Potential for Sensor Systems to Monitor Fruit Physiology of Mango during Long-Distance Transport

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Mango is a widely cultivated tropical fruit crop and exhibits climacteric behavior characterized by changes in respiration and ethylene production during development and ripening. Optimal postharvest ripening depends on many factors, but during shipping to distant high-value markets, ripening generally should be minimized. Monitoring the physiological activity presents possibilities for real-time response and the integration of smart technologies. However, systems are still needed which are portable, economical, and accurate. Optical sensors are low-cost but lack good accuracy, while electrochemical sensors are highly accurate but expensive. Economic nanoparticle sensors are being developed for potential applications in fruit quality monitoring, but they can be complex. This work explores possibilities for development of a monitoring system for climacteric fruits such as mango and presents results on testing of commercially available systems and development of sensors that will fit the criteria.

Keywords: gas sensor, mango fruits, postharvest ripening, transport monitoring

INTRODUCTION

To meet global demands for fresh agricultural produce, it is necessary to optimize production and distribution systems. Considering export of fresh mango fruit (e.g., Thailand-Japan), several factors play a role in determining fruit quality at consumption. As mango is a climacteric fruit, development, maturation and ripening are characterized by respiration rate and ethylene synthesis (Fig. 1). Decreasing respiration during fruit development leads to a minimum, followed by intensification until full ripeness (climacteric peak). The respiration rise is associated with a sharp increase in ethylene production which induces ripening. Mangos are most optimally harvested directly after the pre-climacteric minimum, meaning mature but unripe, after which the fruit then undergoes post-harvest ripening. Cultivation, harvest timing and handling chain conditions all decisively influence the magnitude of the climacteric curve, and thus, final quality of the fresh mango at consumption. Many other internationally traded fruits exhibit similar behavior such as banana, apple, pear, and papaya.

In commercial production of mango, harvest timing is determined by farmers according to fruit size and shape based on their experience and in post-harvest operations, sorting is often dependent on arbitrary factors such as size and color. Thus, shipments can vary with respect to maturity stage causing complications such as accelerated ripening. To optimize production and distribution systems of long-supply chains for fresh export of tropical climacteric fruits, it is necessary to establish monitoring systems from field to market (Kuswandi et al., 2011; Jedermann et al., 2014a). A gap currently exists between pre- and post-harvest research, which inhibits development of comprehensive production-distribution systems to ensure consistent, superior quality. From this, the objectives of the study are defined:

1. Identify and test prospective sensor technologies for implementation in a monitoring system climacteric fruits
2. Develop a non-destructive system for monitoring climacteric behavior which is portable and economical

Presently, possibilities to monitor the climacteric gases, ethylene and CO₂ are primarily with stationary equipment in laboratories (Cristescu et al., 2013). Applying in situ measurement has been hampered by the deficiency of portable units designed to detect the gases at necessary resolutions (Janssen et al., 2014; Jedermann et al., 2014b). Moreover, high humidity inside controlled atmosphere chambers complicates the realization of gas sensing systems that are sufficiently sensitive, reliable, robust and cost-effective. In particular, three measurement technologies have shown promising potential for fruit supply chains and were tested to develop a robust, portable monitoring system: non-dispersive infrared (NDIR) spectroscopy, electrochemical (EC) measurement and nanoparticle (NP) semiconductors (Nagle et al., 2010; Nemade and
NDIR sensors are simple spectroscopic devices often used in gas detection. The main components are an infrared source, a sample chamber or light tube, a wavelength filter, and the infrared detector. The gas is diffused into the sample chamber, and gas concentration is measured electro-optically by its absorption of a specific wavelength in the infrared (IR) range. The IR radiation is directed through the sample chamber towards the detector. The detector has an optical filter in front of it that eliminates all radiation except the wavelength that the selected gas molecules can absorb. Ideally other gas molecules do not absorb IR radiation at this wavelength, and do not affect the amount of radiation reaching the detector.

EC sensors generally consist of electrodes immersed in an electrolyte medium. The sample gas is flowed through the EC cell and becomes solubilized. A redox reaction generates an electric current that is proportional to gas concentration. These sensors are generally very accurate (0.02 ppm) and tend to be used principally for gases which cannot otherwise be detected, or where high levels of accuracy are needed. These sensors may require preconditioning of the sample gas, can be subject to cross interference, and may react to sudden humidity changes. Thus, additional components such as pumps and scrubbers need to be included in the system design.

NP-based sensors function by measuring the change in electrical resistance (proportional to the concentration) as gas is absorbed onto the surface of a nano-layer semiconductor. A typical material used for this type of application is graphene. NP sensors can be used for a wide range of gases and perform well in the detection of gases at low concentrations (up to 1,000 ppm). They are generally low-cost, robust, and stable. However, they are not particularly selective and are not suited to detecting a single gas in a mixture or for use where high concentrations of interfering gases are likely to be present. Cross-interference can be minimized by using filters, calibrating for the specific gas,
and incorporating a delayed response.

Possibilities for monitoring climacteric activity of mango using different sensor technologies were explored and developed. It was expected that a prototype system could be realized and, if reliable functioning and performance could be proven, the sensor unit could be promoted for commercial production. Increasing packing efficiency and avoiding erroneous practices should have a direct, positive impact on fruit export industries and the importing markets by reducing losses and increasing revenues via improved product quality (Ma et al., 2016). Results should improve the status of mango on the world market and allow farmers to obtain premium payment for higher fruit quality. The results should add to the scientific knowledge base with respect to a better understanding of non-invasive detection of fruit physiology. Furthermore, the benefits can be extended not only in the case of mango, but other climacteric fruits as well, and are highly relevant for countries which export tropical fruits.

TECHNICAL CONCEPT

Commercial NDIR sensors were tested for measuring typical CO₂ concentrations for mango and evaluated for integration into the monitoring system. It was decided that these sensors were too low in accuracy, expensive, and had excessive electrical requirements. Thus, the possibilities for using NP sensors were considered in more detail. Although some research exists for using nanotechnology for the detection of ethylene (Esser et al., 2012), this solution was finally considered technically complex for a commercial system at this time. Thus, the use of EC sensors for ethylene measurement was explored. Meanwhile, the possibility for using NP sensors for detection of CO₂ concentration was judged to be feasible (Andô et al., 2015; Wang et al., 2016) and the research was made to develop such sensors together with partners in Japan. A model system was proposed as shown in Fig. 2.

RESEARCH IMPLEMENTATION AND RESULTS

Testing of the ethylene analyzer

Research was conducted in order to evaluate commercial EC sensors for ethylene measurement. A device was obtained for testing, namely the ETH1010-N Electrocatalytic Ethylene Analyzer (ETH) produced by Fluid Analytics, Inc., USA (RelyOn Ltd., Tokyo, Japan). Tests were carried out to evaluate several aspects of the device.

Sensor stability

Test measurements showed stabilization of ethylene measurements until up to 20 min (Fig. 3). When the device is turned off, the electrocatalyst has not charge-stabilized and it requires time to build the charge on the surface of the gold catalyst, i.e., it is a large capacitor due to high surface area. Also, once it has charge-stabilized, the temperature and hydration of the electrocatalyst also needs to stabilize and for that reason the auto-calibration cycling in room air helps accelerate that. In fact, the device does better when it is left on, but perhaps without the pump running. After calibration, the device needs some time to equilibrate. This is on the order of approximately 5 min (Fig. 4). Recalibrating while sampling the same recirculating gas did not seem to affect the measurement (Fig. 5). Even the ethylene concentration decreases as gas is sampled, recalibrating to 30 ppm did not cause the sensor measurement to return to 30 ppm. Temperature and relative humidity sensors are pre-calibrated. Measurements showed the temperature sensor to be particularly stable and accurate (Fig. 6). The resolution was 0.1°C.

Accuracy

Tests were done to evaluate the accuracy of the ethylene sensor. Small amounts of pure ethylene were injected into a closed recirculating 10 L chamber system at varying intervals over 5 h to periodically increase the concentration. Reference measurements were made by sampling gas from the chamber and analyzing by gas chromatograph (Shimadzu GC-8AIF, Kyoto, Japan) with an oven Flame Ionization Detector (FID). The values as measured by the two systems were compared (Fig. 7). It was found that the ETH ethylene reading became unreliable after 25 ppm. At higher concentrations after 30 ppm, the reading decreased until 0. This was the case in all instances with calibration at 0.9, 7 and 30 ppm. According to the manufacturer, the device is designed to operate primarily around and below 10 ppm, unless the gain is reduced. The sensor is set at high gain so that better resolution is achieved in the lower part of the range, which is lower than 1 ppm. For a range of 1 ppm to 30 ppm, the gain needs to be turned down so that the sensor reading does not baseline. Within the range 0–20 ppm, the sensor was found to have reasonable accuracy. Accuracy seemed to improve with calibration at lower value of 0.9 ppm.

Responsivity

From the same tests of the accuracy measurements, the responsivity of the sensor was evaluated (Fig. 8). It was confirmed that the responsiveness of the sensor was very good between 0–25 ppm. At continuous sampling at the same concentration, a slow decline in the reading can be detected, for example between 90–120 min. If a recirculating container is used, there is a steady, but very slow exponential decline due to electrocatalytic reaction (~1–4% reduction at each sample interval, depending on the sampling rate). In a good experiment, where the sampling is done properly, the reading is not expected to drift more than 2%.

Battery life

The device was powered up and left turned on several hours to build up a full charge on the battery. The power supply was disconnected and the device was left to measure at 2-min interval until the battery charge completely ran out. The total time the device ran on a single battery charge was more than 36 h. The battery life was much longer than stated in the specifications for similar devices (~8 h). Perhaps this long battery life is due to the fact that this system was configured without additional components such as the optional CO₂ sensor. The data logged in the internal memory was cleared when the power ran out. When
Fig. 3  Measurements of ambient air for 60 min after powering on the device showing stabilization periods.

Fig. 4  Measurements of ambient air for 20 min after calibration at (a) 1 and (b) 10 ppm showing equalization time.

Fig. 5  Multiple recalibrations at 30 ppm (indicated by x) using the same recirculated gas.

Fig. 6  Plots for temperature during experiments showing high resolution of readings.

Fig. 7  Comparison of values for ethylene concentration obtained from ETH sensor and as measured by gas chromatography (GC-FID): (a) 0.9 ppm; (b) 7.0 ppm.
the device was powered on again, the data was lost. It was evident that for long-term monitoring, extended battery life with continuous saving of event logs would be required.

**Development of a nanoparticle sensor for CO₂**

A thin-film NP sensor was developed together with a Japanese electronics company AgIC Inc. for use in the system to detect CO₂. The NP sensor was constructed by depositing a layer of graphene onto silver electrodes printed on a thin-film PET substrate (Fig. 9). Electrodes were made by inkjet printing a conductive pattern of a silver nanoparticle solution through a commercial inkjet printer (Jabari and Toyserkani, 2016). The sensing principle exploits the change in electrical conductivity of graphene due to gas molecule adsorption. Initial testing was done to check the responsivity of the resistance reading to changes in CO₂ concentration and the effects of environmental variables on the sensor. Additional refinement and tuning of the sensors is ongoing before incorporation into the transport monitoring system.

**Testing of a combined sensor for ethylene, CO₂, temperature and relative humidity**

A combined sensor device, the F-950 (Felix Corp, USA), was obtained for testing which was able to measure ethylene, CO₂, temperature and relative humidity. A supplemental battery pack was fabricated in order to prolong the operating time for long shipment (more than 24 h). The sensor was packed in a commercial box of mangos (Fig. 10) and sent via normal air distribution routes from a packing house in Thailand to the port-of-entry in Tokyo. The shipment included 8 fruits totaling 2,500 g wrapped in conventional foam sleeves and lasted 20 h. Data was logged at 1 min intervals and is displayed in Fig. 11. CO₂ increased considerably during shipment, especially between 10–17 h, due to respiration of the fruits. After 16 h, a sharp spike was observed in ethylene concentration, signaling the induction of the final ripening stage of the fruits. After initial stabilization, temperature and relative humidity remained relatively consistent.

**Research outlook**

The concept of a postharvest monitoring system for fruit transport is finalized and sensors are in development. Commercial EC devices for ethylene have been tested. While these sensors are expensive and require sufficient power supply, they are still the most suitable. Work on NP sensors for ethylene must be further developed in order to produce feasible options. In the next phase, mango fruits
harvested from commercial orchards in Thailand will be used to determine the effect of climacteric behavior on distribution. Fruits will be grouped into lots based on physiological maturity. Three treatments will be tested, where the shipping boxes will contain fruits: (i) all with low respiration (ii) all with high respiration and (iii) with mixed respiration. Two modes of transport will be evaluated: direct delivery to Tokyo by air and commercial carriage to Japan by ship. Concentration of climacteric gases will be monitored inside the packing boxes during transportation using the developed system. Environmental factors such as air temperature and humidity will be evaluated for their influence. Upon arrival in Japan, fruits will be subjected to post-harvest ripening and evaluated for quality and compared with sensor data. The continued work of the consortium and final development of the monitoring system will be presented in future papers.

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