ANTIOXIDANTS: TYPES, PROPERTIES AND MECHANISM

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INTRODUCTION-

The word antioxidant comes from the Greek, anti means against, plus oxys referring to oxidations. The retardation of oxidative reaction by minute quantities of a certain compound was observed in 1797 by Berthollate and again observed in 1817 by Davy. The first report of use of antioxidants in fats by Deschamps in1843. These are typically considered under the general category preservatives are used to prevent the reaction of certain food constituents

Antioxidant 'means a substance when added to food retards or prevents oxidative deterioration of food and does not include sugar, cereal, oils, flours, herbs and spices.

Antioxidants are defined by the united states of "Substance used to preserve food by retarding deterioration, rancidity or discoloration due to oxidation."

WHY TO USE AN ANTIOXIDANT?

Antioxidants are only means of preventing oxidation, Need of an Antioxidants to extent the shelf life of food, Reduce wastages & complaints, Decreases nutritional losses.

AN IDEAL ANTIOXIDANT

Safe in use, Non-toxic, Effective at low concentration, Shouldn't impart foreign flavour, odour, colour to food , Easy to incorporate is substrate, Survive cooking processes-baking/frying,Easily available & cheap,Easy to detect, identify & measure.

TYPES OF ANTI-OXIDENTS-

Primary antioxidants

Operate most directly from mechanistic stand point, All the primary antioxidant used in food with one exception, have one –OH and one OR group in ortho and para position,They are effective at very low concentration,Most effective in animal fat than vegetable fat,They protect fats under ordinary storage conditions but are inactivated during baking or frying .

Synergists

In the absence of primary antioxidant have very little effect on the oxidation of fat ,Synergists may be organic or inorganic and usually in acidic characters,It contain several –OH and –COOH group or both ,Many low molecular weight hydroxy acid or amino acid group exhibit synergistic activity,Regenerate the primary antioxidants Eg . Citric acid, ascorbic acid, lecithin.

Synthetic Antioxidants- Some antioxidants, such as BHA and BHT, are used in combination with resulting synergistic effects.Synthetic antioxidants are easier to use, more reliable, and generally more cost-effective than natural antioxidants .Some of the more popular synthetic antioxidants used are phenolic compounds such as follows:

BHA (Butylated Hydroxy anisole)

- BHA consist of a mixture of 3-tert-butyl 4-methoxyphenol (2 BHA) and 2 tert butyl-4 methoxyphenol (3BHA)
- Readily synthesized by butylation of paramethoxyphenol
- Melting point is near 65^0C
- Soluble in fat but insoluble in water
- BHA is great popularity as a food antioxidant because its ability to remains active in baked and fried food
- The stability of fat containing BHA decreases when they are heated to high temperature
- BHA is not destroyed readily mild basic condition
- It is used in low concentration
- FDA has approved its use in combination with other antioxidants

BHT (Butylated Hydroxy Tolune)

- Chemically BHT is 2,6-di-tert butyl-4-methylphenol
- Purified BHT is white crystalline product which is essential odorless
- It melt at 70^oC and insoluble in water but soluble in organic solvent and fat
- BHT does not impart any odour , taste, colour to fat
- BHT survives heat processing, thus carrying through into finished products.

NDGA (Nordihydroguaiaretic acid)

- NDGA is chemically 2,3-dimetyl-1,4-bis (3,4 dihydroxy phenyl) butane
- NDGA was first isolated in 1942 from a plant Larrea divaricata
- It may be found concentration up to 7% in young twing of plant
- NDGA is a white, crystalline solid, melting at 184-185^{o}c.
- It is soluble in dilute alkali and slightly soluble in water
- Studies indicated that solubility of NDGA in fat is 0.5-0.7%. But when heated at 125-150^{o}c 5 % can be dissolved
- Activity of NDGA is effective in the pH range of 5-6.5 but it is decreases rapidly when pH is increased or decreased

TBHQ (tert-Butylhydroquinone)

- TBHQ is a beige powder or is a white-to-tan crystal
- Its solubility in different solvents declines in the order of alcohol > fats > water
- It is stable to heat and is most effective antioxidant in preventing oxidation of frying oils
- TBHQ mixed with BHA and BHT can increase the smoke point of fats and oils
- FDA has approved the use of TBHQ up to 200 ppm in most foods, based on the food's fat content,
- Use in Vegetable oils Baked and confectionary Products Cosmetics, Margarine Snack foods like Fried Potato chips

NATURAL ANTIOXIDANTS

- ✓ The empirical use of natural compounds as antioxidants very old
- ✓ Can be extracted from plant, microorganisms, and even in animal tissues.
- ✓ Ascorbic acid and tocopherols are important commercial natural antioxidants
- ✓ Natural antioxidants may possess several drawbacks including high usage levels, low antioxidant efficiency, undesirable flavour or odour, and possible loss during processing

Catechins

- Catechins are flavanols, which are also called roanthocyanidins or flavan-3-ols.
- Present in a variety of foods such as wine, tea, fruits and chocolate
- Major catechins such as catechin, epicatechin, epicatechin gallate (ECG), and epigallocatechin-3-gallate (EGCG)

- Catechins are able to inhibit lipid oxidation in red meat, poultry and fish

Anthocyanins

- Anthocyanins, the natural colorants/pigments of fruits and vegetables, are novel, safe, and proven antioxidants
- The positively charged oxygen atom in the anthocyanin molecule makes it a more potent and distinct hydrogendonating antioxidant compared to oligomeric proanthocyanidins (OPCs) and other flavonoids
- Antioxidants critically depends on their ability for electron delocalization and to form resonating structures following changes in pH, which does not take place in other popular antioxidants
- Anthocyanins have been demonstrated to be novel antioxidants and potent inhibitors of lipid peroxidation as compared to other classic antioxidants

Honey

- Honey, a natural product formed from nectar by honeybees
- Evidence indicates that honey can exert several health-beneficial effects such as gastroprotective, hepatoprotective, reproductive, hypoglycemic , antioxidant
- It contains enzymes such as glucose oxidase, diastase, invertase, catalase and peroxidase
- Honey also contains other bioactive constituents such as organic acids, ascorbic acid, trace elements
- The main phenolic and flavonoid compounds in honey include ellagic acid, gallic acid, syringic acid, benzoic acid, cinnamic acid, ferulic acids, myricetin, chlorogenic acid, caffeic acid, hesperetin, coumaric acid, isoramnetin, chrysin, quercetin, galangin, luteolin and kaempferol
- Honey may or can ameliorate oxidative stress in the GIT, liver, pancreas, kidney, testis and plasma

Tocopherols

- ✓ Tocopherols collectively known as tocols,
- ✓ Widely distributed through in plant tissues vegetable and animal fat
- ✓ From wheat germ oil and cottonseed oil isolate three chemically similar compound with different vitamin E activity
- ✓ Antioxidant activity is depend on concentration

- ✓ Antioxidant activity dependent on temperature
- ✓ Activity of tocopherol is not destroyed completely by baking or frying

Ascorbic Acid

- It is gamma lactone of simple sugar acid and structure is determined as 2,3-dienol-1-gluco-furanolactone
- Ascorbic acid is a white crystalline powder and melting point is near to160^{o}c and insoluble in fat
- Ascorbic acid widespread in plant tissues
- Unsuitable for used in butter
- The antioxidant activity of ascorbic acid and its derivative can be depend on their capacity to bind metal ions
- Ascorbic acid is not regarded primarily as antioxidant by FDA

Phospholipids

- Lecithin was the first to a number of material occuring naturally in edible product
- The anti oxidative activity differs variance in functional groups and structures.
- Lecithin and cephalin are important commercial antioxidant, but limited use

Citric Acid

- Citric acid was used in Denmark in soybean oil refining in 1928
- Chemically is 2-Hydroxy1,2,3 propane-tricarboxylic acid
- Readily decomposed by heat but its thermal decomposed product are good synergists
- Highly soluble in water and almost insoluble in fat
- It is non toxic acid and does not impart undesirable odour or flavor in food
- Used in cured meat

MECHANISM OF ANTIOXIDANTS

- The antioxidant may act by
  1) Inactivation of free radical
  2) Complexing with metal ions
  3) By reduction of hydro peroxides
- Antioxidants can slow lipid oxidation by inactivating or scavenging free radicals, thus inhibiting initiation and propagation reactions

- The antioxidants function by the very simple and effective method of donating hydrogen atom to free radicals and thus terminating their life

The antioxidant molecule represented by AH, in which 'H' is the active hydrogen

$$ROO\cdot + AH \rightarrow ROOH + A\cdot$$

$$RO\cdot + AH \rightarrow ROH + A\cdot$$

$$R\cdot + AH \rightarrow RH + A\cdot$$

Antioxidants donate hydrogen atoms to the lipid radicals and produce lipid derivatives and antioxidant radicals that are more stable

- Antioxidant radicals are capable of participating in termination reactions with peroxy, oxy and other antioxidant radicals

$$ROO\cdot + A\cdot \rightarrow ROOA$$

$$RO\cdot + A\cdot \rightarrow ROA$$

$$A\cdot + A\cdot \rightarrow AA$$

- Formation of antioxidant dimmers (dimerization)
- This effectively stops the autocatalytic free radical chain mechanism as long as the antioxidant is present in its nonradical form.

Synergism in Lipid Oxidation

Synergism occurs when mixtures of antioxidants produce a more pronounced activity than the sum of the activities of the individual antioxidants when used separately.

To have maximum efficiency, primary antioxidants are often used in combination with

(1) other phenolic antioxidants, or with

(2) various metal chelating agents

Kinds of Metal Chelators

Metal chelators deactivate trace metals that are free or salts of fatty acids by the formation of complex ion or coordination compounds.

1. Phosphoric acid
2. Citric acid
3. Ascorbic acid
4. Ethylene-Diamine-Tetra-Acetate (EDTA)

Factors Affecting the Efficiency of Antioxidant

1. Oxidation potential should be high
2. Reduction potential should be low
3. Stability to pH and processing.
4. Should be Solubility in oil

References (if any)