# $^{\rm EFFECTS}$ of twelve antioxidants in three levels of concentration in lard at $^{70^{\circ}\rm C}$ in an oxidation accelerated test

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## SUMMARY

34 samples of lard were stored at 70°C for 16 days and their oxidation rate was evaluated daily by the peroxide index. One extra-sample without treatment, refrigerated lard, was kept at 4°C to be a control. The antioxidants and concentrations tested were: BHT, BHA, citric acid, propyl gallate and an antioxidant mixture (at 0.005%, 0.010% and 0.020% in weight); KRAKI A200, guarana, ascorbic acid (0.010%, 0.030%, 0.060%); distilled soybean (at 0.1428%, 0.4286% and 0.8572%), ROSMANOX 4942 and ROSMANOX-E 4943 (0.010%, 0.060% and 0.120%). The reduction of the oxidation rate was more effective with the samples treated with distilled soybean oil (0.8572%, 0.4286% and 0.1428%), ROSMANOX-E 4943 (0.120% and 0.060%), propyl gallate (0.020% and 0.010%), BHA (0.020% and 0.010%) and the antioxidant mixture (0.020% and 0.010%). The distilled soybean oil is a natural source of tocopherol. ROSMANOX is a rosemary extract and ROSMANOX-E contains rosemary and vitamin E (both are from Sanofi, Germany). KRAKI is an antioxidant blending from Kienast & Kratschmer Ltda (Brazil). These results show that oxidation reaction can be retarded by careful use of natural or synthetic antioxidants.

Keywords: antioxidants, natural antioxidants, oxidation

# INTRODUCTION

Lipid oxidation is one of the major causes of changes in meat products. Oxidative deterioration can occur by exposing lipids to oxygen, light, heat, ionizing radiation, metal ions, metalloprotein catalyst and enzymes (lipoxygenase). The antioxidant action of one substance may be exerted by reacting with free radicals, chelating catalytic metals, and also by acting as oxygen scavengers (Shahidi and Wanasundara, 1992).

Generically, an antioxidant can be classified like natural or synthetic. Many antioxidants are or contain phenolic compounds that act by free radicals elimination and/or chelating metals. Some of the most used synthetic phenolic antioxidants are: butylated hidroxytoluene (BHT), butylated hidroxyanisole (BHA), tertiary-butylhydroquinone (TBHQ) and propyl gallate. Examples of natural phenolic antioxidants include: flavonoid compounds (myricetin, quercetin), cinnamic, elagic and tannic acid derivatives, coumarins, tocopherols, and polyfunctional organic acids. Compounds with synergistic effect are: citric acid, phosphoric acid, thiodipropionic acid and its esters, lecithin, amino acids, biotin, niacin, ascorbic acid, nicotinic acid, p-aminobenzoic acid, polyphosphates and ethylenediaminetetraacetic acid (EDTA) (Shahidi and Wanasundara, 1992; Watts, 1954). In nature, many substances show antioxidants properties. Herbs, spices and vegetable antioxidants like rosemary, sage, oregano, onion, mustard, ginseng, pepper, sesame seeds, green tea and barley leaves have been widely researched. It's well known that antioxidation action from natural spices changes with species, origin, use (integral, ground, ethereous, aqueous, alcoholic extracts) and with the type of substrate. However, the use of these spices may be limited by strong smell and/or taste conferred to foods (Ramanathan and Das, 1993; Park et al., 1992; Liu et al., 1992; Sanofi, 1992; Watts, 1954). To determine the activity of an antioxidant one can use foods tested under normal storage conditions or under accelerated oxidation. (Shahidi and tr and Wanasundara, 1992). This work is in attempt to test the efficacy of traditional synthetic and natural antioxidants used by food industries.

#### Materials and Methods

Samples of lard were weighed in beckers, received the antioxidants and were perfectly homogenized. One extra-sample without treatment, refrigerated lard, was kept at 4°C to be an auxiliary control. The other samples were storage at 70°C (Abdullabekova et al., 1987). The oxidation development was checked daily by peroxide index during 16 days.

The concentrations used to BHT, BHA, propyl gallate and antioxidant mixture were chosen according to brazilian and north-american legislations (BRASIL, 1971; FSIS/AAFHV, 1993). The mean value tested of 0.010% corresponds to maximal limit accepted to addition in fats. The shortest value (0.005%) is related to this limit half. The highest value (0.020%) corresponds to limit concentration doubled. To the antioxidant mixture developed, the sum BHA + propyl gallate + citric acid observed the levels 0.005%, 0.010% and 0.020% on fat weight. Citric acid was tested at 0.005%, 0.010% and 0.020%. Ascorbic acid and alpha-tocopherol (vitamin E, natural occurrent in distilled soybean oil) have addition limit of 0.030% on fat weight, and were tested at 0.010%, 0.030% and 0.060%. Distilled soybean oil (DSO) contains 6 to 9% of total tocopherols in its composition (Augusto, 1988). 7% of tocopherols was the basic percentage used to calculate the DSO addition in lard, so the levels used to DSO were 0.1428%, 0.4286% and 0.8572%. The concentrations of compounds: KRAKI A-200 (tested at 0.010%, 0.030% and 0.060%), ROSMANOX 4942 and ROSMANOX E-4943 (at 0.030%, 0.060% and 0.120%) were chosen by manufacturer recommendations. Ground and integral guarana was tested at 0.010%, 0.030% and 0.060% due to the absence of legislation for its use and because it is a product consumed in wide scale. The antioxidants used and their respective manufacturers were: BHA, propyl gallate, rosemary extracts ROSMANOX 4942 and ROSMANOX E-4943: Sanofi do Brasil Ltda and Sanofi Germany (Brazil/Germany); BHT: Pena Branca Alimentos (Brazil); KRAKI A-200: Kienast & Kratschmer Ltda (Brazil); distilled soybean oil: Olvebra Industrial (Brazil); guarana: Agrofaza Ltda (Brazil); ascorbic and citric acids: Universidade Federal de Santa Maria (Brazil). The technique utilized to peroxide index determination was described by Terra & Brum (1988).

#### **Results and Discussion**

Table 1 shows the results obtained with lard under accelerated oxidation conditions (70°C) during 16 days. Statistical analysis (Tukey test) was applied to results (Table 2). The best treatments showed smaller means to peroxide index. The antioxidant action retarding the oxidation process was more clear in the firsts 10 days, when were observed smaller peroxide indexes. The auxiliary-control kept refrigerated at 4°C did not change. Only the sample with propyl gallate at 0.020% had peroxide indexes so down at 70°C. Table 2 shows the performance of each antioxidant and concentration, with the correspondent peroxide value placed in crescent order. Generally, the best performances were related to more elevated antioxidant concentrations. From natural antioxidants tested, ROSMANOX E-4943 and distilled soybean oil show best results, comparable to propyl gallate (the best from synthetics). The guarana did not retard the oxidation development. Treatments whose means were bigger than 144.312 meq/kg (control mean) did not show significative difference from this, that is, did not affect the oxidation rate.

#### Conclusions

Reduction of oxidation rate was more effective in samples added of propyl gallate (at 0.020% and 0.010%), ROSMANOX-E 4943 (at 0.120% e 0.060%), distilled soybean oil (at 0.8572%, 0.4286% and 0.1428%, corresponding to tocopherols at 0.060%, 0.030% and 0.010%), BHA (at 0.020% and 0.010%) and with the antioxidant mixture (at 0.020% and 0.010%). Generally, bigger values of concentration were not significantly different from intermediate concentration (limited by legislation). Distilled soybean oil can be used on control fat oxidation due to its elevated tocopherol content, with confirmed antioxidant action. This possibility of use to distilled soybean oil opens new perspectives to utilize this subproduct from vegetable oil industries. The rosemary extract ROSMANOX E-4943 also was effective, confirming studies from other authors about rosemary action, which was more clear in vitamin E added product than in ROSMANOX 4942, denoting synergistic interaction to this combination. Guarana did not show antioxidant effect at tested concentrations. The limiting conditions to natural antioxidants persist to be mainly their characteristic of marked taste and smell. The antioxidant mixture showed inferior performance to its individual components also tested: propyl gallate and BHA, meaning that there were no synergistic interactions between its components (propyl gallate, BHA and citric acid) at tested conditions. The high test temperature (70°C) may have been the cause for the low performance antioxidant action to KRAKI A-200, ascorbic and citric acids.

### Acknowledgements

To the brazilian industries: Minuano Alimentos (from Lajeado, RS); Sanofi do Brasil (from Cosmópolis, SP); Leperg (from Porto Alegre, RS); Pena Branca (from Caxias do Sul, RS); Olvebra Industrial (from Eldorado do <sup>Sul</sup>, RS); Klemm & Cia Ltda (from Santa Cruz do Sul, RS); Kienast & Kratschmer Ltda (from São Caetano do <sup>Sul</sup>, SP) and Agrofaza Ltda (from Mauês, AM).

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