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Fish Processing by Ozone Treatment - Is Further Investigation of Domestic Applications Needful?

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Over the years globally, the trends of fish product utilization have been diverse. On the other hand, a number of process technologies have helped to actualize fish product development. Besides ozone processing showing high preservation promise, ozone after declared Generally Recognized As Safe (GRAS), has steadily evolved up to domestic facilities for home use. Recent tests performed on a domestic facility reported promising results on some characteristic properties of ozone-processed shrimp with storage time. In this terse opinion communication, the need for further investigations into other commercially available domestic ozone facilities is justified.

1. Introduction: Fish Processing Methods – A Modest Tabulation

Over the years globally, the trends of fish product utilization have been diverse. In particular, fish products have served great healthful uses owed to their chemical composition, providing global population with nourishment as well as industrial by-product resources (Okpala et al., 2014; Okpala, 2017a, d&e; Sen, 2005). To advance human health and product development, various food process technologies have been developed and evolved over time, probably to overcome the deficiencies of the traditional conventional methods such as drying, salting up to typical refrigeration (Hall, 1997; Okpala et al., 2014; Okpala, 2015a; Sen, 2005).

Table 1: Some fish processing technologies by class with some terse remarks

Technology name	**Technology class**	**Terse remarks**
Modified Atmosphere Packaging	Non-thermal	The use of headspace gases to bring about food preservation
Minced Processing	Non-thermal	Considerable recovery of edible fish flesh from waste using bone separator
Retort Pouch	Thermal	Sealing of already prepared fish product using flexible multilayer plastic
Irradiation	Non-thermal	The application of ionizing radiation energy of liberated electrons for targeted fish shelf preservation
Ozone treatment	Non-thermal	The application of generated ozone on fish products targeted product shelf preservation
Microwave	Thermal	The use of electromagnetic waves ranging between 300 MHz and 300GHz converted to heat, aimed at fish product preservation

Examples of promising food technologies applied to fish products include Modified Atmosphere Packaging (MAP), Minced processing, Retort Pouch, Irradiation, Ozone treatment, and Microwave (Hall, 1997; Okpala, 2014 and 2015b; Sen, 2005). Some fish processing technologies by class with some terse remarks have been summarized in Table 1. Whilst these food processes possess both merits and demerits regardless of class, that is, non-thermal up to thermal, all put together have received massive research attention/interest across the globe and have either individually and/or collectively played diverse function(s) towards fish product development (Hall, 1997; Okpala et al., 2016a-c; Okpala, 2016a-b; Sen, 2005).

2. Ozone Processing declared 'GRAS' and thereafter

Figure 1 shows the technological progress of ozone since discovery indicating key inventors, locations and context/situation. From the early times when ozone was recognized as odour, assigned 'O_3' as simplest formula, early applications to food and non-food materials, it was only when US Food Drug Administration (FDA) declared it as 'Generally Recognized As Safe (GRAS)' and amended their food additive regulations to ensure that either aqueous and/or gaseous ozone would be safe, that the globe embraced this bio-based broad-spectrum antimicrobial. Since then, pursuits have continued for ozone to attain more environmental friendly process (O'Donnell et al., 2012; Okpala, 2017a-b).

Ozone in food industry remains driven by factors such as consumer and processor acceptability, environmental impact, food safety and shelf life extension, as well as regulatory and legislative concerns. It is well understood that to obtain optimal results, ozone is better discharged on a fresh produce (O'Donnell et al., 2012; Okpala, 2014 and 2015b). Whilst the chemical and physical properties of ozone has greatly influenced its efficacy, how ozone is generated today, whether it is corona discharge or ultraviolet methods, has not so much deterred researchers from attempting its application on wide range of foods such as fruits and vegetable, grains, meat, seafood as well as non-food aspects such as food industry sanitization, water treatment, food waste and odour treatment and so on (O'Donnell et al., 2012; Okpala, 2015b and 2017a). In addition to ozone already considered as non-destructive to biochemical properties of fish flesh, it is also ascribed among most powerful oxidizing substances commercially available (Okpala, 2014, 2015a and 2017a).

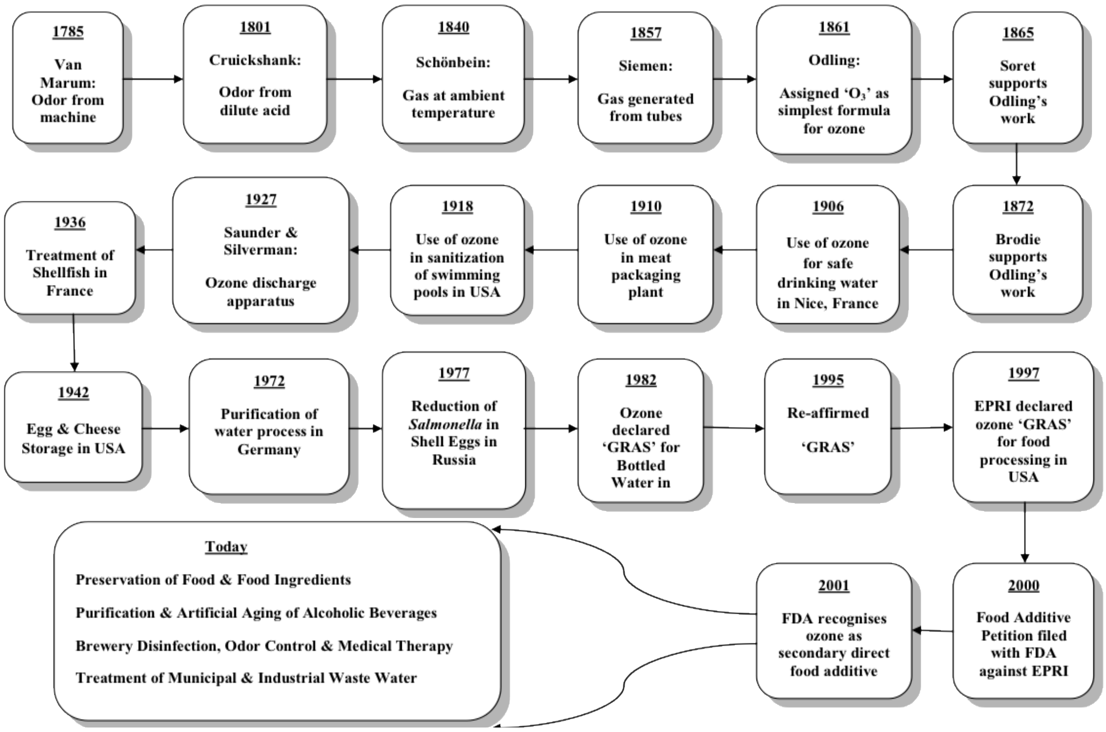

Figure 1: Technological progress of ozone since discovery indicating key inventors, locations and contexts/situations.

3. Ozone Discharge up to Applications/Treatments

Ozone discharge occurs in three forms, namely: corona, ultraviolet and electrochemical. The most common is the corona type, which is widely applied in either laboratory and/or industrial settings. Ozone reaction processes have been well discussed by other authors (Goncalves, 2009; Guzel-Seydim et al., 2004a&b; Kim et al., 2003; O'Donnell et al., 2012). Ozonation – when ozone is pumped into liquid/water medium at specific flow rate and time – has also been reported elsewhere (Jiang et al., 1998). As a triatomic molecule, ozone, not only classed as allotrophic modification of oxygen, it remains in gaseous form at refrigerated/room temperature with oxidation-reduction potential of 2.07 v (Kim et al., 2003). Respectively, concentration ratio of ozone in gas and water is 1.13 and 0.26 – all of which are dependent on water temperature (Okpala, 2017d). Whilst ozone stays more stable in gas compared to aqueous (O'Donnell et al., 2012; Tomiyasu et al., 1985), if there be high pH in medium to interfere with stability of ozone molecule, its stability in water would take place with an increase in pH (O'Donnell et al., 2012; Okpala, 2017d; Ouederni et al., 1987).

Figure 2 shows the schematic diagram for set-up of ozone generator highlighting corona discharge approach/methodology. The connection of various components is shown, from oxygen cylinder up to the electrodes (high and low tension). Also shown is the use of about 4% used to capture excess ozone, which has been reported (Okpala et al., 2015; Okpala, 2017d). Some ozone application on food material(s)/product(s) by purpose/type(s) are presented in Table 2. It is shown that nature of ozone on foods, i.e., aqueous and gas, focus on decontamination as well as shelflife extension (Kim et al., 1999; Kim and Yousef, 2000; O'Donnell et al., 2012; Okpala et al., 2015; Okpala, 2017d).

Some ozone-food processing facilities are presented in Table 3. It is showed that regardless of ozone application/combinations, whilst ozone discharge on food process facilities/system involve equipment surfaces, confectionary plants, sanitizer for dairy/food plants up to domestic types, the microbial reduction still remains considerable. Clearly, there is useful evidence of microbiological efficacy of ozone when applied on food and non-food surfaces. This microbiological efficacy of ozone treatment has also been dealt with in Khadre et al (2002), especially how it relates with reactivity, temperature and pH. Anyways, considering the working operation of ozone generator regardless of application, whilst the passage of air through generated feed gas can result in production of 1 – 4% ozone, the use of pure oxygen can equally result in production of up to between 6 – 14% ozone. Notwithstanding this, the free radicals well known to associate with ozone are the core of its high reactivity and oxidizing power (Guzel-Seydim et al., 2004 a&b; Khadre et al., 2001; Kim et al., 1999; Kim and Yousef, 2000; O'Donnell et al., 2012; Okpala, 2014 a&b; Okpala, 2017d).

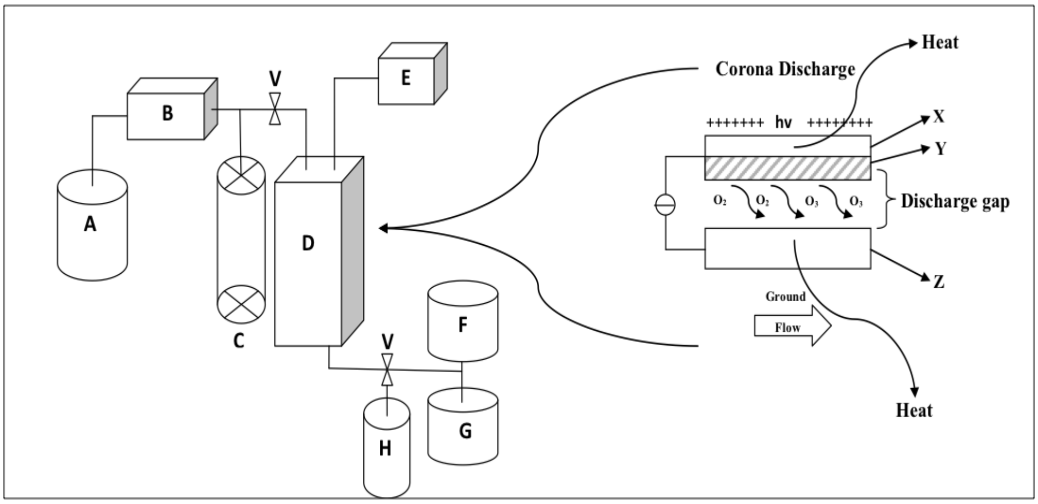

Figure 2: Schematic diagram for set-up of ozone generator highlighting corona discharge instrument; Key: A= Oxygen cylinder; B= Flow Rate Controller; C= Bubble Type Flow Meter; D= Ozone Generator; E = Transformer; F& G= Excess Ozone Traps (4% KI); H= Rotating Vessel (90 rpm); V = Valve; X= High Tension Electrode; Y= Dielectric; Z= Low Tension Electrode (Adapted from Okpala et al., 2015; and Okpala, 2017d).

Despite the differences in production of ozone, its concentration in particular is believed not to go up beyond the point where both the rate of formation equals with that of destruction. Therefore, there is a higher chance that the storage of gaseous ozone would be almost impossible given its nature of spontaneous degradation into oxygen atoms (Goncalves, 2009; Guzel-Seydim et al., 2004 a&b; Jiang et al., 1998; Okpala et al., 2015). Particularly, as per this current communication, the use of domestic types of ozone application has been of increasing/keen interest to the author. Also, in the view that this facility type is now commercially available around the world, it therefore becomes more imperative for makers of ozone equipment to continue to search for 'best' safe applications that would deliver the needs of consumers as well as industry. Also, the use of domestic ozone facility contributes well to the fact that ozone is gaining stronger grounds as a sanitizing agent for the food industry (Okpala, 2017d).

Table 2: Some ozone treatment applications on food material(s)/product(s) by purpose/type(s).

Ozone treatment/type	**Food material Product**	**Purpose of application**	**References**
Aqueous	Meat; beef; fish, poultry meat	1) Decontamination 2) Extension of shelflife and quality	O'Donnell et al. (2012) Okpala et al. (2015) Okpala (2017d)
Aqueous and gas	Applies; blackberries; strawberries and grapes	1) Decontamination; 2) Extension of shelf-life and quality improvement	O'Donnell et al. (2012) Kim et al. (1999) Kim and Yousef (2000)
Gas + vacuum + Heat	Eggs	1) Hyper-pasteurization process; 2) Decontamination	Kim et al. (1999) Kim and Yousef (2000) Okpala (2017d)

Table 3: Some ozone-food processing facilities with microbial reduction impact

Ozone application/combinations	**Food process facility/system**	**Microbial reduction impact**	**References**
Ozone (aqueous)	Food processing equipment surfaces	Up to 95% microbial plate count reduction	O'Donnell et al. (2012)
Ozone + H_2O_2	Confectionary plant; Hatchery equipment; Packaging film	Up to between 95 – 99% microbial plat count reduction	Kim et al. (2003) O'Donnell et al. (2012)
Ozone (aqueous)	Domestic ozone facility; Sanitizer for dairy and food plants	Up to between <3 - <5 log reduction	Okpala (2014a-b) Okpala (2017d) O'Donnell et al. (2012)

4. Domestic Ozone Facility used for Fish Processing: Some Reported Points

As quest for societal welfare continually rises, the food industry continues to pursue innovative design of bio-based materials (Okpala, 2017d). Clearly, relevant literature presents ozone treatment as promising preservative candidate for the fish industry. The declaration of ozone as GRAS by FDA, not only paved way for its application to the fish industry, but also, has greatly contributed to advance this preservative technology (O'Donnell et al., 2012). Health regulatory standards continually advise manufacturers of ozone generating facilities to authenticate, establish, and verify the optimum amounts that would produce significant effects on food. This is because the concentration of residual quantities of ozone in direct contact with food flesh has to be insignificant (O'Donnell et al., 2012; Okpala, 2014 and 2017a).

In recent times, ozone use has evolved up to household generating devices capable of purifying tap water, and clean fruits and vegetables. This form of ozone process technology (OPT), not only an additional intervention and promising for food industry, the author recently used a household ozone-generating device (O_3 Fresh^{TM}, Model SQ-8-BA, Ovoproducts, Leicestershire, UK) to investigate ozone-processed shrimp subject to iced storage. Complying with European Council Directive 73/23/EEC and 93/68/EEC (as amended), this device is commercially available and increasingly situated in many home kitchens. It has built-in ozone concentration discharge of 100 mg/h into water, wash and spin capacity of 4 L, and three exposure levels/wash cycles of 1, 3, and 5 min – all fixed by manufacturer. Typically, by adjusting ozone exposure/wash cycles, the treatment levels can be determined (Okpala, 2014; Okpala, 2017a-c,&e).

To operate this facility (at ~ 25 °C), the shrimp (fish) product was placed in the evenly perforated removable basket and filled with (recommended) tap water up to the indicated level. When wash cycles is switched-on, the removable basket revolves/spins concurrently with ozone discharge to ensure rapid, regular and even distribution of ozone constituent particles within the water medium (Okpala, 2014, 2015b, 2016, 2017a-b). The characteristic properties determined on the tested ozone-processed shrimp samples ranged from chemical, physical, and microbiological parameters. The resultant data showed promising preservation trends (Okpala, 2014, 2015b, 2016, 2017a-b). Besides the characteristic trends showing promising preservation potential of the household ozone facility with storage time (Okpala et al., 2016b), there were some energy considerations of ozone-processed shrimp, such as total energy, which showed no significant differences (Okpala et al. 2015). The authors understood that it was fairly difficult to ascertain the total energy outcomes in the ozone-processed shrimp, which in that publication was indicated as good justification for future research.

5. Concluding Remarks: Is Further Investigation Needful?

To best of author's knowledge, it appears that only shrimp product has been tested using domestic ozone facility. The latter, whilst increasingly becoming commercially available and promising candidate for food safety, the results evidenced on one fish-food type (that is, shrimp) would definitely not suffice to make strong food technological case, but can only be for a start. As a matter of fact, other domestic/home ozone facilities that may or may not resemble that reported by the author, might well possess different concentration discharge as well as treatment levels/wash cycles. This creates avenue for new research questions to emerge, which according to Okpala (2017c), may help to actualize specific (researchable) objectives, and then consolidates to build-up an overall aim. In this context therefore, there is need to encourage other researchers to use domestic ozone facilities to engage in further studies.

It is important that such further studies are warranted to involve other commercially available domestic ozone facilities, to test it on a wide range of economically important fish products not only to generate more robust data towards product development but also to authenticate, consolidate and validate the preservation potential of domestic facility in food processing technology.

Acknowledgments

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References

Goncalves, A.A., Ozone: an emerging technology for seafood industry, Brazilian Archives of Biology and Technology, 52(6), 1527-1539. DOI: 10.1590/S1516-89132009000600025.

Guzel-Seydim, Z.B., Bever, P.I., Greene, A.K., 2004a, Efficacy of ozone to reduce bacterial populations in the presence of food components, Food Microbiology, 21(4), 475-479. DOI: 10.1016/j.fm.2003.10.001.

Guzel-Seydim, Z.B., Greene, A.K., Seydim, A.C., 2004b, Use of ozone in the food industry, LWT-Food Science and Technology 37(4), 453-460. DOI: 10.1016/j.lwt.2003.10.014.

Hall, G.M., (2nd Ed.), 1997, Fish Processing Technology. Blackie Academic & Professional, London, United Kingdom (ISBN: 978-1-4613-111-3).

Jiang, S.T., Ho, M.L., Jiang, S.H., Lo, L., Chen, H.C., 1998, Color and quality of mackerel surimi as affected by alkaline washing and ozonation, Journal of Food Science 63(4), 652-655. DOI: 10.1111/j.1365-2621.1998.tb15805.x.

Khadre, M.A., Yousef, A.E., Kim, J.G., 2001, Microbiological aspects of ozone applications in food: A review. Journal of Food Science 66(9), 1242-1252. DOI: 10.111/j.1365-2621.2001.tb15196.x.

Kim, J.G., Yousef, A.E., 1999, Application of ozone for enhancing the microbiological safety and quality of foods: A review, Journal of Food Protection, 62(9), 1071-1087. DOI:10.4315/0362-028X-62.9.1071.

Kim, J.G., Yousef, A.E., Khadre, M.A., 2003, Ozone and its current and future application in the food industry, Advances in Food and Nutrition Research, 45, 167-218. DOI: 10.1016/S1043-4526 (03)45005-5.

O'Donnell, C., Tiwari, B.K., Cullen, P.J., Rice, R.G. (Eds.), 2012, Ozone in Food Processing, Wiley-Blackwell, Chichester, United Kingdom (ISBN: 978-14444334425).

Okpala, C.O.R., 2014, Investigation of quality attributes of ice-stored Pacific white shrimp (Litopenaeus vannamei) as affected by sequential minimal ozone treatment, LWT Food Science and Technology 57, 538-547, DOI: 10.1016/j.lwt.2014.02.007.

Okpala, C.O.R., W-S. Choo, G.A. Dykes, 2014, Quality and shelf life assessment of Pacific white shrimp (Litopenaeus vannamei) freshly harvested and stored on ice, LWT Food Science and Technology 55, 110-116, DOI: 10.1016/j.lwt.2013.07.020.

Okpala, C.O.R., 2015a, The physicochemical changes of farm-raised Pacific white shrimp (Litopenaeus vannamei) as influenced by iced storage, Food and Nutrition Science 6(10), 906-922, DOI: 10.4236/fns.2015.610095.

Okpala, C.O.R., 2015b, Quality evaluation and shelf life of minimal ozone-treated Pacific white shrimp (Litopenaeus vannamei) stored on ice, Journal für Verbraucherschutz und Lebensmittelsicherheit 10(1), 49-57, DOI: 10.1007/s00003-014-0904-x.

Okpala, C.O.R., Bono, G., Abdulkadir, A., Madumelu, C.U., 2015, Ozone (O3) Process Technology (OPT): An Exploratory Brief of Minimal Ozone Discharge applied to Shrimp Product, Energy Procedia 75, 2427-2435. DOI: 10.1016/j.egypro.2015.07.206.

Okpala, C.O.R., 2016, Lipid autoxidation in ozone-processed crustacea under cold storage: A treatise, Lipid Technology, 28(5-6), 93-95, DOI: 10.1002/lite.201600026.

Okpala, C.O.R., Bono, G., Geraci, M.L., Sardo, G., Vitale, S., Schaschke, C.J. 2016a, Lipid oxidation kinetics of ozone-processed shrimp during iced storage using peroxide value measurements, Food Bioscience 16:5-10. DOI:10.1016/j.fbio.2016.07.005.

Okpala, C.O.R., Bono, G., Cannizaro, L., Jereb, P., 2016b, Changes in lipid oxidation and related flesh qualities of white shrimp (Litopenaeus vannamei) during iced storage: Effects of the use of increasing ozone exposures, European Journal of Lipid Science and Technology 118 (12), 1942-1951. DOI: 10.1002/ejlt.201500347.

Okpala, C.O.R., 2017a, Home ozone processing – protecting healthful lipids in seafood, International News on Fats, Oils & Related Materials (INFORM), 28(2), 28-31.

Okpala, C.O.R., 2017b, Changes in some proximate, colour and textural characteristics of ozone-processed shrimp: Combined effects of increasing ozone discharge and iced storage, Iranian Journal of Fisheries Sciences. (in-press).

Okpala, C.O.R., 2017c, Reflecting in the woods: can it help to enhance the formulation of (our) research questions? BioResources Online Journal (http://nscu.edu/bioresources) (In-press).

Okpala, C.O.R., 2017d, Ozone delivery on food materials incorporating some bio-based processes: A succinct synopsis, Advanced Materials Proceedings (In-press).

Okpala, C.O.R., 2017e, Changes in some biochemical and microbiological properties of ozone-processed shrimp: Effects of increased ozone discharge combined with iced storage. American Journal of Food Technology (In-press).

Ouedemi, A., Mora, J.C., Bes, R.S., 1987, Ozone absorption in water: Mass transfer and solubility, Ozone: Science and Engineering, 9, 1-12. DOI: 10.1080/01919518708552384.

Roth, J.A., Sullivan, D.E., 1981, Solubility of ozone in water, Industrial & Engineering Chemistry Fundamentals, 20, 137-140. DOI: 10.1021/i100002a004.

Sen, D.P., 2005, Advances in Fish Processing Technology. Allied Publishers Private Ltd., India (ISBN: 81-7764-655-9).

Tomiyasu, H., Fukutomi, H., Gordon, G., Kinetics and mechanism of ozone decomposition in basic aqueous solution, Inorganic Chemistry, 24, 2962-2966. DOI: 10.1021/ic00213a018.