Kinetic approach of natural antioxidant depletion during thermal oxidation

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Natural antioxidants are largely applied for the increase in the thermal stability of organic products. The depletion of additive is a major problem that determines the quality of materials for long term usage. The present approach depicts the efficiency on natural antioxidants obtained by extraction from several herbs belonging to labiatae class. The kinetic parameters of thermal oxidation (induction period, demioxidation time and activation energy) were evaluated and discussed for characterization of antioxidant depletion.

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1. Introduction

The necessity of friendly stabilized materials promotes the addition of natural antioxidants into various materials and foodstuff for health preservation [1]. The direct benefit of biocompatible antioxidants consists in the reduction of synthesis antioxidant borne illness and significant shelf-life extension of various stabilized products. The efficiency of natural antioxidants is investigated for different applications in the improvement of material oxidation resistance in accordance with their perfect compatibility with human body.

The spice and herb extracts promote free radical scavenging [2] by the presence of some classes of compounds: phenolic acids, phenolic diterpenes and flavonoids. Their antioxidant efficiency involves the activity of phenolic functions that may easy remove proton and catch free radical.

The correlation between the structures of phenolic antioxidants and their stabilization efficiency has been already pointed out based on the kinetic studies [3-8]. The complexity of composition revealed for various extracts from plants determines a large range of effectiveness, because of the relative proportion between active components (for example [9]). However, the cascade mechanism [10] through which intermediates with antioxidant features are formed, characterizes a high contribution of carnosic acid and its derivatives in the blocking activity on oxidation process chain.

Nowadays, there is a strong interest in isolating antioxidants from natural sources for the protection of biological media and the improvement of resistance against oxidation [11]. Among these, Rosemary has been reported to possess remarkable antioxidant properties [12]. This direction is contrast with the addition of synthesis antioxidants, like butylated hydroxytoluene – BHT – and its related compounds, which have suspected to cause or promote negative health effects [13].

Our previous investigation on the antioxidant efficiency of flavonoids has pointed out the general features of the protective action promoted by natural extracts [14]. This paper presents the kinetic approach of the labiatae extracts with the peculiar attention on rosemary powder.

2. Experimental

Several labiatae extracts (rosemary, sage, oregano, thyme, mint, lemon balm, sweet marjoram, sweet basil) were prepared by room temperature extraction in ethanol followed by the removal of solvent under vacuum. The solid extracts were separately added into neat paraffin (0.25 % w/w) by vigorous grinding accompanied by sample wetting with some drops of chloroform in quartz mortal. The stabilized samples consisting of paraffin and extract powder were dried in a dissicator at room temperature for 24 h.

Aliquots of about 2 mg of each composition were subjected to the chemiluminescence investigation according to pre procedure presented in an earlier paper [14]. The testing temperature was 160^0C. In spite of high temperature applied to all the present chemiluminescence measurements, the thermal stability of additives was not affected. The reliable results on effective stabilization were obtained due to the satisfactory reproducibility of CL measurements and compound stability.

3. Results and discussion

Numerous types of naturally obtained antioxidants with various activities were identified [15, 16] for replacing synthesis antioxidant compounds.

The value of plant extracts is assessed by the most kinetic parameter, oxidation induction time. The efficient competition of antioxidant components for free radical abstraction may be viewed by the records of chemiluminescence determination of time dependence of CL intensity. In Fig. 1, several CL curves are presented. Their relative positions indicate the peculiar antioxidant activities. It may be easy noticed that the remarkable contribution of additive to the thermal stabilization of organic substrate was obtained with sage and rosemary extracts.

However, the oregano and thyme extracts can not be ignored for the inhibition of oxidation caused by the destructive conditions of usage. In Table 1 the kinetic parameters that depict the specific antioxidant activity of each studied extract along the degradation process. The phenolic constituents of extracts protect efficiently the host substrate and the propagation of degradation chain advanced as delaying process with a diminished rate. The first upper group of extracts gathers the most efficient antioxidant natural additives, which cover the large areas of health care formulations. The other four extracts may be used as oxidation retardants for the extension of shelf life.

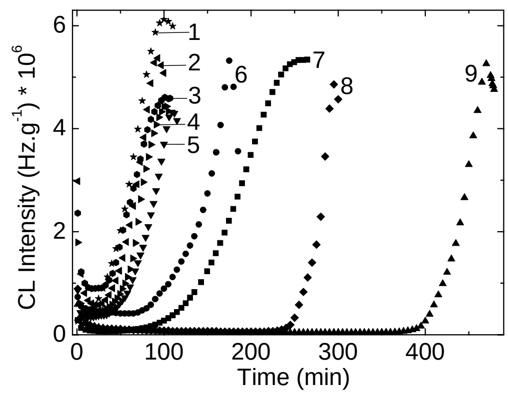


Fig. 1. CL curves for oxidation of modified paraffin: (1) blank; (2) marjoram; (3) basil; (4) lemon balm; (5) mint; (6) thyme; (7) oregano; (8) sage; (9) rosemary.

Table 1. Kinetic parameters for thermal oxidation of parafin.

Type of extract	Oxidation induction time (min)	Demioxidation time (min)	Maximum oxidation rate ($Hz.g^{-1}.min^{-1}$)
Blank	32	62	101275
Rosemary (Rosmarinus officinalis)	423	440	64284
Sage (Sage officinalis)	269	278	53940
Oregano (Origano vulgare)	134	183	51197
Thyme (Thymus vulgaris)	119	150	25859
Mint (Mentha piperita)	59	84	38079
Lemon balm (Melissa officinalis)	57	71	114576
Sweet marjoram (Majorana hortensis)	50	69	23502
Sweet basil (Ocinum basilicum)	40	63	20287

The stabilization capacity of natural extracts of labiatae herbs is tightly related to the specific activity of each component [17] higher values of kinetic parameters belonging to the first four tested extracts demonstrate the role of components as chain breakers either during induction period, or on propagation stage.

The proficiency on the modification in time dependency of protection level is related to the consumption of antioxidant during stabilization accomplishment. The subject of antioxidant consumption during thermal oxidation of organic basic substrates is a controversial matter, because some papers have reported first-order kinetics [18, 19], while other articles have stated zero-order kinetics [20, 21]. On the other hand, no data on the decay of natural antioxidants are available. The lack of this concern has stimulated the reaction order determination for the depletion of natural antioxidants consisting of rosemary extract.

The consumption rate was approached on the basis of zero and first kinetic orders for which the following equations can be written:

$$\text{zero order:} \quad -\frac{dc}{dt} = k$$

$$\text{first order:} \quad -\frac{dc}{dt} = k.c$$

The integration of these equations over the antioxidant concentration range from c_0 (initial concentration) to c_{cr} (critical concentration) gives the dependencies of rate constants on antioxidant concentration and depletion time:

zero order: $k = \dfrac{c_0 - c_{cr}}{t_i}$

first order: $k = \dfrac{\ln c_0 - \ln c_{cr}}{t_i}$

The evaluation of rate constants was done on the chemiluminescence curves obtained for paraffin stabilized with rosemary extract at different concentrations (Fig. 2).

The improvement in the thermal stability of host substrate is provided by the increasing initial concentration of added rosemary extract. The critical concentration of additive was determined as the intercept of line dependency of induction time on concentration (Fig. 3).

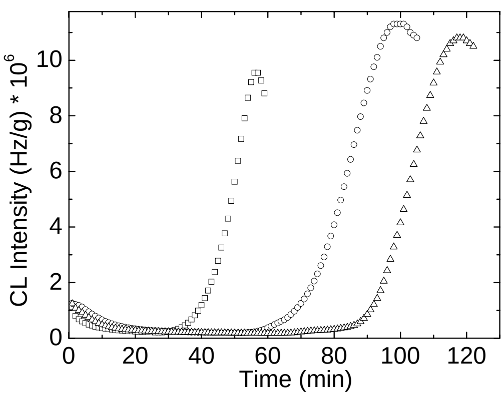


Fig. 2. Isothermal CL curves recorded for paraffin in the presence of rosemary extract (air, 185^{0}C): (□) 0.50 %; (○) 0.75 %; (Δ) 1.00%.

Applying Oswald's integral method (the method of invariant rate constant) to above equations, it was possible to calculate the values of rate constants for thermal oxidation of paraffin modified with different concentrations of paraffin (Table 2).

It may be noticed that the rate constant values obtained on the hypothesis that oxidation process takes place as a first order reaction depend on the initial concentration of Rosemary extract. They became lower as Rosemary extract concentration rises. Thus, the hypothesis of first order reaction for stabilizer consumption is not followed. On the other hand, the rate constants obtained starting from the assumption of zero-order reaction are independent of extract concentration and the half-life of Rosemary extract content obeys a linear dependency as it is shown in Fig. 3. It can be concluded that the antioxidant disappears in paraffin by zero-order kinetics.

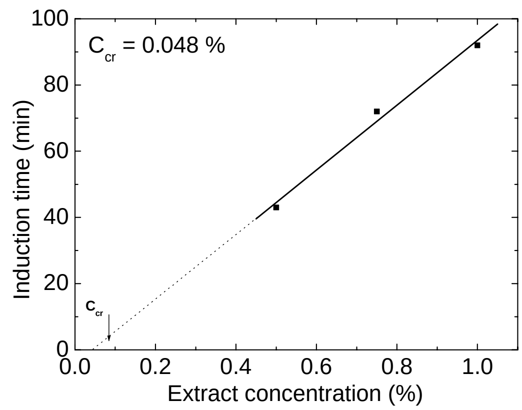


Fig. 3. Dependence of oxidation induction time on Rosemary extract concentration for thermal degradation of stabilized paraffin in air and 185^{0}C.

The comparison of stabilization contribution of synthesis (BHT) and natural antioxidant (rosemary extract) is presented in Fig. 4. Disregarding their antagonist effects on alive tissues, the kinetic parameters that characterize the oxidative protection are quite different (Fig. 5 (a) and (b)). Rosemary extract exhibits undoubted higher peculiarity in relation to the inhibition of oxidation.

Table 2. Rate constants for antioxidant (rosemary extract) depletion at 185^{0}c.

Extract concentration c_0 (%)	Induction time t_i (min)	Rate constant	
		assuming zero order reaction (% w/w. min^{-1}) * 10^2	assuming first order reaction (% w/w. min^{-1}) * 10^2
0.50	43	1.051	5.449
0.75	72	0.975	3.817
1.00	92	1.035	3.300
Mean value	-	1.020	-

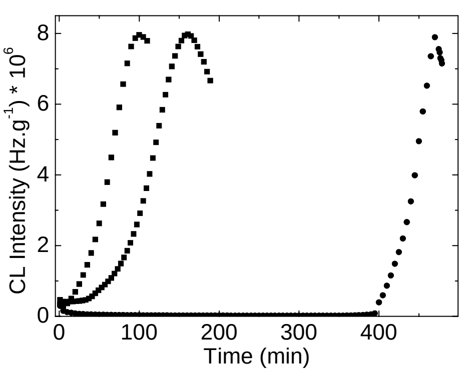


Fig. 4. CL curves recorded for (■) blank, (●) BHT, (▲) rosemary extract.

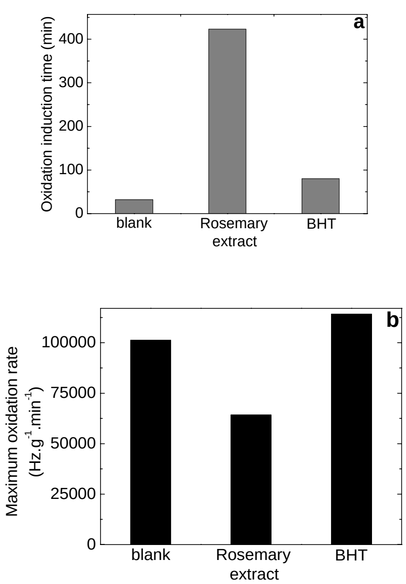
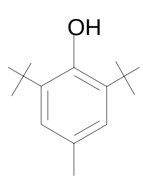
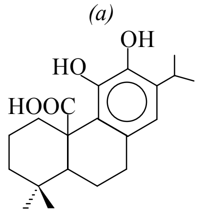


Fig. 5. Comparison of kinetic parameters in the thermal oxidation of paraffin in different states of stabilization.



(a)



(b)

Fig. 6. Molecular structures of butylated hydroxytoluene (a) and carnosic acid (b).

Though the both protective systems present phenolic structures (Fig. 6), the influence of the other part of molecule is prominent. The existence of other double bonds with which it is possible to resonate for obtaining conjugated structure. This configuration is proving more beneficial for the scavenging of radicals appeared during degradation.

4. Conclusions

The addition of labiatae extracts to the organic substrates improves the quality of materials due to the contribution of antioxidant component to the delaying of oxidation. The depletion of additive obeys the kinetic of zero-order.

These results may be extended to any other materials that are subjected to the thermal degradation. The efficient preservation of initial features and the improvement in the thermal resistance of organic environments are favorable overlapped on the biological acceptance of this kind of antioxidants.

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