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ABSTRACT

Chicken meat has a high nutrient content. However, its quality is easy to be degraded. The degradation is normally characterized by the formation of metabolite gases (NH3 and H2S) as deterioration indicators. Sensors detect phenomena better than human senses. This study aimed to classify meat quality based on gas formation during meat storage. In addition, a kinetics model of gas changes was determined. The gases were detected using a set of equipment consisting of Raspberry Pi and Metal-Oxide-Semiconductor (MOS) gas sensors. Samples were put in a 10 x 10 x 10 (cm) black container. MOS sensors were put inside the box to detect the gases at room temperature for 24 hours, with data collection being recorded every hour. Obtained data were then analyzed using Principle Component Analysis (PCA) for quality classification. The study showed that the quality of chicken meat was classified into three groups with a total variance of more than 95%. PC1 explained 88.2%, and PC2 explained 9.0%. The constant rate of H2S and NH3 changes followed the first-order kinetics with a constant rate of 0.2641 and 0.2925, respectively. The equation for H2S and NH3 changes were Ct = 1.70 e0.2641t and Ct = 1.00 e0.2925t, respectively.

1. INTRODUCTION

Broiler chicken meat is in great demand by the public as a source of protein and nutrition that is easy to obtain and relatively inexpensive. The high nutrition in chicken is caused by its content of protein, fat, carbohydrates, minerals, and other substances that are beneficial to the human body (Kusumaningrum et al., 2013). The demand for healthy, nutritious, and safe chicken meat is increasingly growing in Indonesia. According to data for 2020, the average per capita consumption of purebred chicken in one week has increased compared to the previous year by 6.42 percent (Direktorat Jendral Peternakan dan Kesehatan Hewan, 2021). The high demand for chicken meat should be accompanied by high quality control, considering that chicken meat is susceptible to microbial spoilage.
and contamination from chicken manure.

One of the main indicators that determine the freshness of meat during storage is the concentration of sulfur compounds such as hydrogen sulfide (H$_2$S) and biogenic amines such as ammonia (NH$_3$), which are the two main metabolites of microbial decarboxylation of amino acids (Nitiyacassari et al., 2021). After slaughter, the blood circulation of the animal will be stopped and followed by the cessation of the respiration process (Huff-Lonergan et al., 2010). The meat will undergo an anaerobic glycolysis process which causes a decrease in the pH value and protein autolysis produces amino acids that make the meat susceptible to microbial spoilage (Fu et al., 2019). Protease produced by spoilage microbes and meat enzymes can decompose meat (Huff-Lonergan et al., 2010) so that a volatile aroma is formed after the chicken is slaughtered. Under these conditions, volatile compounds such as NH$_3$ and H$_2$S will be formed. The formation of spoilage gases can measure the degree of meat spoilage and indirect bacterial contamination. With spoilage gas indicators, it is possible to monitor the freshness of the meat in the market by measuring the gas concentration in the chicken meat directly in the field.

Monitoring of chicken meat quality degradation has great potential for developing cheap, easy, and portable control technology. Many analytical techniques to monitor meat spoilage have been developed, including Fourier Transform Infrared (FT-IR) spectrometry (Vasconcelos et al., 2014), High Performance Liquid Chromatography (HPLC) (Okarini et al., 2008), and Gas Chromatography–Mass Spectrometry (GC-MS) (Wettasinghe et al., 2001). However, using these instruments requires more complicated preparation and need a longer time. Most of these methods require sophisticated instrumentation and cannot be implemented in situ in the field.

Therefore, an analysis system that can evaluate meat quality in a fast, simple, economical, and portable way is required. In this research, the MOS gas sensor coupled with Arduino (microcontroller) and Raspberry Pi is chosen to monitor volatile compounds associated with chicken meat spoilage to meet the need for reliable sensing devices that are sensitive, simple, and inexpensive. MOS was chosen considering its advantages, such as low cost, quick response time, chemical and thermal stability, and easy fabrication. This study aims to classify the level of freshness of chicken meat using MQ 136 and MQ 137 types of sensors. In addition, the kinetic analysis will also be carried out to predict changes in the evolution of NH$_3$ and H$_2$S gases from chicken meat during storage.

2. MATERIALS AND METHODS

2.1. Sample preparation
This research was conducted at the Bioindustry Laboratory, Department of Agricultural Industrial Technology, Faculty of Agricultural Technology, Gadjah Mada University. In this study, broiler chicken breast was used as the sample. The chicken meat was purchased directly from a slaughterhouse in Yogyakarta, Indonesia. Meat was brought to the laboratory tightly closed and in fresh condition. A total of 150-200 g of breast meat were sliced from the chicken carcass and used as a measurement sample.

2.2. Detection equipment
The main equipment in this research was a set of self-designed gas detection equipment. The main parts of this equipment are the sensor system, microcontroller (Arduino), Raspberry Pi, and monitor. Two types of resistive metal oxide (MOS) gas
sensors, namely MQ 135 and MQ 136, were used to sense the smell of gas emitted by chicken meat samples during observation. These two sensors were metal oxide semiconductors, the most frequent materials for gas sensing purposes (Andre et al., 2022). These sensors had a resistance value that would change along with the changes in the detected gas concentration, resulting in a change in the voltage on the device. The final reading from the gas detection tools is the NH$_3$ and H$_2$S concentration in ppm after being converted to the calibration equation and would be stored in a computer database.

The two sensors were installed in an acrylic container sizing of 10 cm x 10 cm x 10 cm with a tight lid. A sample of chicken meat to be detected for gas evolution was placed in the acrylic container in the measurement process. Referring to the datasheet from the manufacturer, the selectivity of the two gas sensors is shown in Table 1.

**Table 1.** Type and selectivity of gas sensors used

| Sensor type | Gas selectivity                  |
|-------------|---------------------------------|
| MQ 135      | NH$_3$, alcohol, NOx, CO$_2$, benzene |
| MQ 136      | Hidrogen sulfida (H$_2$S)        |

Raspberry Pi 3 B+, installed with a MySQL database, was used to store sensor reading data by the Arduino microcontroller (Nugroho et al., 2020). The R language program then reads the data stored in the database to classify the meat freshness using the PCA method. The schematic diagram of the data flow can be seen in Figure 1, and the complete diagram of the equipment is shown in Figure 2.

**Figure 1.** Data flow diagram of the developed gas detector

**Figure 2.** Schematic diagram of the sample chamber, sensor chamber, and sensor system
2.3. Measurement Procedure
Chicken meat samples were placed in a container equipped with the gas sensor. Both gas sensors (MQ-136 and MQ-137) would be exposed to the gases released by the measured chicken meat. The sensor would then respond to the gas output from the meat, which resulted in a change in the voltage value on the equipment. The magnitude of this voltage change depended on the concentration of gases released by the meat. On the other hand, the concentration of these gases depended on the level of freshness of the meat being tested. The change in the voltage value was then converted to calculate the ratio of resistance \( \frac{R_s}{R_o} \) (Qiu & Wang, 2017), where the \( \frac{R_s}{R_o} \) ratio would be entered into the calibration equation to obtain the gas concentration value in ppm. Gas measurements were carried out every hour for 24 hours of storage at room temperature with three replications.

2.4. Data analysis
PCA was used to analyze the data stored in the MySQL database to classify the level of freshness of chicken meat for 24 hours of measurement. The results of this analysis were in the form of a graph depicting groups of freshness levels of chicken meat samples. Kinetic analysis was used to determine the rate constant of change in gas concentrations of \( \text{NH}_3 \) and \( \text{H}_2\text{S} \) measured during the study. All reaction orders, namely 0\(^{\text{th}}\), 1\(^{\text{st}}\), and 2\(^{\text{nd}}\) orders, were analyzed using equations 1, 2, and 3, respectively.

\[
C_t - C_o = kt \tag{1}
\]

\[
\frac{C_t}{C_o} = e^{kt} \tag{2}
\]

\[
\frac{1}{C_o} - \frac{1}{C_t} = kt \tag{3}
\]

where \( C_o \) was the initial gas concentration value, \( C_t \) was the gas concentration value at any time, \( t \) was the storage time, and \( k \) was the constant value of the rate of change of concentration. The suitability of the reaction order was determined based on the coefficient of determination \( (R^2) \) and RMSE (Root Means Square Error).

3. RESULTS AND DISCUSSION

3.1. Sample Freshness Classification
Principal component analysis (PCA) was carried out to evaluate the volatile gas spoilage markers (\( \text{NH}_3 \) and \( \text{H}_2\text{S} \)) of raw chicken meat at room temperature. This analysis resulted in a PCA score with two main components (PC1 and PC2). Two components explained more than 97.20% of the total variance, PC1 explained 88.2%, and PC2 explained 9.0%, as shown in Figure 3.

From Figure 3, it can be seen that based on the evolution of \( \text{NH}_3 \) and \( \text{H}_2\text{S} \) gases, the age or length of storage time for chicken meat samples occupies different groups. Based on the results of this analysis, in general, the quality of the meat was divided into three groups, namely the 0-9 hours measurement group, 10-20 hours, and 21-24 hours. The first group (0-9 hours) could be categorized as fresh meat, the second group (10-20 hours) could be categorized as non fresh meat, and the third group (21-24 hours) could be categorized as spoiled meat. The results of this study were quite
close to the results reported by Nitiyacassari et al. (2019), that chicken meat at room temperature rotten after 10 hours of storage based on changes in pH, texture, Total Volatile Base (TVB) 0.021%N, and Total Plate Count (TPC). Asmara et al. (2019) reported that based on the characteristics of color and texture, the level of freshness of chicken meat could be categorized into three classes, namely fresh (0-4 hours after slaughter), medium fresh (4-6 hours after slaughter), and not fresh (more than 6 hours after slaughter). Meanwhile, Li & Suslick (2016) found that chicken meat stored at 24 °C experienced a decrease in freshness when it entered the 12th hour. Mikš-Krajnik et al. (2015) stated that chicken breast meat stored at 21 °C entered the early stages of decay after 12 hours of storage, followed by the production of sulfide compounds. Based on the results of this study, the length of time for the freshness limit of chicken meat, which was 9 hours, this value laid in between the results from the two research above. These differences may be caused by sample factors, the basis of the assessment criteria, and storage temperature.

3.2. Kinetic Analysis of NH₃ and H₂S Changes
Raw chicken undergoes spontaneous decay under aerobic conditions at room temperature through two different pathways, namely glycolysis and proteolysis simultaneously at different speeds. Meat spoilage microorganisms catabolize glucose and lactate to produce ethanol and fatty acids through oxidation or glycolysis. The catabolism of nitrogen compounds and amino acids which are secondary metabolic reactions, leads to the formation of sulfides (Wettasinghe et al., 2001). The increase in ammonia content (NH₃) along with storage time is a meat quality indicator for the beginning of the deterioration process, which is positively correlated with an increase in the number of microbes (Kozacinski et al., 2012). The formation of NH₃, H₂S, and VOC (volatile organic compounds) gases result from protein metabolism by bacteria such as Bacillus, Clostridium, and Pseudomonas (Kartika et al., 2018). Figure 4 shows the changes in the concentration of H₂S and NH₃ of the chicken meat samples tested in this study.
Up to the 9th hour, the increase of H$_2$S and NH$_3$ gases was still relatively small, where the concentration of the two gases was only around 16 ppm. However, entering the 10th hour, both gases consistently increased significantly and continued to rise until the 24th hour. At the 24th hour, H$_2$S gas concentration increased by more than 4000% and NH$_3$ gas by more than 7000% compared to the 9th hour, this meant that the increment were more than 260% and 460% per hour for H$_2$S and NH$_3$, respectively. According to Alexandrakis et al. (2012), the formation of hydrogen sulfide (H$_2$S), dimethyl sulfide, and ethanol compounds could be used as criteria for testing the spoilage of Irish chicken meat stored at 4 °C using the SPME (Solid Phase Micro Extraction) technique. Production of carbon disulfide and dimethyl sulfide began to form on the 4th and 8th days for chicken meat stored at 4 °C.

The increase in ammonia level as a result of the use of free amino acids by microbes produced by-products in the form of sulfides, indoles, and amines that caused the changes in the characteristics of meat spoilage, in the form of a foul odor and an increase in pH (Adams & Mos, 2005). Free amino acids and sulfur compounds were volatile and very appropriate as chicken spoilage biomarkers because they could be detected instrumentally before organoleptic changes occur in the product (Alexandrakis et al., 2012).

The rate constant (k) for the formation of NH$_3$ and H$_2$S was obtained from kinetic equations of zero, first, and second orders. The relationship between gas concentrations (C) of H$_2$S and NH$_3$ with time (t) can be seen in Figure 4. The calculation results of the rate constant (k) value, the prediction equation, the coefficient of determination (R$^2$), and the RMSE value (Vasconcelos et al., 2014) are presented in Table 2.

From Table 2, it can be seen that the order that has the highest R$^2$ value and the lowest RMSE is the first order, both for NH$_3$ and H$_2$S gases. Therefore, it could be concluded that the changes in gas concentrations of NH$_3$ and H$_2$S followed the first order kinetics equation. Some literature stated that the kinetics of changes in food processing followed a first and second order patterns (Asropi et al., 2019). The same result was also found in Olivera et al., (2013) research. Research on the kinetics of quality changes in chicken meat (Rabeler & Feyissa, 2018) and beef processed food products by heating, followed a first-order kinetics (Ling et al., 2015). Research on the kinetics of color and texture changes in beef also followed a first-order kinetics (Olivera et al., 2013).
Table 2. Value of rate constant ($k$) and kinetic equation of gas change $H_2S$ and $NH_3$

| Parameter | Order | Rate constant | Kinetics equation | $R^2$ | RMSE  |
|-----------|-------|---------------|-------------------|-------|-------|
| $H_2S$    | 0     | 14.264 ppm.h$^{-1}$ | $C_t = 14.264 t + 1.70$ | 0.7026 | 129.92 |
|           | 1     | 0.2641 h$^{-1}$ | $C_t = 1.70 e^{0.2641 t}$ | 0.9653 | 100.55 |
|           | 2     | -0.0344 ppm$^{-1}$ h$^{-1}$ | $1/C_t = 0.588—0.034 t$ | 0.8809 | 244.73 |
| $NH_3$    | 0     | 20.174 ppm.h$^{-1}$ | $C_t = 20.174 t + 1.00$ | 0.6209 | 220.68 |
|           | 1     | 0.2925 h$^{-1}$ | $C_t = 1.00 e^{0.2925 t}$ | 0.9796 | 53.11 |
|           | 2     | -0.0561 ppm$^{-1}$ h$^{-1}$ | $1/C_t = 1—0.0561 t$ | 0.9134 | 364.70 |

Figure 5 shows the relationship between changes in gas concentrations during storage: (a) $H_2S$, (b) $NH_3$

4. CONCLUSION

From the results of this study, it could be concluded that the constructed equipment using gas sensors MQ-136 and MQ-137 could detect the evolution of $NH_3$ and $H_2S$ gases produced by chicken meat during room air storage. Analysis of chicken meat quality grouping could be done using PCA and resulted in 3 groups, namely the fresh meat group (0-9 hours), non-fresh meat (10-20 hours), and rotten meat (21-24 hours). From the results of kinetic analysis, it was found that the evolution of $NH_3$ and $H_2S$ gases followed the first order kinetic equation with quite high accuracy.

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