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Frying disposal time of sunflower oil using hybrid electronic nose-fuzzy logic approach

Rohit Upadhyay*, Sneha Sehwag, Hari Niwas Mishra

Agricultural & Food Engineering Department, Indian Institute of Technology Kharagpur, Kharagpur, 721302, West Bengal, India

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ABSTRACT

An electronic nose (e-nose), equipped with 18 metal oxide semiconductor (MOS) sensors (L, T, and P types), was used to monitor the disposal time of deep fried sunflower oil stabilized with natural antioxidants. E-nose was interfaced with chemometrics and fuzzy logic analyses to rank and screen the most effective MOS sensors against headspace volatiles of fried oils. The chemical indices of rancidity *viz.*, total polar compounds (TPC) and triglyceride dimers-polymers (TGDP), among others, were measured and correlated with e-nose based rancidity index (odor index). The inherent clustering of oil samples with varying degree of rancidity was deconvoluted by principal component analysis and hierarchical clustering on principal components. Six MOS sensors (LY2/G, LY2/AA, LY2/GH, LY2/gCT1, T30/1, and P30/1) were screened and ranked using fuzzy logic analysis. A good relationship was noted between rancidity indices and odor index (R^2>0.85). Upon reaching threshold discard limit of TPC (25 g/100 g oil), the frying disposal time was determined to be approximately 16 h (15.5 h (chemical test) *vs.* 16.24 h (e-nose)). The hybrid e-nose-fuzzy logic approach could substitute the existing chemical methods and integrated for on-line quality inspection of cooking oils.

1. Introduction

Lipid oxidation is the major cause of quality deterioration of cooking oils which affects their nutritional and organoleptic attributes, shelf stability, and safety (Jaswir, Man, & Kitts, 2000). Deep frying of oils leads to slow accumulation of harmful polar and polymeric compounds and hence necessitates the estimation of disposal time. Official chemical methods *viz.*, peroxide value (PV), free fatty acid (FFA), and total polar compounds (TPC) are routinely used to examine thermo-oxidative alterations in fried oils. Literature review indicates an extensive list of spectroscopic methods to measure lipid oxidation (Muik, Lendl, Molina-Díaz, & Ayora-Cañada, 2005; Armenta, Garrigues, & de la Guardia, 2007; Talpur et al., 2015). Nevertheless, these methods are laborious, destructive, environmentally unsafe, and often require complex spectral pretreatment which lead to conflicting results (Bendini et al., 2007). This necessitates the need to develop a simple, non-invasive, and reliable method to overcome the drawbacks of conventional and spectroscopic methods.

Sensory panels can provide qualitative and quantitative descriptions of foods and their performance depends upon right training (Gan, Man, Tan, NorAini, & Nazimah, 2005). However, sensory tests are time-consuming, expensive, and often suffer subjectivity and panel fatigue. Over last decade, considerable research was undertaken to develop an electronic nose (e-nose) that can provide low-cost and rapid sensory information about freshness and quality of foods (Esposto et al., 2009; Pacioni, Cerretani, Procida, & Cichelli, 2014). E-nose consists of metal oxide semiconductor (MOS) sensors that imitate the human olfactory system to assess the rancid defects in food products (Aparicio, Rocha, Delgadillo, & Morales, 2000; García-González & Aparicio, 2003; Chatterjee, Bhattacharjee, & Bhattacharyya, 2014). Till date, the e-nose instrument is scarcely explored to monitor the rancidity and disposal time of cooking oils used for frying.

The presence of different MOS sensors illustrates the versatility of e-nose in detecting volatile organic compounds (VOCs). However, Chatterjee et al. (2014) reported that multiple sensors in e-nose often lead to poor sample discrimination and hence, necessitates the need to filter the most responsive sensors while analyzing the odor fingerprints of food samples. An interesting resolving approach would be to interface the e-nose with fuzzy logic analysis which is widely used in sensory tests to rank the

* Corresponding author.
E-mail addresses: ruv.16jy@gmail.com, rohit.upadhyay@iitkgp.ac.in (R. Upadhyay).

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linguistic data of sensory panels (Bevilacqua, Ciarapica, & Marchetti, 2012; Routray & Mishra, 2012; Jaya & Das, 2003). The hybrid e-nose–fuzzy approach could screen the most effective MOS sensors to describe the rancidity in frying oils. In addition, it also can allow rapid estimation of chemical rancidity indices by establishing the relationship between e-nose and chemical tests.

In this work, we proposed to study an e-nose system in tandem with fuzzy logic analyses to monitor the frying disposal time of SO. This work is an extension to our previous investigations where natural antioxidants *viz.,* oleoresin sage (SAG), rosemary, and ascorbyl palmitate (AP) were tested to stabilize SO against oxidative deteriorations (Upadhyay & Mishra, 2015a, 2015b, 2015c, 2015d, 2016a, 2016b). The rancidity indices (TPC and polymeric compounds, FFA, and Rancimat induction period (IP)) of SO were measured using official methods. Lastly, an e-nose based rancidity index called odor index was determined and quantitatively correlated with rancidity indices. The hybrid e-nose-fuzzy logic approach could serve as a rapid and non-invasive way to monitor the frying quality of cooking oils.

2. Materials and methods

2.1. Materials

A fresh lot of SO (refined, bleached, and deodorized without added antioxidants), an oil dispersible formulation of SAG (Moroccan variety), and AP (>99% purity) were supplied by Synthite Industries Limited (Kerala, India). The content of active antioxidant components in SAG *viz.*, carnosic acid and carnosol were determined to be 11.20 and 5.33 g/100 g extract, respectively, as previously reported (Upadhyay & Mishra, 2014). The initial quality parameters of SO *viz.,* PV (AOCS Cd-853, 2004), TPC (IUPAC 2.507, 1987), FFA (AOCS Ca 5a-40, 1994), and fatty acid composition (AOAC., 2000) were 1.5 milliequivalents O_2/kg oil, 4.32 g/100 g oil, 0.07 mg KOH/kg oil, and 6.3 g/100 g C16:0, 3.6 g/100 g C18:0, 21.7 g/100 g C18:1, 68.4 g/100 g C18:2, 1.71 g/100 g C18:3, respectively (Upadhyay and Mishra, 2016a). Analytical grade reagents *viz.,* n-hexane, tetrahydrofuran (THF), petroleum ether, diethyl ether, and silica gel (70–230 mesh, 5% moisture content) were purchased from Merck (Mumbai, India). Fresh potatoes were purchased from a local store in Kharagpur (West Bengal, India) for frying.

2.2. Preparation of oil blend for frying

SO (without added antioxidant) was mixed with SAG (1289 mg/kg oil) and AP (218 mg/kg oil) to obtain an antioxidant stabilized SO blend (SOB) for frying experiments. The levels of SAG and AP were previously optimized to obtain a stable SOB (Upadhyay & Mishra, 2016a). For blending, SO (5.0 kg ≈ 5.45 L) was homogenized (T25 ULTRA-TURRAX®, IKA® India Private Limited, Bangalore, India) with accurately weighed SAG (6.445 g) and AP (1.09 g) in glass bottles followed by stirring for 20 min at 50 °C in water bath. Once homogeneity achieved, SOB was removed from water bath and later subjected to frying treatment (Upadhyay, Sehwag, & Mishra, 2017). Before frying, SOB was divided into two sets of oils *viz.,* test and training set. It was important to train the e-nose sensors against volatiles of fried oil. Therefore, it was first trained using a duplicate set of deliberately rancid SOBs (total 5 namely T1, T2, T3, T4, and T5). Training set of SOBs (50 mL each) were deliberately aged in a rancidity accelerating chamber equipped with UV light at high temperature (60 °C) for 1 (T1), 2 (T2), 3 (T3), 4 (T4) and 5 (T5) days. Once aging completed, they were removed from rancidity chamber and heated at 180 °C for 5 h (ensuring that TPC cut-off limit of 25 g/100 g oil was crossed) and later submitted to e-nose training.

2.3. Frying experiments

An open pan frying of potatoes chips was performed using test set of SOB. Before frying, the raw potatoes were thoroughly washed, peeled, and sliced (diameter: 7.0 cm, thickness: 0.3 cm, on average). A stainless steel pan fryer (height: 5.5 cm, diameter: 20.5 cm) was used over conventional kitchen electric plate equipped with thermostat. Each batch (ca. 50 g) of potato slices was deep fried for 5 min (inter-batch interval ≈ 30 min) in 2.5 L of SOB at 180 ± 2 °C. The oil temperature was continuously monitored using a digital thermometer attached to a steel probe. SOB was continuously heated for 9 h/day over 2 consecutive days. After every hour of frying, ca. 20 g of fried SOB was filtered into a screw-cap vial and refrigerated (−20 °C) until chemical and e-nose analyses. At the end of day, SOB was allowed to cool down to room temperature and kept covered. It should be noted that the stainless steel pan fryer was kept opened during frying. All frying trials including training set were performed in duplicate.

2.4. E-nose analysis

2.4.1. Instrument

The change in rancidity index (as headspace VOCs) of training and test set of SOBs was captured using Fox 4000 e-nose system (Alpha MOS, Toulouse, France). It consisted of a fully automated HS 100 auto-sampler (Alpha MOS, Toulouse, France), an array of 18 MOS sensors and an electronic unit for data acquisition. The MOS sensors consisted of L-type (LY2/LG, LY2/G, LY2/AA, LY2/GH, LY2/gCTI, LY2/gCT; short chain volatile fatty acids and aldehydes), P-type (P10/1, P10/2, P40/1, P30/1, P30/2, P40/2, PA2; aliphatic non-polar molecules) and T-type (T30/1, T70/2, T40/2, T40/1, TA/2; polar alcoholic and chlorinated compounds) that respond to wide variety of VOCs (Oliveros et al., 2002). Firstly, e-nose analysis was trained to identify the signal patterns of rancid VOCs using training set of SOBs (T1, T2, T3, T4, and T5). Later, the test set of SOBs (SR0–SR18) collected during frying (0–18 h) were analyzed.

2.4.2. Operating procedure

Five grams of oil sample was transferred into a 20 mL glass vial having Teflon septum in the screw cap. Each sample undergoes a 30 min thermo-incubation to generate and equilibrate headspace VOCs. The accumulated VOCS were injected into Fox 4000 e-nose system using an auto-sampler at a flow rate of 150 mL/min. The VOCs were carried by purified air (carrier gas) at 5 psi to sensors. The sensor response was defined as the relative change in the resistance $\Delta R/R$ value (which is change in the resistance of MOS sensor relative to its base value). The data were recorded for 120 s followed by a recovery period (420 s) to allow the sensors to return to the baseline resistance. The signal response ($\Delta R/R$) of all the 18 MOS sensors was recorded in duplicates for training and test sets of SOBs. For each sensor, an absolute value of maximum $\Delta R/R$ was extracted to generate an odor map. Later, the $\Delta R/R$ values were used to rank the sensors using fuzzy logic analysis.

2.5. Fuzzy logic analysis

To screen and rank the most sensitive MOS sensors against VOCs, their response values ($\Delta R/R$) were considered analogous to sensory score in fuzzy interpretation. In the fuzzy logic analysis, weightage or importance is given to certain attributes in food products (Jaya & Das, 2003). Since this analysis process has been replicated in sensor screening, it was required to assign statistical weightage to fried oils. All the oil samples were given equal weightage, *i.e.*, test (fresh (0 h) and fried (1–18 h)) and training set (T1–T5) of SOBs were considered equally important. It is imputable