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SHORT COMMUNICATION

Influence of natural and synthetic antioxidants on the degradation of Soybean oil at frying temperature

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Abstract The effect of several natural and synthetic antioxidants to retard the formation of polar compounds and thermo-oxidation at prolonged frying temperatures was studied. Antioxidants, including butyl hydroxyl toluene (BHT), *ter*-butyl hydroxyquinone (TBHQ), α- and γ-tocopherols, tocopherol mixture (α, β, γ and δ), sesamol, β-sitosterol, β-sitostanol, γ-oryzanol, curcumin, rosemary extract and sucrose acetate isobutyrate (SAIB) were tested in refined soybean oil without added any additives recovered from refinery. Rosemary extract and SAIB were showed a considerable effect on both polar compound formation and secondary oxidation. These compounds increased the oxidative stability of oil for more than 30 % compared to conventional synthetic antioxidants. Oils treated with SAIB showed higher color retention after 6 h heating compared to the oils added with BHT, TBHQ and tocopherols. Curcumin, sesamol and γ-oryzanol showed higher antioxidant potential compared to other antioxidants. Preliminary results obtained from this study have clearly demonstrated that SAIB and rosemary extracts are more commercially viable antioxidants to increase the stability of frying oils.

Keywords Frying · Antioxidants · Rosemary extract · Sucrose acetate isobutyrate (SAIB)

Highlights • The effect of several natural and synthetic antioxidants to retard the formation of polar compounds and thermo-oxidation at prolonged frying temperatures was studied.
• All antioxidants were tested in refined soybean oil without added any additives that was recovered from refinery.
• Rosemary extract and sucrose acetate isobutyrate (SAIB) were showed a considerable effect on both polar compound formation and secondary oxidation.
• Curcumin, sesamol and γ-oryzanol showed higher antioxidant potential compared to other synthetic antioxidants.
• SAIB and rosemary extracts are more commercially viable antioxidants to increase the stability of frying oils.

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Introduction

The frying process involves immersion of food material in hot oil at a temperature range of 150 to 190 °C (Choe and Min 2007). Frying leads to degradation of oil by accumulating polar compounds, which involves a set of physicochemical reactions such as thermo-oxidation, hydrolysis and polymerization (Orozco et al. 2011; Tena et al. 2014). Polar compounds include oxidized, dimerized and polymerized triacylglycerols along with diacylglycerols and free fatty acids. They originate from triacylglycerols and increase the rate of degradation of oil. Eventually, through mass transfer process these degradation products accumulate in the fried food and reduce the nutritional quality of both oil and food (Qing Zhang et al. 2012). Quantification of the polar compounds is the most reliable method for monitoring the degree of degradation of frying oils (Gertz 2000). On the other hand, studying the effect of antioxidants on polar compound formation during the frying process is one of the most important areas of lipid research. Secondary oxidation products such as aldehydes and ketones formed during thermo-oxidation lead to complete degradation of frying oil. Antioxidants could be useful to retard the formation of these secondary oxidation products. But, most of the natural antioxidants and synthetic antioxidants were found to be ineffective at a prolonged frying temperature because of their low thermal stability (Marmesat et al. 2010). So, studying the efficacy of different plant-based antioxidants such as sesame lignans, rosemary and sage extracts in frying process is a growing interest in the commercialization of the frying oil industry (Gertz 2004; Lee et al. 2008). This leads to the formation of antioxidant emulsions, blending with different oils and screening of unconventional antioxidants for increasing the stability of frying oils (Aladedunye and Przybylski 2014a, 2014b; Tironi and Añón 2014). The limit of the addition of synthetic antioxidants to refined edible oils is limited to 0.02 % by different food laws (FSSAI 1998). However, most of the studies discussed the efficacy of antioxidants in higher limits (up to 0.1 %) and testing the effect of those additives in the refined oil, which already contains synthetic antioxidant that causes a synergistic or antagonistic effect on the antioxidant activity. Synergistic effect leads to higher activity of targeted antioxidant to be studied by reacting with the already added antioxidant, while on the contrary, the antagonistic effect leads to lower activity of targeted antioxidant. This will lead to obtain underestimation or overestimation of targeted antioxidant effect (Choe and Min 2009). This necessitates studying the targeted antioxidant effect in the frying oil devoid of any other added antioxidants and also at the same concentration. The present study investigates several natural and synthetic antioxidants on the degradation of refined soybean oil at frying temperature and evaluates the antioxidant activity in the total polar compound formation and secondary oxidation in the oil.

Materials and methods

Refined soybean oil without added any synthetic antioxidants was recovered from the Sakthi soya group (Pollachi, India). Tocopherols mixture (α, β, γ, and δ), α -tocopherol, γ-tocopherol, β-sitosterol, β-sitostanol, and sesamol were purchased from Sigma (Milan, Italy). γ-oryzanol was bought from Tokyo chemical industries (TCI, Japan). Butyl hydroxyl toluene (BHT), ter- butyl hydroxyquinone (TBHQ) and Curcumin were purchased from Alfa Aesar (Hyderabad, India). Rosemary extract (Herbalox, type O) was provided by Kalesc Inc. (Miami, U.S), and Sucrose acetate isobutyrate (SAIB 100) was supplied by the Eastman Chemical company (Tennessee, U.S).

All solvents and chemicals of highest purity grade were purchased from Spectrochem (Bangalore, India). Silica gel 60 and thin-layer chromatography (TLC) Aluminum plates (20 × 20 cm) with silica gel 60 F254 were from Merck (Darmstadt, Germany).

Sample preparation

A standard amount of 0.02 % of each antioxidant added to 20 g oil samples in different steel vessels (30 ml capacity) and heated on a hot plate assembled with a temperature sensor (IKA, India) at 180 °C for 2 h by maintaining exact frying temperature throughout the study. In addition, the temperature in at different parts of the oil was monitored through the temperature reader and also occasionally stirred to maintain the exact temperature with little error. A control sample without added any antioxidant was heated at same conditions mentioned above. All experiments were performed thrice, and all oil samples were cooled down after heating and subjected to further characterization immediately.

Quantification of polar compounds

Polar compounds in all samples were quantified by column chromatography method according to the official IUPAC procedure (IUPAC 1979). Briefly, 500 mg of oil dissolved in 2 ml of hexane/diethyl ether 90:10 (*v*/*v*) was loaded onto a packed silica gel column containing 15 g of stationary phase. The non-polar fraction containing the unoxidized triacylglycerol (TAG) was eluted with hexane/diethyl ether 90:10 (*v*/*v*), and the solvent was evaporated. The polar compounds were then eluted with diethyl ether and finally dried under nitrogen gas. The efficacy of separation was checked by TLC by using precoated silica gel plates eluted with hexane/diethyl ether 80:20 (*v*/*v*) and visualized by exposure to iodine vapors.

p-Anisidine value (*p*AV) and conjugated diene value (CD)

It can be defined as 100 times the optical density measured at 350 nm in 1 cm cuvette of a solution containing 1 g of the oil in 100 ml of the solvent mixture. *p*AV of all samples were determined by standard AOCS official method Cd (18)–90 (AOCS 2003). CD values of all oil samples were determined according to the standard IUPAC method (IUPAC 1987).

Statistical analysis

One way ANOVA analysis was performed by using the SPSS 16.0 version software. All the analysis was performed in triplicate and the results were expressed as mean ± SD.

Results and discussion

Effect of antioxidants on polar compound formation

Figure 1 showed the effect of various antioxidants on the formation of polar compounds in the refined soybean oil at frying temperature after 2 h. Fresh soybean oil showed 4.00 ± 0.25 % polar compounds while heated oil showed 24.20 ± 0.75 %, which is the nearest proposed limit (> 24 %) for the deterioration for frying oils. Usually, this limit acquires by oils after 20–25 frying cycles in the real time frying operations (Bansal et al. 2010; Aladedunye and

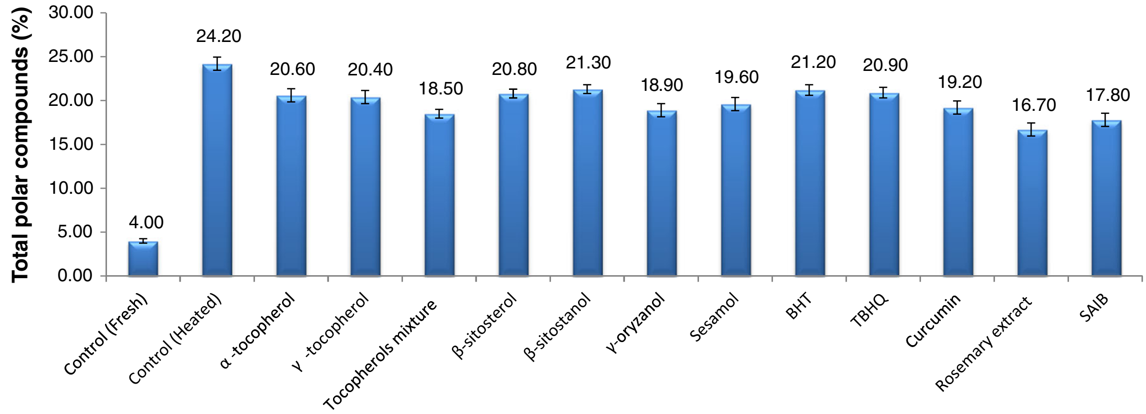

Fig. 1 Effect of different antioxidants on the formation of polar compounds in soybean oil at frying temperature after 2 h(*). *Statistically significant difference between control and samples ($p < 0.05$)

Przybylski 2014a, 2014b). But, in our study, the soybean oil was attained to have 24 % of polar compounds within 2 h of heating at frying temperature. This higher value explains the influence of steel vessel on the extensive degradation of oil utilized in this study (Freitas et al. 2009). Moreover, Tocopherols, sitosterol, BHA and BHT showed only a little effect at frying temperature, with respective to the polar compound formation (Fig. 1). These results clearly explain the ineffectiveness of conventional antioxidants during the prolonged frying process. Interestingly, sitostanol that is a saturated form of sitosterol also found to be ineffective similar to those explained earlier. From the recent past, stanols have gained much importance for their higher thermal stability and antioxidant capacity over sterols (Aydeniz and Yılmaz 2013). But, our results showed that sitostanol could not show greater effect compared to sitosterol at frying temperature.

Tocopherols mixture was showed a higher reduction in the polar compound formation compared to individual tocopherols. A mixture of tocopherols limited the polar compound level to 18.50 ± 0.50 %, which is mainly caused by the synergistic effect of different tocopherols. On the other hand, γ-oryzanol, a principle bioactive compound of rice bran oil, sesamol from sesame oil and curcumin, a major compound from turmeric have shown a significant effect on the polar compound formation. These results suggest the oil industries can choose these compounds to increase the thermal stability of oils.

In this study, we identified rosemary extract and SAIB as the most thermally stable antioxidants for frying process. Soybean oil added to the same concentration (0.02 %) of rosemary and SAIB showed that they limited the polar compound formation to 16.70 ± 0.75 % and 17.80 ± 0.70 % respectively as against 24.20 ± 0.75 % of polar compound formation respective to the control sample. One-way ANOVA results showed that the difference between the control (heated) and all samples are significantly different at $p < 0.05$. Especially, rosemary, SAIB, tocopherol mixture added samples are significantly different from BHT, TBHQ, and sitosterol added samples. This showed that rosemary and SAIB produce about 30 % more stability in comparison with a control sample with respective to the total polar compounds. Antioxidant properties of rosemary extracts are well known due to the contents of diterpenes (10–15 %) including carnosic acid and carnasol (Robbins and Sewalt 2005). On the other hand,

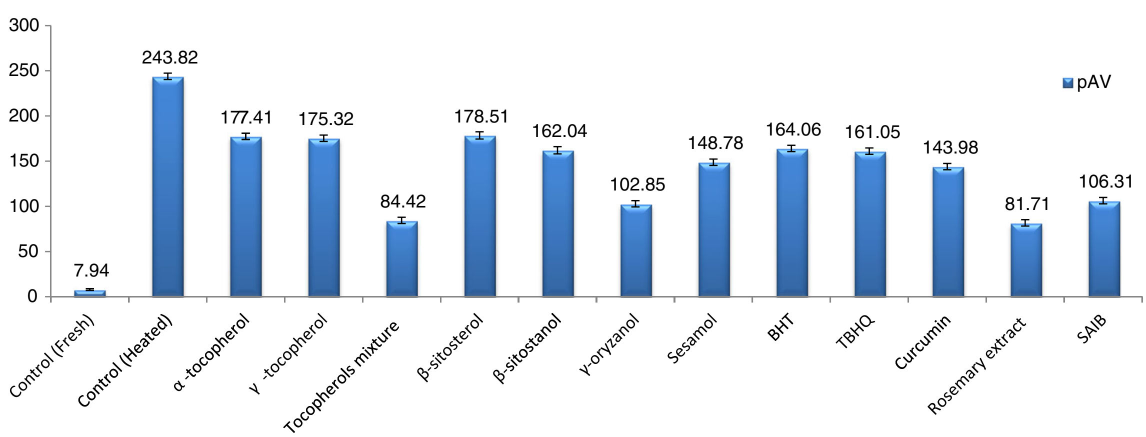

Fig. 2 Effect of different antioxidants on secondary oxidation (in terms *p*AV) of soybean oil(*). *Statistically significant difference between control and samples ($p < 0.05$)

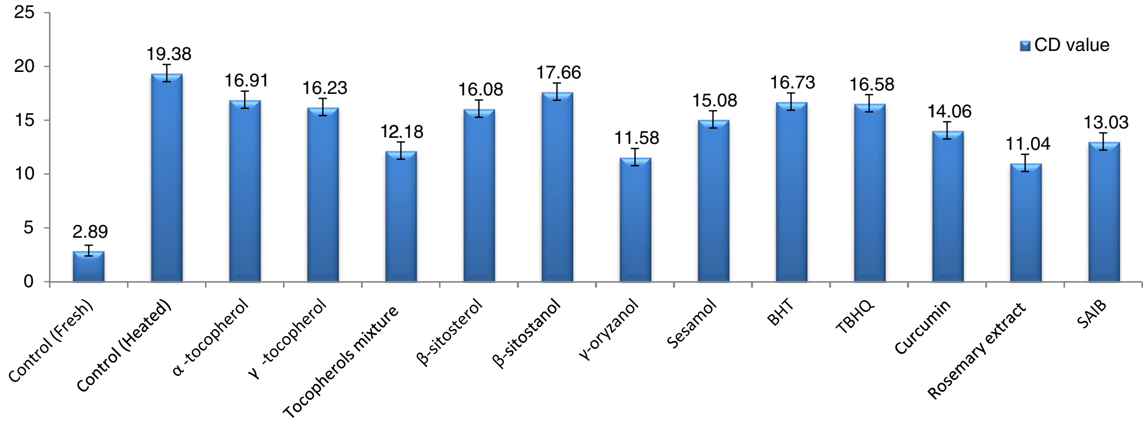

Fig. 3 Effect of different antioxidants on secondary oxidation (in terms of CD value) of soybean oil(*). *Statistically significant difference between control and samples ($p < 0.05$)

SAIB is a food additive that is used in the beverage industry. Toxicological studies showed SAIB is one of the safest food additives with maximum acceptability up to 2000 ppm (Reynolds and Chappel 1998; Myhr et al. 1998). However, SAIB is not a general choice of antioxidant for oil processing industries besides several other compounds. But, in this study, we utilized SAIB because of its high thermal stability (> 200 °C) and lipophilicity, and found that it is a best replacement to many other synthetic antioxidants (Reda 2011).

Effect of antioxidants on oxidation of oils

The oxidative stability of frying oil is an important factor in determining the shelf-life of fried products during storage (Jung et al. 2014). Thermo-oxidation of frying oils involves both primary and secondary oxidation. But, secondary oxidation continues because of the least stability of peroxides at frying temperature. Oxidation further proceeds to the formation of minor compounds, including aldehydes, ketones, and dienes. This is one of the main reasons for rejecting the peroxide value or fatty acid profiling for studying the frying oil degradation. On the other hand, *p*AV values give information about the secondary oxidation products such as carbonyl compounds formed at the end of the oxidation. In addition, *p*AV and diene values provide reliable information about the degradation of oils at frying temperature compared to peroxide values (Tompkins and Perkins 1999). *p*AV and diene values of oils treated with different antioxidants have shown in Figs. 2 and 3 respectively. *p*AV and diene values showed extensive degradation of the control sample within 2 h (7.94 ± 1.0 to

Fig. 4 Physical appearance of soybean oil with different antioxidants after 6 h heating at frying temperature

243.82 ± 3.5 of *p*AV and 2.89 ± 0.5 to 19.38 ± 0.8 of CD) without the addition of any antioxidants. But oils added to the tocopherol mixture, γ-oryzanol, SAIB and rosemary extract showed significant resistance towards secondary oxidation. All these values are significantly different at $p < 0.05$, inferred from statistical analysis. In the agreement with earlier studies (Che Man and Jaswir 2000), rosemary extracts showed a potent antioxidant capacity towards the secondary oxidation (Fig. 2). Moreover, tocopherol mixture and γ-oryzanol that showed higher polar compound formation compared to SAIB, could lower the oxidation compared with SAIB treated oils. Similarly, even though Rosemary showed higher activity than SAIB, color retention of the oil added with SAIB was higher than rosemary even after heating the oils for 6 h (color measurements have not taken as oil was 100 % polymerized). Additionally, oils added with BHT, TBHQ, sterol and tocopherols completely lost their color (Fig. 4). These major color deviations occur due to the formation of polymerized triacylglycerols. Our results clearly explain the anti-polymerizing activity of SAIB over many other antioxidants. Moreover, curcumin and sesamol were found to be better antioxidants than BHT, TBHQ, and tocopherols. These results strongly support their highest effectiveness to increase shelf life of oils in continuous frying operations compared to commonly utilizing synthetic antioxidants.

Conclusion

In this study, we analyzed the influence of several conventional and unconventional antioxidants to inhibit the degradation of soybean oil at frying temperature. In this process, we found tocopherols mixture, rosemary extract, and SAIB could reduce the total polar compound formation and also secondary oxidation in the oils at about more than 30 % compared to other antioxidants. Similarly, γ-oryzanol and curcumin showed a considerable effect on the frying oil quality. Preliminary results of this study concluded that rosemary extract and SAIB are the most commercially viable antioxidants to maximize the stability of frying oils. Testing of these antioxidants in real time frying process with different food materials and storage stability studies are currently underway.

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