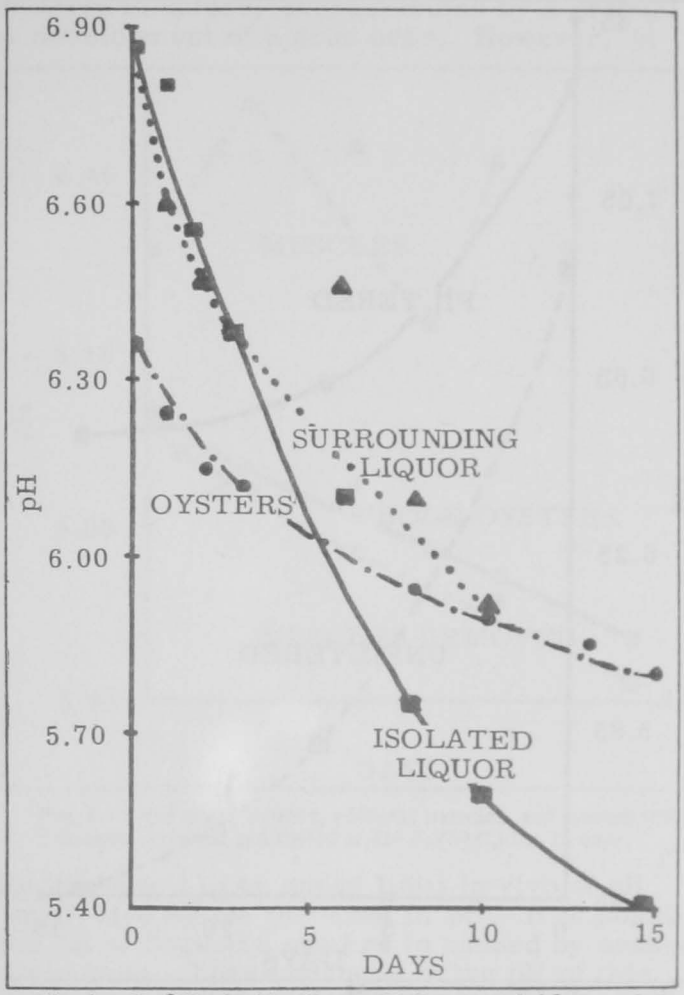

Fig. 4 - pH of (1) shucking liquor, (2) liquor exuded from and allowed to remain in contact with washed oysters, and (3) oyster meats stored at 41° F. (5° C.) for 15 days.

The initial pH values of both the shucking liquor and the liquor exuded after washing were higher than the initial pH of the oyster meats. The data are plotted in figure 4. In agreement with previous findings by Pottinger (1948, 1951), the pH values of the oyster meats and contact liquor were about equal after 11 days of refrigerator storage. Contrary to expectations, the pH of the shucking liquor decreased at a much more rapid rate than that of the oyster meats or of the contact liquor. However, while the odor of the oysters and contact liquor was the typical sour one, that which developed in the shucking liquor was predominantly "fishy," resembling that which develops in heat-treated oysters in which no drop in pH takes place. Both the shucking liquor and the contact liquor became very turbid.

Since the shucking liquor was not filtered, it probably contained suspended finely-divided particles of oyster tissue which may have supplied both substrate and enzyme systems. Furthermore, Yonge (1926, 1927, 1928) found that the digestive process in the oyster is not confined to the digestive glands, but may be carried out by freely moving phagocytes which may appear in the liquor. The greater drop in pH of liquor as compared to oysters can probably be attributed to its lower buffering capacity. Further study of shucking liquor was made in which some of the liquor was filtered through S&S black ribbon paper. Filtering immediately increased the initial pH of the liquor from 6.90 to 7.30, and as may be seen in figure 5, the pH of the filtered liquor decreased at a slower rate than than that of the unfiltered liquor.

Adductor Muscle and Soft Tissues: To determine the part played by glycolysis in the adductor muscle on the rate and amount of souring in the shucked oyster, the adductor muscle was dissected from some of the oysters and the pH values followed and compared for the whole oysters, adductor muscles, and oysters with muscles removed, all of which were stored at 41° F. (5° C.) for 15 days.

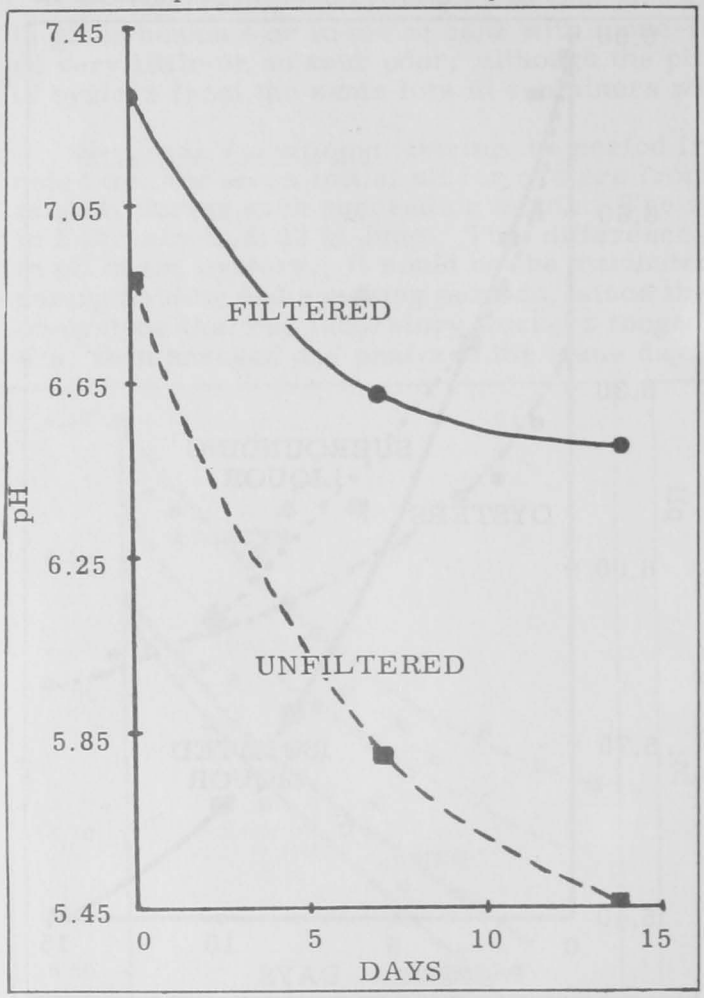

Fig. 5 - pH of filtered and unfiltered shucking liquor stored at 41° F. (5° C.) for 15 days.

The results of this study are presented in figure 6. Removing the muscles did not affect the initial pH of the remainder of the oyster meats, nor did it seem to have any effect on the rate of pH drop during storage for the 15-day period. The pH value of the muscles was initially higher than that of the whole oysters and oysters with muscles removed, and it remained high throughout the study. While the typical sour odor developed in the soft tissues, a "rancid fish" odor was detected in the muscles before eventual putrefaction.

Unwashed Oysters Stored in Own Shell Liquor: Observations were made on two lots of shucked oysters stored unwashed in their own shucking liquor in closed metal friction-top cans at 41° F. (5° C.). The pH decreased in these just as it did in drained washed oysters from the same lots, and the typical sour odor developed in each. This is contrary to the findings of King and his associates (1945) who reported putrefaction rather than souring in oysters stored in their own shucking liquor without washing. It is interesting also to note that while this liquor developed a "rancid fish" odor when it was stored separately from the oysters in glass beakers with aluminum foil covers, it developed a sour odor when allowed to remain in contact with the oysters. In both cases there was an eventual decrease in pH.

Homogenate of Whole Oysters: Changes of pH in homogenates of oysters were also followed with the objective of evaluating the possibility of using homogenized samples for certain other phases of experimentation with oysters in this laboratory. The shucked oysters were homogenized in a Waring blendor and the homogenate then stored in closed metal friction-top cans at 41° F. (5° C.). However, it was found that these blended samples did not follow the spoilage pattern of oysters which were stored unhomogenized. Instead of the usual drop, the pH increased from 6.02 to 6.20 by the eleventh day of storage, at which time there was an extreme ""rancid fish" odor. It was assumed that spoilage predominating in the homogenized oysters was oxidative, involving unsaturated fats which were exposed by blending, since high pH values and a fishy odor are characteristic of oxidative spoilage which has been found by Gardner and Watts (1956) to occur in cooked oysters.

DISCUSSION

The foregoing observations indicate that the spoilage pattern of whole refrigerated Southern oysters is similar, in general, to that reported for oysters in other locations. This spoilage is fermentative in nature, characterized by a gradual and continuous decrease in pH and the development of a sour odor. However, in the Southern oysters a seasonal variation has been found in initial pH and in pH values at intervals during storage. No particular odor or quality rating of Southern oysters can be correlated with a given pH value during all seasons of the year.

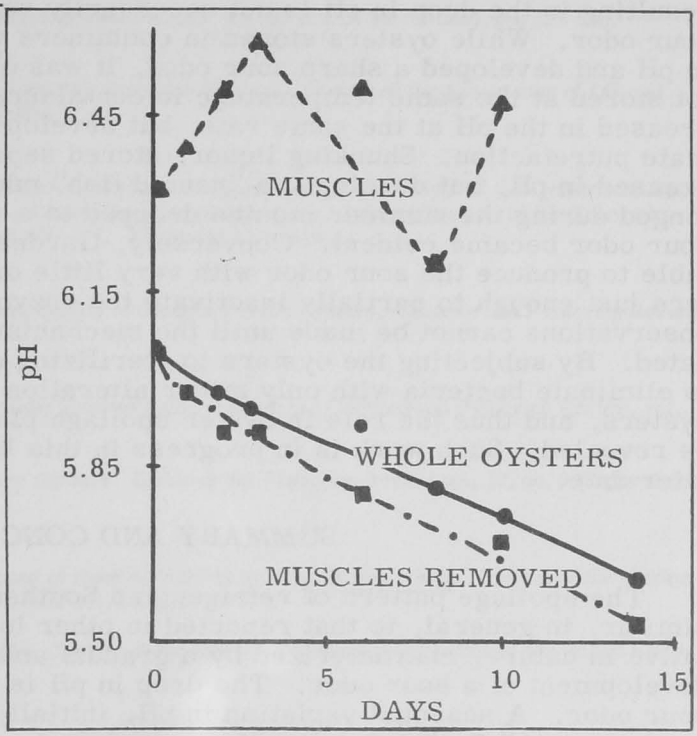

Fig. 6 - pH of whole oysters, adductor muscles, and oysters with muscles removed and stored at 41° F. (5° C.) for 15 days.

It is interesting to note that the pH, measured initially and at intervals during subsequent storage, is much lower during the summer months when the glycogen content of the oysters is at a minimum. Kokubo (1929) observed that the pH of the blood and pericardial fluid of the oyster (Ostrea gigas) decreased in early summer and increased in winter. He reported that the pH of these body fluids rapidly decreased when the oyster was subjected to respiration in water of high acidity, the lower limit in vivo being pH 5.40. Under these conditions the CO_2 content of these body fluids was increased. When oysters were subjected to respiration in water of high alkalinity, the pH of blood and pericardial fluid of the oysters rapidly increased to an upper limit in vivo of pH 8.45, and the CO_2 content remained unaffected by the increase in pH. It is possible that the seasonal variation in initial pH of Southern oysters is caused by seasonal change in pH of the water of the oyster beds. These changes in the pH of this water should be followed in any future work to shed further light on the value that can be assigned to pH as a test for quality of oysters.

Another possibility is that the composition of the oyster during the summer months, or spawning period, is such that the more acid parts of the organism contribute more to the pH of the whole oyster than they do during the winter months. For example, the style and the stomach were found by Yonge (1926-1927) to be the most acid parts of the oyster, with a pH of 5.2 and 5.5, respectively. It would be interesting to follow the seasonal pH of the various tissues and to compare these values with the pH of the whole oyster.

The initial pH of the adductor muscle, although higher than that of the soft tissues, apparently has no effect on the initial pH of the whole oyster, since the initial pH values of whole oysters and of oysters with muscles removed were identical. Furthermore, glycolysis in the adductor muscle appears to have no effect on the rate of souring in the whole oyster. This stands to reason, since the percentage of glycogen in the adductor muscle has been found by Hatanaka (1941) to be small as compared to that in the soft tissues. Ashikaga (1949) reported that glycogen in the whole oyster decreased to only 3 percent of the original after five days and was lost entirely after ten days when oysters were held at 37° F. (2.8° C.). After 5 and 25 days at 2°-4° F. (-17° to -15° C.), the percentages of glycogen remaining

were 83 percent and 63 percent, respectively. However, when fresh adductor muscles were stored at 6-9° F. (-14.5° to -12.8° C.), they contained about 71 percent of the original glycogen after three days. When the muscles were dried and preserved, the loss of glycogen was only 8.25 percent even after two years.

Considerable evidence has been accumulated to indicate that acid production resulting in the drop in pH is not necessarily related to the development of the sharp sour odor. While oysters stored in containers with tight-fitting covers decreased in pH and developed a sharp sour odor, it was observed that oysters from the same lot stored at the same temperature in containers with loose-fitting covers also decreased in the pH at the same rate, but developed little or no sour odor before ultimate putrefaction. Shucking liquor, stored separately from oyster meats, also decreased in pH, but developed a "rancid fish" odor rather than a sour odor. Oysters tonged during the summer months dropped to a very low pH (5.52-5.69) before a sour odor became evident. Conversely, Gardner and Watts (1956) have found it possible to produce the sour odor with very little or no drop in pH by heating the oysters just enough to partially inactivate the enzyme catalase. Explanations of these observations cannot be made until the mechanisms involved in spoilage are elucidated. By subjecting the oysters to sterilizing doses of radiation it may be possible to eliminate bacteria with only minor alteration of the enzyme systems within the oysters, and thus the role in oyster spoilage played by these two mechanisms may be revealed. Such work is in progress in this laboratory and will be reported on a later date.

SUMMARY AND CONCLUSIONS

The spoilage pattern of refrigerated Southern oyster meats was found to be similar, in general, to that reported in other locations. This spoilage is fermentative in nature, characterized by a gradual and continuous decrease in pH and the development of a sour odor. The drop in pH is not necessarily correlated with the sour odor. A seasonal variation in pH, initially and at intervals during subsequent storage at 41° F. (5° C.), has been observed, with the values being lowest during the summer and highest during the winter.

Spoilage patterns and pH changes have been followed also in oyster liquor held under various conditions as compared to oyster meats, in the adductor muscles as compared to the soft tissues, in washed and unwashed oysters, and in homogenized oysters.

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OYSTER DRILL--THE OYSTER'S ENEMY

The oyster drill is one of the most serious problems facing the oyster industry, and effective control methods would be a tremendous boon to growers and harvesters of this shellfish.

The oyster drill, Urosalpinx cinerea, may add variety to its oyster menu in the form of mussels and barnacles. There is also evidence that cannibalism occurs among adult drills, and a variety of other mollusks, such as soft and hard clams, and scallops may also fall before this voracious predator. At times even small crabs, the carrion of fish or such lower invertebrates as encrusting bryozoans are devoured.

--"Sea Secrets," The Marine Laboratory, University of Miami, Coral Gables, Fla.