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Research Article

Effect of Different Synthetic Antioxidants in the Stability of Palm Oil on Deep Fat Frying of Instant Noodles

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Abstract

The effect of three different synthetic antioxidants viz.-Tertiary Butylated Hydroxyquinone (TBHQ), Butylated Hydroxyanisole (BHA), Butylated hydroxyquinone (BHT) in the stability of palm oil on deep fat frying of instant noodles was well studied at ambient condition taking peroxide value and acid value as the objective parameters to measure the oxidation of frying oil. Soaked cake(cut noodles with soup) as frying samples were taken then fried in Refined Bleached Deodorized (RBD) palm oil of standard grade at 170 - 180°C. The RBD palm oil was analyzed for its physiochemical parameters. The fried noodles were also analyzed for moisture content, acid value (AV), peroxide value (PV), density (gm/cc). The three synthetic antioxidants in their proportion 100 ppm, 150 ppm, 200 ppm mixed in RBD palm oil in three batches. Oil sample collected in each hour of frying, it was found that higher the proportion of antioxidants lesser was the oxidation of frying oil which increased the stability. For three antioxidants the frying quality was analyzed such as AV, PV, and specific gravity and control sample oil was taken as without using antioxidant. The results showed that TBHQ of 150 ppm was statistically positive significance over two antioxidants (BHA and BHT) on the basis of AV and specific gravity where correlation coefficient (r), r > 6 PE. In case of BHA and BHT while using 200 ppm it extended the stability of frying oil upto 14 and 16 hrs respectively on the basis of AV. It was statically positive significant (r > 6PE) but in case of PV it extended upto 12 hr and 14 hr which was not statistically positive significance where r < 6PE. In conclusion 150 ppm of TBHQ was more significance over BHA and BHT to control the oxidation of oil on the basis of PV, AV and specific gravity.

Keywords: *TBHQ; BHA; BHT; Refined Bleached Deodorized (RBD); Acid Value; Peroxide Value; Saponification Value; Density, Stability*

Introduction

Fats and oils, important and the most concentrated source of energy furnishing about 9 kilo calories/gram of oils and fats as compared with 4 k.calories per gram each furnished by protein and carbohydrate [1]. Since Fats and oils have higher energy value, foods containing a high proportion of fat form a compact energy source and thus give variety of our preparations of foods [2]. Fats and oils are oxidative in nature even at room temperature [3]. When they are stored for a long period, they undergo oxidation and become rancid. Autoxidation is the major cause of rancidity of fats and oils [4]. Sanders [5], States that oxidative rancidity leads to the formation of both unpalatable and toxic compounds, and is thus nutritionally undesirable. Different classes of substances occurring in oxidized fat have been shown to have toxic effects and physiological disorders [6]. Additional data on human subjects supports the concept that lipid peroxides may inhibit other metabolic systems, particularly glycolysis accounting oxygen toxicity [7]. Therefore it is necessary to control oxidation of oils and fats.

Deep fat frying is a process in which the food is cooked by immersion in hot oil more than 170°C. Despite the fact that the deep fat frying industry is well-established and highly automated, the deep fat frying process is considered to be an art rather than a science (Blumenthal, 1991). It is a complex process. During deep fat frying, thermal, oxidative, and hydrolytic reactions take place resulting in physical and chemical changes in the oil and the formation of new compounds [8]. Regarding the control of oxidative deterioration of fats and oils, a number of methods have been developed. Many problem of oxidation can be solved or at least kept under control, by adequate technological interventions by food manufacture. Choice of the appropriate operational condition is very often crucial to the keeping quality of foods otherwise easily oxidized. The correct packing material, use of inert atmosphere and suitable storage condition are ways to retard the oxidative deterioration. There are however, many situations where reasons do not allow one to utilize any of these ways of protecting food against oxidation. In many of these desperate situations, well known antioxidants are very useful. Antioxidants are a good all-around remedy against the lipids oxidation in foods, or oils and fats [9]. Synthetic antioxidants are used. In recent years, the possible toxicity of synthetic antioxidants has been investigated by several workers [10]. Therefore, emphasis has been given for using natural antioxidants rather than synthetic antioxidants. The objectives of this research are to analyze the change in physiochemical parameter (AV, PV, Specific gravity, Saponification value) of palm oil in each hour of frying using different concentration of antioxidants (TBHQ, BHA, BHT) on deep fat frying of instant noodle and to recommend these for industrial purposes according to the result obtained.

Material and Method

Materials

Cut cake (noodles) Cut cake (60 - 62 gm). Palm Oil (RBD), Synthetic Antioxidants (Tertiary Butylated Hydroxyl Quinone (TBXQ), Butylated Hydroxy Anisole (BHA), Butylated Hydroxy Toluene (BHT), specific fryer with temperature controller and Thermometer.

Methods (Analytical)

Physical and chemical parameter analysis

Estimated of Peroxide Value The frying oil was analysed for Peroxide Value at interval of one hour followed the procedure by AOAC, 2005 (41.1.16) [11].

Estimation of Acid Value Acid Value of frying oil was determined by titration method according to AOAC, 2005 official method (41.1.23) [11].

Estimation of specific gravity Specific gravity of palm oil was determined by pycnometer followed by AOAC, 2005 (41.1.05) [11].

Estimation of Saponification Value The Saponification value of frying oil was determined by the procedure of Rangana [12].

Data Analysis

Data analysis was done by SigmaXL, a statistical add in for excel 2007.

Importance of peroxide value and acid value in assessing food quality and food safety

Fats and oils in foods oxidized during processing, circulation and preservation. This reaction causes deterioration in taste, flavour, odour, colour, texture and appearance, and a decrease in the nutritional value of foods (Frankel E.N., lipid oxidation. The oily Dundee. 1988). Furthermore, the reaction can induce food poisoning. Therefore, from a food quality and food safety perspective, this oxidation reaction must be suppressed. Instant noodles are a fried food, and therefore instant noodles content a lot of fat and oils. In 1964 and 1965, Japan had a food poisoning epidemic caused by the degradation of the fat and oil in instant noodles [13]. Many people who ate the degraded instant noodles develop acute symptoms such as diarrhoea, nausea, abdominal pain, fatigue, and headache, but fortunately, no one die. After the incidence the ministry of health and welfare, currently the ministry, Labour and welfare, in Japan set standards for instant noodles in the food sanitation Law to protect against food poisoning and to control the quality of instant noodles. In that law, peroxide value (PV) and acid value (AV) were chosen as useful indices to control food safety and quality, and the standard values of PV and AV were set at no more than 30 mequiv/kg and 3 respectively. These values were chosen because they indicate stage of fat and oil deterioration. After setting these values, there has been no reported cases food poisoning caused by instant noodles in Japan. At the initial stage of fat and oil deterioration, the reasons for measuring PV and AV are very different because of the different mechanism underlying the formation of hydroperoxides and FFA from fat and oil. Hydroperoxides is formed by the oxidation of fats and oils. Whereas FFA is formed by the hydrolysis of fat and oil. PV is an index to quantity the amount of hydroperoxides in fat and oil. Several studies have reported that secondary oxidized oil product is generally toxic [14]. Also, weakly oxidized fats and oil at levels of only 100 mequiv/kg of PV are neurotoxic. Therefore, the formation of hydroperoxides, the primary oxidized product of fat and oil, must be suppressed to protect against the oxidation of fat and oil and the formation of secondary oxidized products from both food quality and food safety perspectives. Meanwhile, AV is an index to measure the amount of FFA. The FFA themselves are not toxic; however, the presence of FFA affects food quality. Consequently, measuring both indices is indispensable to control food quality and safely.

There is currently a movement worldwide to use only AV to control food quality and safety.

For example, the 36th session of the Codex on Food Additives and Contaminants help at Rotterdam. The Netherlands, in 2004 expressed the opinion that PV is not safety factor As a result; the 28th session of the Codex Committee on Method of Analysis and Sampling held at Budapest, Hungary, in 2005 determined that only AV is the useful as an index of fat and oil deterioration to control the quality and safety of instant noodles. PV was not recommended as an index in this standard (ALINIRM 05/28/23, 2005), this is very dangerous, because there is evidence that the oxidized products of fat and oil formed from deteriorated fat and oil are the real cause of food toxicity [14]. Furthermore, it is impossible to predict the magnitude of the PV from the AV because the underlying mechanisms of formation are completely different.

During the storage, many kinds of reactions, such as oxidation, hydrolysis, polymerization, cyclization, and β-scission can occur in the fats and oils. It is very difficult to determine how the individual reaction interacts to form toxic compounds. Almost all of these reactions, however, relate to oxidation and proceed via the formation of lipid hydroperoxides. Consequently, protecting against the formation of lipid hydroperoxides is the best way to maintain food safety and quality. In the Food sanitation Law of Japan, PV is set to no more than 30 mequiv/kg because deteriorate instant noodles with a PV as low as 100 mequiv/kg have caused food poisoning in Japan [13]. A PV value of 100 mequiv./kg might not be very high, but animal studies reveal that this level of deteriorated fat and oil is neurotoxic. During the oxidation of fat and oil, sudden oxidation is the propagation period, occurs after the induction period. More the antioxidants are consumed during the induction period. Although 30 mequiv/kg is much less than 100 mequiv/kg. once the sudden oxidation starts during the propagation period the 100 mequiv/kg level would be reached soon after the 30mequiv/kg level. Furthermore, this initial stage of PV alteration cannot be estimated by changes in AV because the two, indices do not increase simultaneously. Consequently, setting a criterion of 30 meqiuv/kg for PV in instant noodles is important to control food safety.

It is not sufficient to monitor food deterioration with AV alone to maintain food quality and food safety. We conclude that PV must be adapted as an index in the Codex standard for instant noodles.

Relationship between PV and AV in Instant Noodle

The concept for measuring PV and AV are completely different. It is now accepted that the secondary oil oxidized products such as polymerized oil, cyclic fatty acid, hydroperoxy alkenal and hydroxyl alkenal are main cause of toxicity in oxidized oil. Therefore, the formation of lipid hydroperoxide, the primary oil oxidized product, must be suppressed to prevent the formation of the secondary oil oxidized products in Instant Noodle. In Japan, PV is hired to monitor the formation of the primary oil oxidized product, namely lipid hydroperoxide. On the contrary, AV is measured to keep the food quality. During the food processing and storage, free fatty acids are formed in the noodle by the hydrolysis of the oil. Free fatty acid itself is not a very toxic compound; however, it becomes a cause of the reduction of flavour and taste. The purpose of measuring AV is to check the free fatty acid level in Instant Noodle [15] Japan proposed the food standard of Instant Noodle that contains PV and AV to the Codex Regional Coordinating Committee for Asia to make it international standard. However, several representatives of Asian countries did not accept the proposal from Japan. Particularly, including PV in the standard was opposed because they recognized that the PV and AV would increase together during the deterioration of Instant Noodle and measuring AV is enough to keep the food safety and quality. As mentioned above, the concepts for measuring PV and AV are completely different and PV is an essential item to keep the food safety. Consequently, 218 kinds of fried type Instant Noodles were collected from commercial base of all over the world and measured PV and AV of them to grasp the deteriorated situation of Instant Noodles sold in the market. Furthermore, the relationship between PV and AV values was investigated to confirm the truth of other countries opinions. All the measured values on PV and AV are plotted in figure 1. These results show that the both values are spread to wide range and some of them exceed the criteria (PV: 30 meq/kg and AV: 3) established in Food Sanitation Law in Japan. Since almost all samples were sold in cool condition, the samples exceeding 30 in PV might be exhibited under strong light for a long period. On the other hand, the samples exceeding 3 in AV might be stored under high humidity. Light and moisture strongly affect the degradation of oils, made a deteriorated Instant Noodle, which is as same as deteriorated Instant Noodle caused food poisoning in 1964, with sunlight and high temperature and succeeded in reappearing the food poisoning with the sample. Consequently, it would be said that cutting light or sun light is the most important way to preserve Instant Noodle even the material of the package film can suppress the UV and water transmission. In figure 8, if the both PV and AV increase simultaneously during storage, the approximating curve against these plots must become ever- increasing curve. However, the plots are not scattered like that. The coefficient of correlation for PV and AV was calculated with Pearson's product-moment coefficient of correlation and the result was -0.1083. This value means that the plots are scattered in the downward-sloping and the correlation between PV and AV is poor because the coefficient of correlation is lower than zero and the absolute value is near zero. Consequently, the coefficient of correlation reveals that PV and AV do not form simultaneously in the oil of Instant Noodle during the deterioration. Furthermore, the P value was also calculated and the value was 0.1106. This value also explains that the relation between PV and AV is not significant because the value was bigger than 0.05. Therefore, analysing only AV cannot grasp any deteriorated situation of the oil in Instant Noodle and analysing both PV and AV has a strong and significant meaning. We conclude that PV is also an indispensable factor to keep the food safety and quality of Instant Noodle [15].

Increase PV in the oil of Instant Noodle

A great number of studies concerning the oxidation or heating of the oil have been carried out so far. These studies are mainly separated to three types of studies.

The most popular study is that the oil is heated at more than 250°C under oxygen omitted circumstances such as under nitrogen, carbon dioxide, etc. This kind of heating forms polymerized oil and cyclic fatty acid without containing oxygen molecular in the structure. These compounds are very toxic; however, these compounds are not oxidized compound. Furthermore, it must be said that these study conditions are not realistic. Consequently, these results are not available when the food toxicity of the oil is discussed.

The oxidations of the oil under atmospheric condition are also carried out. In this degradation, the oxidation of the oil proceeds by radical chain reaction via lipid peroxyl radical. Therefore, the compound formed in this reaction contains oxygen molecular in it. These studies are separated to two types of studies. One is heating the oil over 100°C and the other is less than that. Taking account of the accumulation of lipid hydroperoxide (PV) in the system, the heating temperature is important point. For instance, the temperature usually hired for deep-fry and stir- fry is around 180°C and the lipid hydroperoxide is decomposed easily under this condition. As the result, the PV of the oil does not increase it and the secondary oil oxidized products are formed instead of that. However, it has been reported that the polymerized oil and cyclic fatty acid are not accumulated much in the system. Frankel., *et al*. measured the cyclic fatty acid level in the oil used at fast foods restaurant and found that 0.1-0.5% of total fatty acid was changed to cyclic fatty acid.

The oxidation heated at less than 100°C accumulates lipid hydroperoxide in the system because the rate of the formation of lipid hydroperoxide is faster than the rate of the decomposition of that. Normally, this kind of oxidation is called "autoxidation". The autoxidation also proceeds under atmospheric condition and accumulates the lipid hydroperoxide (PV) in the system at first. The amount of the lipid hydroperoxide finally reaches to the top, after that, it starts to decrement because the rate of the formation of lipid hydroperoxide becomes slower than the rate of the decomposition of that. The reaching level depends on the kinds of fatty acids consisting of the oil, heating temperature, etc. The decomposed lipid hydroperoxide forms aldehyde, ketone, alcohol, alkane, etc. It is now accepted that the hydroxyl alkenal and hydroperoxyl alkenal formed in autoxidation is very strong toxic compounds. Therefore the autoxidized oils are also toxic [13, 16,17].

Results and Discussion

Effect of different concentration of TBHQ on Acid Value

The acid values measured at regular interval of time (1 hr) of different concentration of TBHQ are shown in figure 1.

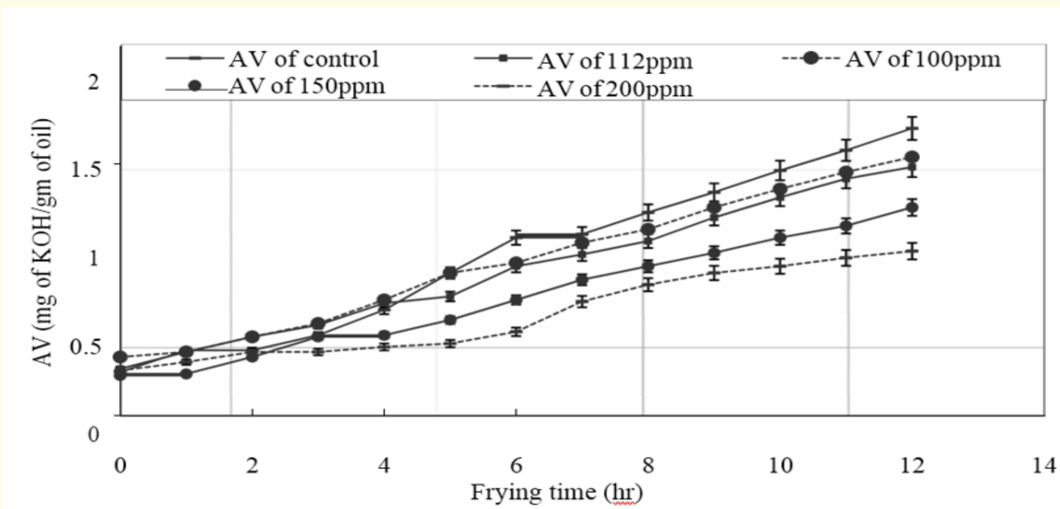

Figure 1: *Change in acid value with respect to frying time (hr) of oil using different TBHQ concentration.*

In figure 1, it was found that acid value (AV) increased with increased in frying time whether there was used of TBHQ or not and found significance difference. There was inversely proportion between acid value and antioxidants proportion (upto 200 ppm). NS recommends the AV of oil upto 1 mg of KOH/gm of oil; it was found that TBHQ of 200 ppm was more stable for rise in AV which extended the stability of oil upto 12 hr while that of control (without using TBHQ) extended upto 6 hr but the correlation coefficient (r) became decreased while increase in concentration of TBHQ upto 200 ppm i.e. 0.99750, 0.99628 and 0.97518 of 100 ppm, 150 ppm and 200 ppm respectively. All the concentration are statistically significance at 95% of confidence level where r < 6PE (probability error) refers.

Effect of different concentration of BHA on Acid Value

The acid values measured at regular interval of time (1 hr) of using 100 ppm, 150 ppm and 200 ppm of BHA represented graphically in figure 2.

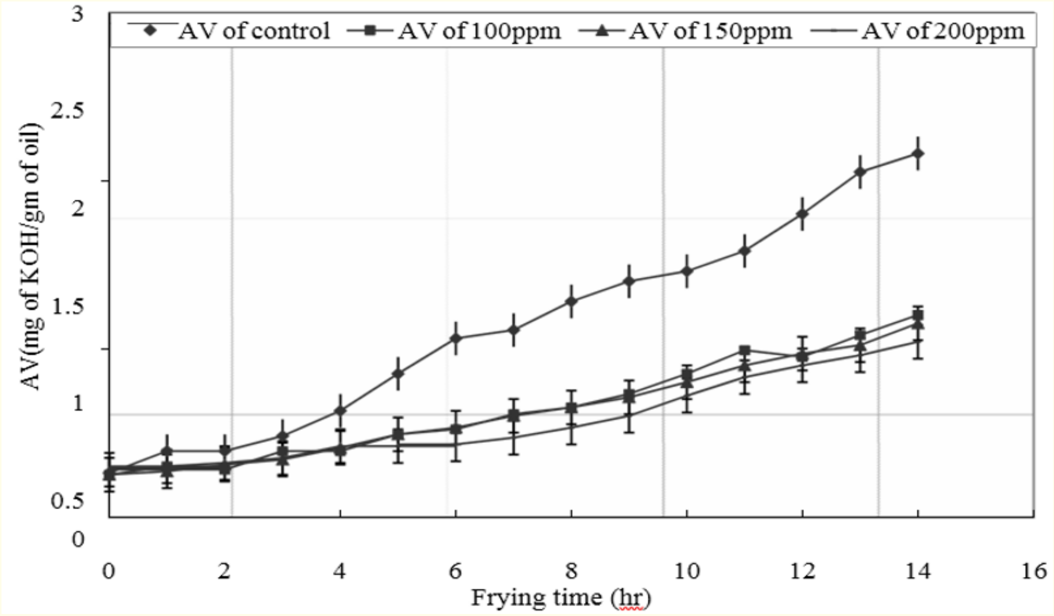

Figure 2: *Change in acid value with respect to frying time (hr) of oil on different concentration of BHA.*

While using BHA of different concentration it was found that decrease in AV with increase in concentration of BHA up to 200 ppm. The concentration of 200 ppm shows more stable than others concentration it increased the stability of frying oil up to 14 hr while that of control (without using BHA) was 6 hr and which was 2 hr more that of TBHQ (using 200 ppm) but the correlation becomes decrease with increase in concentration up to 200 ppm, it shows the strong positive correlation on 150 ppm concentration of BHA, correlation coefficient was found to be 0.98533, 0.99163 and 0.96483 of 100 ppm, 150 ppm and 200 ppm respectively. All concentration are positively statistical significance at 95% level of confidence where r > 6PE.

Effect of different concentration of BHT on Acid value

The acid value measured at regular interval of time (1 hr) using 100, 150 and 200 ppm of BHT are represented graphically in figure 3.

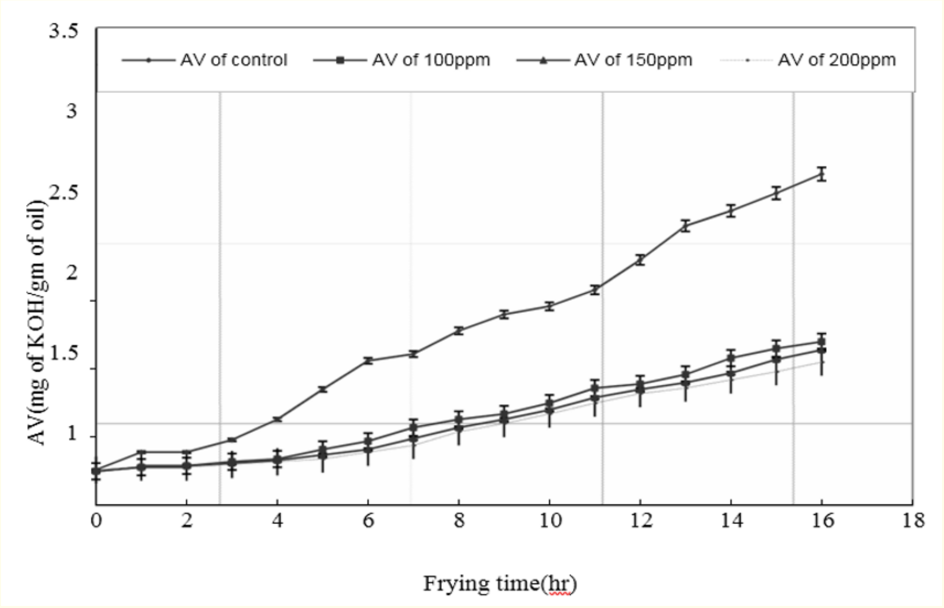

Figure 3: *Change in acid value with respect to frying time (hr) of oil on different concentration of BHT.*

It was found that AV reached to its limit within 16 hr while using BHT of 200 ppm and that of control (without using BHT) reached within 6 hr.

BHT was more significance than TBHQ and BHA on the basis of AV. It increases the AV around 1 mg of KOH/gm of oil (Nepal Standard) within 16 hr while 200 ppm concentration BHT was used. And also same result obtained as above mention two antioxidants but 100ppm BHT was positively strong significance than 150 and 200 ppm having correlation coefficient 0.98518, 0.97619 and 0.96641 respectively where r > 6PE It also found that by increased antioxidants concentration increased the stability time of frying oil.

In any frying situation there is obvious rise in acid value with increase in frying time. Although there is no any supporting literature regarding the correlation between release of free fatty acid and concentration of antioxidants which was evident during dissertation work and found strong positive relation for control and weak positive correlation for the oil of 200 ppm. Free fatty acid itself is not a very toxic compound; however it impairs flavor and taste of itself and the product. The purpose of measuring AV is not significant in aspect of public health but it is regarded as the quality parameter of oil. Here result obtained shows the positive correlation between the decreases in rise in AV against increase in antioxidants concentration.

Effect of different concentration of TBHQ on Peroxide Value

The Peroxide value measured at regular interval of time (1 hr) using TBHQ of 112 ppm, 100 ppm, 150 ppm and 200 ppm different are represented graphically in figure 4.

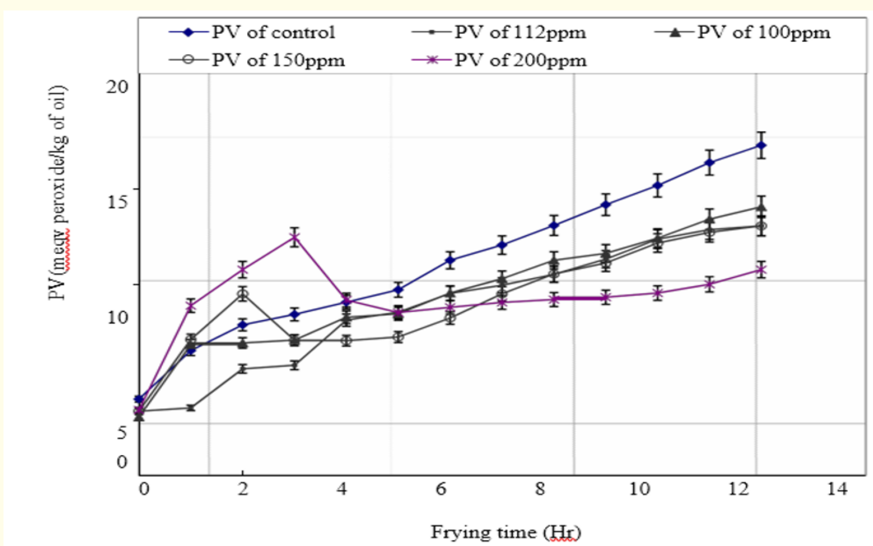

Figure 4: *Change in peroxide value with respect to frying time (hr) of oil using different TBHQ concentration.*

As shown in graph above, it was found that rise in peroxide value (PV) became decrease with increase in TBHQ concentration. PV increases abruptly at first hour of heating and reaches its maximum peak on 200 ppm concentration then decrease gradually. It increases the stability of oil on the basis of PV up to 11 hr while that of control reaches to its standard limit within 5 hr. But 150 ppm TBHQ is statistically significance than 112, 100 and 200 ppm and correlation coefficient was found to be 0.90723, 0.095214, 0.97246 and 0.86014 that of 112, 100, 150 and 200 ppm respectively where r > 6PE.

Effect of different concentration of BHA on Peroxide value

The Peroxide value measured at regular interval of time (1 hr) of 100, 150, 200 ppm concentration of BHA and control (without using BHA) represented graphically in figure 5.

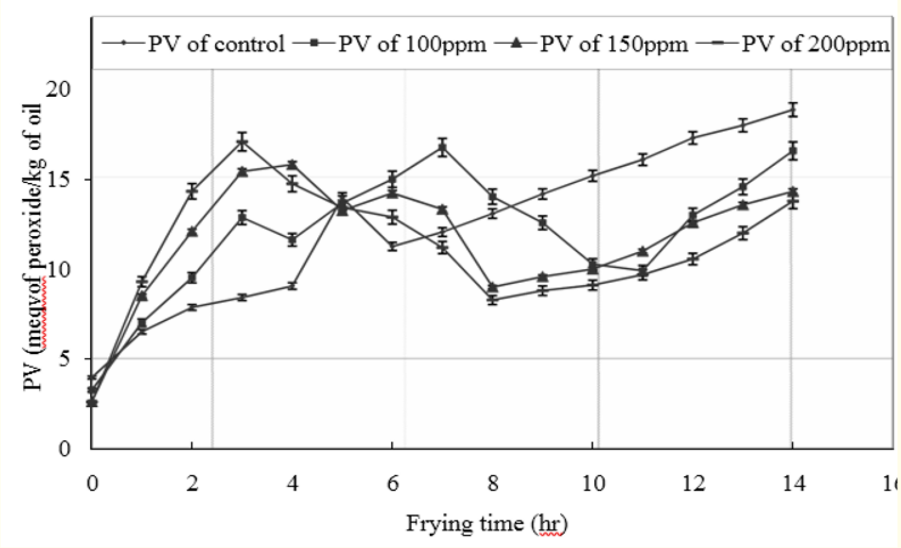

Figure 5: *Change in peroxide value with respect to frying time (hr) of oil using different BHA concentration.*

While using BHA of different concentration it did not extend the stability of frying oil in comparison with TBHQ. It also increased the stability upto 11 hr which is same as TBHQ but rise in peroxide value become decrease while increase the antioxidant concentration(compare with control) on the basis of statistically analysis there is no statistically significance in any concentration of BHA where r < 6PE.

Effect of different concentration of BHT on Peroxide value

The Peroxide value measured at regular interval of time (1 hr) using 100, 150, 200 ppm concentration of BHT and control (without using BHT) represented graphically in figure 6.

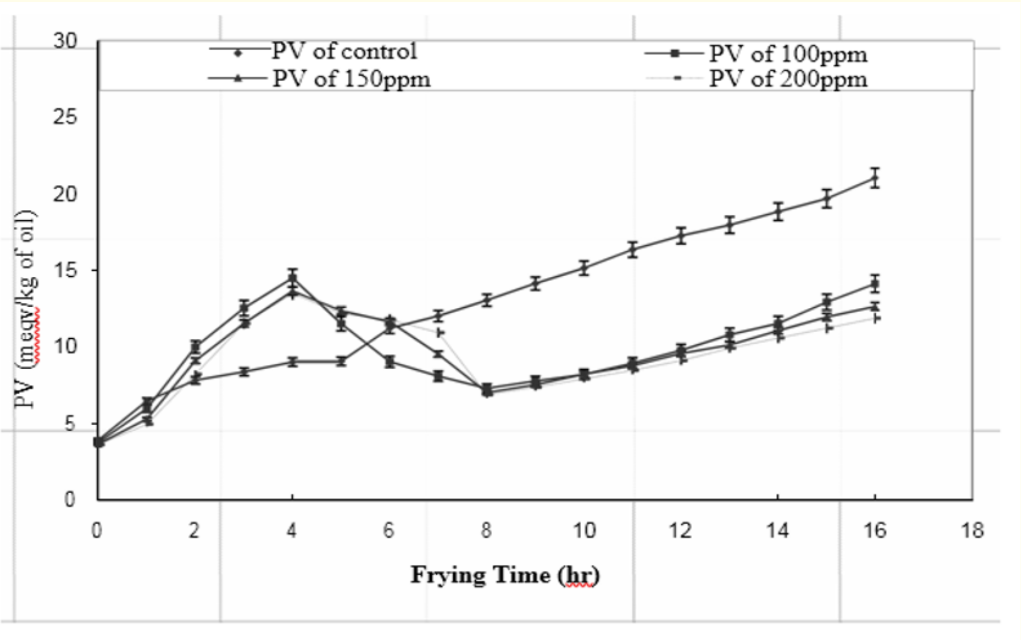

Figure 6: *Change in peroxide value with respect to frying time (hr) of oil using different concentration of BHT.*

BHT extends the stability of frying oil upto 13 hr which was more significance than TBHQ and BHA. But on the basis of statistically analysis it was not significance where r < 6PE. correlation coefficient (r) was found to be 0.44372, 0.40017 and 0.34972 respectively that of 100, 150 and 200 ppm and 6PE was found to be 0.81253, 0.84972 and 1.00004 respectively. TBHQ of 150 ppm concentration having correlation coefficient 0.904012 was more significance than that of BHA and BHT. Almost all to the oxidation reactions proceed via formation of lipid peroxides. Therefore, to prevent the formation of lipid hydroperoxide is the best way to keep the food safety and quality. It also shown that the increasing concentration of antioxidants increasing the stability time of frying oil.

Comparison of acid value and specific gravity using different concentration of BHT

The acid value and specific gravity measured at regular interval of time (1 hr) using 100, 150 and 200 ppm of BHT.

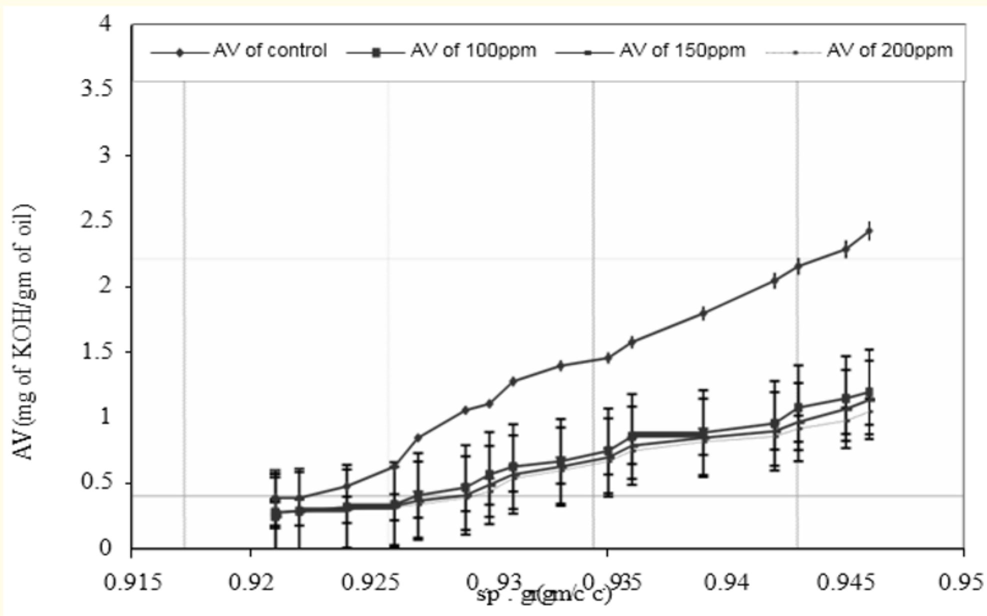

Figure 7: *Change in acid value against specific gravity of frying palm oil using BHT of different concentration at 170 to 180°C.*

It was found that 150 ppm of BHT was found to be statistical significance over 100 and 200 ppm BHT where r< 6PE for all cases.

It is found that 150 ppm TBHQ is more statically significance than 150 ppm of BHA and BHT. It is well known fact that the specific gravity of oil increase with increase in frying time while frying the noodles, it increases the moisture content in oil which increases the specific gravity of oil. The specific gravity of oil slowly increases with increase in antioxidants.

Comparison of acid value and peroxide value using different concentration of TBHQ

The acid value and peroxide value measured at regular interval of time (1 hr) of different concentration of TBHQ. It was found that acid value increased with increased in peroxide value with frying time in certain limit. Peroxide value increased with increase in acid value in first hour of heating then peroxide value became decreased then again increased it was the beginning of secondary oxidation. There was not perfect relation between these two parameters. But correlation coefficient was found to be 0.98871, 0.99650, 0.99318 and 0.96503 respectively that of 112, 100, 150 and 200 ppm where r < 6PE for all cases and at 100ppm it was found more statistically significance than other concentration of THHQ.

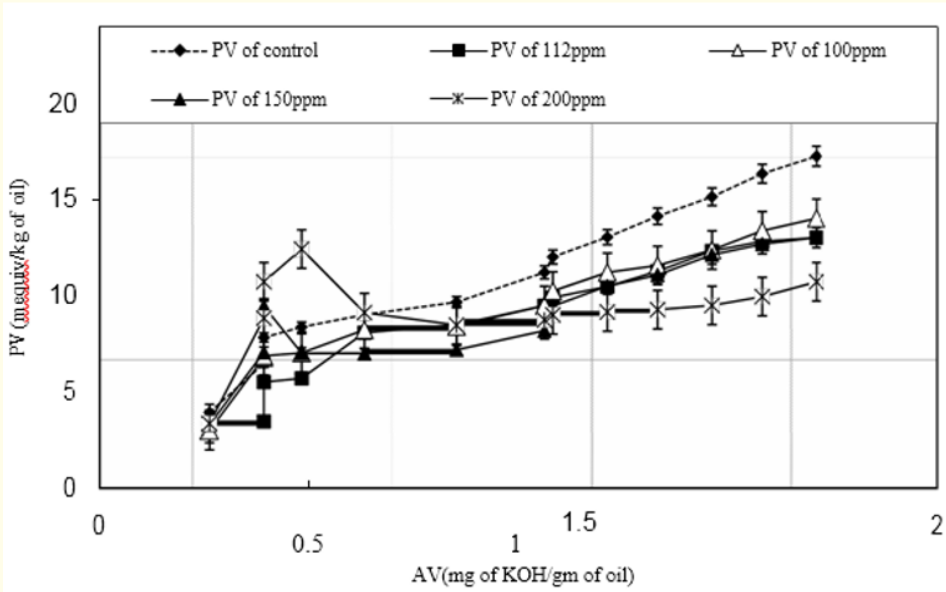

Figure 8: *Relation of AV against PV on different concentration of TBHQ.*

Conclusion and Recommendation

Conclusion

The study suggests that higher the concentration of antioxidants delayed the rise in AV, PV and specific gravity of frying oil to some extent. 150 PPM antioxidant is shows signification results than any other concentration on which 150 ppm of BHT was found more significant than TBHQ and BHA which extend the shelf life of oil beyond 12 hr which was compared to 7 hr of TBHQ and 10 hr of BHT. If we consider Acid value and peroxide vale as human health indicator and food safety indication 150 ppm of BHA is recommended to frying food industry.

Recommendation

1. Higher the concentration of antioxidants delayed the rise in PV, AV and specific gravity of frying oil to some extent.
2. BHT was found to be statistically significant over TBHQ and BHA to stable the PV of frying oil
3. TBHQ was found to be statistically significant over BHA and BHT to stable both AV and PV of the frying oil.
4. Concentration of 150 ppm TBHQ was found to be the most significance over BHA and BHT to stable the frying oil which extended the stability upto 12 hr on the basis of acid value.
5. Concentration of 200 ppm BHT was found to be statistically significant over TBHQ and BHA which extend the stability of frying oil up to 16 hr, according to Codex.
6. While using the TBHQ of 150 ppm it increased the stability of oil 6 hr more than that of control (without using TBHQ) and while using BHT it increased the stability 9 hr more than that of control (without using BHT).
7. It is recommended to use 150 ppm of TBHQ to the industry to control oxidation of oil considering both Acid Value and Peroxide Value.

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