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Gas phase fumigation methods to enhance the functional properties of wheat flour- a review

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Abstract
Ozone gas, chlorine and peroxides are used as fumigants to enhance the functionality of wheat flour. Compare to chlorine and peroxides, ozone residues and toxicity are very less in ozone treated flour and ozone is more effective to enhance the functional properties of wheat flour. This paper reviews the efficacy of ozone fumigation in wheat flour along with chlorine gas and peroxides.

Keywords: Gas phase fumigation, wheat flour

Introduction
Amongst all food grains wheat is the most widely grown cereal grain, occupying about 17 percent of the total cultivated land as well as consumed as a staple food by 35 percent in the world. Asia produces more than half of the developing world’s wheat crop. At present the largest wheat producers are China, India, the United States, Russia, and France. Cereal grains are important food grains and major food for human diet throughout the world, among cereals, wheat is third highest globally (Jin Mei *et al.*, 2016) [6]. According to FAO world cereal production in 2016 stands at 2544 million tones while wheat production is 732.1MT which is increasing significantly year wise. With increasing production rate storage has became major uprising challenge.

Wheat is a unique cereal because of its ability to form viscoelastic dough. The quality of different end products depends mainly on the quality of wheat used in the preparation. The quality requirement of wheat for the preparation of different products varies considerably. Several wheat varieties are grown in different parts of the world and each year new varieties are cultivated. Some wheat varieties yield weak, soft, sticky and more extensible dough which manifest difficulty in dough handling and processing.

According to World Bank Report (1999), each year post-harvest losses in India amount to 12 to 16 million metric tons of food grains and around Rs 50,000 crores every year are lost due to improper storage of food grains. Commonly grains are stored in the traditional storage structures like Kanaja, Kothi, Sanduka, earthern pots, Gummi, Kacheri etc as well as in the modern storage structures like warehouses at the controlled atmospheric conditions (Nithya *et al.*, 2011) [11].

Temperature and humidity plays an important role for safe storage of wheat grains (Karunakaran *et al.*, 2001) [7] as well as for the quality preservation (Fourar-Belaifa *et al.*, 2011) [3]. Generally wheat grains harvest at temperature is 25-30°C and moisture content greater than 13–14 per cent provides ideal conditions for the proliferation of insects in stored grains (Nopsa *et al.*, 2015) [12] as the condition suitable for most insect pests is at temperature around 30°C, with a relative humidity of 40 to 80 percent.

Hence, to get rid of these pests and insects infestations implementation of proper pest management technique is very much crucial to ensure safety of stored grain. In integrated pest management technique along with the execution of other steps like cleaning, uniform distribution, moisture and temperature management fumigation plays an important role to eliminate unwanted insects and pests. Gas Phase Fumigation is a process to suffocate or poison pests inside enclosed area which is completely filled with sufficient concentration of gaseous pesticides at specific pressure and temperature. It is very important during storage as well as during transportation of grains in order to keep away exotic pests like caterpillars, moths, weevils, flour beetles etc. which may cause quality degradation and further spoilage of entire grain bulk leading to major grain loss.

Fumigants act on all insect life stages by diffusing through the spaces between grain kernels as well as into the kernels themselves. Hence, these fumigants are able to penetrate into places that are inaccessible to insecticide sprays or dusts. Due to their highly toxic nature they are classified as restricted use pesticides and are applied only by certified and licensed fumigators. From the last quarter of the 20th century many compounds has been withdrawn which were formally used as major fumigants due to their various hazardous health and environmental effect like:

1. Methyl bromide: The fumigant with the widest range of applications was prohibited worldwide to be used as a fumigant in 2015 under the directive of the Montreal Protocol on ozone-depleting substances (Bell, 2000) [1].
2. Ethylene dibromide: It was banned in 1983 as a fumigant by U.S. Environmental Protection Agency owing to its relatively non-volatile nature and potentially hazardous level detection in several finished grain-based products by governmental food-monitoring laboratories.

At present, only two fumigants are registered for use in stored grain by EPA (Environmental Protection Agency): phosphine and chloropicrin.

1. Phosphine: EPA has classified phosphine as a Group D, not classifiable as to human carcinogenicity.
2. Chloropicrin: At the national level, chloropicrin is regulated by the EPA as a restricted use pesticide. Because of its toxicity and carcinogenicity, distribution and use of chloropicrin is available only to licensed professionals and specially certified growers who are trained in its proper and safe use.

Along with these registered fumigants there are others are also available which are used as a potential pest infestation fumigants described below:

1. Chlorine gas
2. Nitrogen peroxide
3. Hydrogen peroxide
4. Ozone
5. Sulfuryl fluoride
6. Propylene oxide
7. Ethyl formate
8. Carbonyl sulphide
9. Hydrogen cyanide
10. Carbon disulphide
11. Cyanogen
12. Methyl iodide

Among all these fumigants mostly used at commercial level are ozone and chlorine and peroxides. According to FSSAI (Food Safety Standard Authority of India, 2011) rules the moisture content of wheat flour should be around <14%, wheat flour itself is a long term storage product because it is not an ideal environment for the growth of microorganisms. However, when it is processed into different food products, water is added and even totally reserved in them; thus the microorganisms will proliferate immediately and lead to the degeneration of the final product and it is one of the important reasons for short shelf life of wheat based food products. Because of lower water content of wheat flour, poor thermal conductivity and small spaces between flour particles, it is very difficult to inactivate microorganisms in wheat flour by applying traditional sterilization methods such as thermal treatment, ultraviolet and microwave irradiation. So there is a great need for gas phase fumigation methods to inactivate microorganisms and thereby enhance the functional properties of wheat flour and this phenomenon provides the concept of low–bacteria wheat flour.

These gas phase fumigation treatments of wheat grains or wheat flour applied in the form of gas dissolved in water in washing and tempering steps. Number of studies revealed that the biochemical composition and technological properties of wheat flour and flour yield are not effected by these fumigation methods. Furthermore, a significant decrease in energy required for milling and starch damage, and changes in functional properties are observed.

Desvignes *et al.* (2008) [2] studied the changes in common wheat grain milling behavior and tissue mechanical properties following ozone treatment (10g/kg) of common wheat grains and observed the significant reduction in energy required for milling without affecting the flour yield and found changes in technological flour properties of wheat such as starch damage reduction, reduction in extensibility of aleurone layer.

Ozone

Ozone is a strong oxidant, natural fumigant, antimicrobial agent and powerful disinfectant. It is composed of three molecules of oxygen combined together and used for sterilization of equipment and packaging material, surface decontamination, storage and preservation of foods in food industry and it is recognized by US as GRAS in 1997 (Man Li *et al.*, 2013).

Ozone treatment for wheat grain and wheat flour had positive effect on quality parameters, volume and weight, height, skin color, skin structure, external appearance and internal structure and ozone treatment is beneficial to enhance the functional properties of wheat flour.

Jin Mei *et al.* (2016) [6] studied the effect of ozone treatment on medium hard wheat flour quality and performance in steamed bread making and observed the significant increase in carboxyl contents of wheat flour, wet gluten content, strength of wheat dough, falling number and whiteness of wheat flour, significant decrease in α-amylase activity, peak viscosities, hot paste viscosity, and cold paste viscosity and also altered the gelatinization temperature.

Ozone fumigation treatment time and ozone concentration are important factors affecting the rheological and functional properties of wheat flour used as a major ingredient for baking industry. Ozone can be used as an oxidizing agent and added to flours to accelerate natural maturing conditions. Desvignes *et al.* (2008) [2] found that ozone treatment (10 g/kg) of common wheat grains before milling process significantly reduced (by 10 to 20%) the required energy at the breaking stage with out changing flour yield.

Min Li *et al.* (2013) studied the effects of ozone gas fumigation treatment on the inactivation of microorganisms and physicochemical changes in wheat flour during the storage and found that TPC (Total Plate Count) slightly reduced in wheat flour after treatment.

Zsuznanna Laszo *et al.* (2008) found that the increase of concentration of ozone increased the changes in the color and dough properties like falling number and gluten flattering or degree of softening.

Min Li *et al.* (2012) investigated the effects of ozone treatment on the microorganism mortality in wheat flour and shelf-life of fresh noodles as well as the physicochemical properties of wheat flour and textural qualities of cooked noodles. Results showed that the total plate count (TPC) can be largely reduced in wheat flour exposed to ozone gas for 30 min and 60 min. Whiteness of flour and noodle sheet, dough stability, and peak viscosity of wheat starch were all increased by ozone treatment. Free cysteine content in wheat flour was shown to decrease significantly as the treatment time increased and remarkable protein aggregates were In addition, ozone treated noodles were generally higher in firmness, springiness, and chewiness, while lower in adhesiveness. Microbial growth and darkening rate of fresh noodles made from ozone treated flour were delayed significantly.

Ozone in combination is more effective treatment when compare to the ozone alone in applications of food industry. For example, Zsuznanna Laszo *et al*. (2008) investigated the Effects of direct ozone treatment, UV treatment and combined 0_3 /UV treatment on the color, microbiological, and organoleptic properties of milled wheat flour and concluded that, only combined treatment resulted in flour suitable for consumption and more changes observed in terms of quality of dough, color of flour (whiter flour), and significant reduction in microbial counts of flours.

Chlorine gas

Chlorination of soft wheat flour was introduced in the early 1930s and is necessary to produce high-ratio cakes with optimum quality characteristics. The chlorine gas reacts with the flour in a rapid, surface-dependent reaction (Yamazaki and Kissell 1978) [16]. Essentially all flour components (gluten, starch, lipids, water solubles, and pentosans) are modified chemically during the reaction (Stauffer 1990) [14]. The use of chlorine gas in a flour mill poses safety concerns.

Chlorine is a very strong oxidizing agent and disinfectant that reacts with flour components and destroys flour pigments, results in whiter flour. Many soft flours can be treated with chlorine gas or chlorine dioxide gas to improve their keeping qualities and cake-making properties and such flours absorb increased amounts of sugar and oil. All purpose flour is generally treated with chlorine gas and bleaching compounds generate undesirable chlorinated substances in flour and wheat based food products (Zsuzsanna Laszlo *et al*., 2008) [17]. Chlorine gas and chlorine dioxide are common disinfecting, bleaching chemicals and oxidizing, chlorinating agents used in flour industry to improve the quality of flour. Chlorine gas is considered as “generally recognized as safe” (GRAS) recognized by US.

Food and Drug Administration established the use levels for chlorine gas as food additive. Number of studies revealed that the effect of chlorine as fumigant for wheat flour. The action of chlorine gas in wheat flour results the starch depolymerization, and it is responsible for the improved baking qualities of bleached flour. Studies on chlorine gas fumigation on wheat flour not concluded the effect of chlorine residues in chlorinated flour. Generally the problems associated with chlorine treated flour are toxicity of chlorinated flour, presence of chlorinated proteins and lipids and other chlorine compounds. The number of studies found that the chlorine gas phase fumigation of wheat flour at commercial level does not pose a significant human health risk but the effect of chlorine and reaction with other flour components have not been studied.

The level of chlorine gas is important for flour treatment, number of studies revealed that the low level of chlorine gas reduced the pH, pigments in bleached flour, and improved the baking properties than the higher level of chlorine gas treatment on wheat flour (Meera kweon *et al.,* 2009) [10].

Peroxides

Nitrogen peroxide and hydrogen peroxides are used to enhance the functionality of wheat flour. Hydrogen peroxide is a strong oxidizing agent and used as a bleaching agent in foods such as wheat flour, edible oil, egg white and also used as antimicrobial agent and sterilizing agent.

Hydrogen peroxide is known to increase the viscosity of flour water suspension. The increase in viscosity (oxidative gelation) of the water-soluble fraction of flour is known to involve the enzyme peroxidase (Hoseney and Faubion 1981) [5]. The heat treatment of the flour was assumed to have denatured the indigenous peroxidase. Therefore, both hydrogen peroxide and peroxidise were added to the heat-treated flour. Effect of Hydrogen Peroxide Plus Peroxidase on the Properties of Heat-Treated Flour were presented in Table. 1. This treatment reduced the surface pitting in the crust and greatly improved the grain. Cakes containing hydrogen peroxide also had a desirable white crumb colour. Although the volume index increased from 107 to 114, it was lower than that of cakes made with the chlorine-treated flour. Neither higher levels of hydrogen peroxide nor holding the batter for 20 min before baking to allow greater enzyme activity produced larger cakes.

Table 1: Effect of Hydrogen Peroxide Plus Peroxidase on the Properties of Heat Treated Flour.

Sample	Hydrogen peroxide	Peroxidise units	Volume index	Grain score
Chlorinated control	0.00	0	120a	9
Untreated control	0.00	0	110bc	5
Heat-treated	0.00	0	108c	10
Heat-treated	0.05	380	114ab	9
Heat-treated	0.10	380	114ab	9
Heat-treated	0.20	380	113bc	9

a. Per cake batter made from 200 g of flour.

b. Means in a column with the same letter are not significantly different *(P= 0.05).*

c. Score of 1 indicates extremely poor grain; score of 10 indicates excellent grain.

Recently, Manu and Prasada Rao (2011) [9] reported that peroxidase/H_2O_2 was able to cross-link glutenin subunits, through disulfide bonds and dityrosine bonds. In addition to gluten, wheat flour contains albumin and globulin proteins, which are low in molecular weight (20- 60 kDa). Starch is the major component (70- 80%) in flour. It has been reported that peroxidases catalyse the formation of protein-protein, carbohydrate-carbohydrate and protein carbohydrate interactions in wheat (Wang and Denise, 2004) [15]. Peroxidase and Hydrogen peroxide treatment changes the molecular weights of albumins and globulin proteins as well as protein digestibility, and glycemic index of dough and chapattis. Peroxidase catalyzes the oxidation of a number of aromatic amines and phenols in the presence of hydrogen peroxide.

Sadako Takasaki *et al.* (2005) [13] investigated the effect of hydrogen peroxide and peroxidase to wheat flour dough on dityrosin formation and mixing characteristics wheat flour and found that dityrosine cross-links are increased in gluten with added hydrogen peroxide or hydrogen peroxide plus peroxidase and this conjugation can lead to polymerization of the proteins in wheat-flour dough. This is only the reason that the application of hydrogen peroxide with combination of peroxides enhances functionality of wheat flour.

Gould *et al.*, 1989 studied the effect of Alkalie Hydrogen Peroxide(AHP) on mixographic performance of dough containing high fiber cereal-plant fractions such as com or wheat bran, oat or soybean hulls, sugar beet pulp, com cob chaff, ground com cobs, and distiller's spent grains was improved. Dough in which AHP-treated com bran replaced 10% of flour exhibited 40-50% higher mixograph peaks than straight-flour dough over a wide absorption range. Other AHP-treated materials tested also increased the mixograph peak height, but to a lesser extent. Untreated materials and highly purified celluloses decreased the mixograph peak height. At high moisture levels, AHP-com bran also greatly reduced the mixing time required to reach the mixograph peak.

The dosage of hydrogen peroxide is limited to the amount sufficient for the purpose of food processing and food grade only can be used as a processing aid. The Joint FAO/WHO expert committee on food additives (JECFA) had evaluated the safety of hydrogen peroxide in 1980 and considered that the less concentration of hydrogen peroxide does not result in severe toxicity and number of studies revealed that the removal of residual amount of hydrogen peroxide. Combinations of two or more peroxides are used in gas phase fumigation method for increasing the functionality of wheat flour.

Conclusion

Ozone is an effective fumigant for insect killing, mycotoxin destruction and microbial inactivation which has a minimal or no effect on grain and flour quality than other fumigants and studies have demonstrated that ozone which is a natural agent, may offer unique advantages for grain processing along with addressing growing concerns over the use of harmful pesticides. This review paper demonstrated that the ozone gas is an effective fumigant to enhance the functional properties of wheat flour among all gas phase fumigation methods. Compare to chlorine and peroxides, ozone residues and toxicity are very less in ozone treated flour and ozone is more effective to enhance the functional properties of wheat flour.

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