Thermochimica Acta, 231 (1994) 161–168
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01359-B

Antioxidant properties of lignin and its fractions

T. Kasprzycka-Guttman * and D. Odzeniak

Department of Chemistry, University of Warsaw, Pasteura 1, 02–093 Warsaw (Poland)

(Received 31 March 1993; accepted 14 May 1993)

Abstract

Antioxidant properties of lignin in edible oils such as arachide oil have been investigated. Reaction kinetics were measured by differential scanning calorimetry (DSC) and experiments entailed heating the pure oil or oil to which substances suspected of inhibiting oxidation, i.e. lignin or its fractions, had been added, with subsequent comparison of the thermograms obtained. Similar experiments were carried out for arachide oil with addition of the well known inhibitor 2,6-di-*tert*-butyl-4-methylphenol (BHT). Measurements described in this report prove that lignin and its fractions can be regarded as inhibitors in free radical auto-oxidation.

INTRODUCTION

Differential scanning calorimetry DSC is a very useful method for the kinetic study of chemical reactions. Isothermal data of a single run deliver very important knowledge such as the enthalpy ΔH, induction time t_i, rate constant k and half-life time $t_{1/2}$ for a constant temperature.

This report deals with the influence of lignin and its fractions upon oxidation of edible oils. Special stress was put on induction time and activation energy which delivered some knowledge as to whether lignin's influence upon the studied reaction was limited only to induction time [1] or applied to the whole process including induction step and auto-oxidation.

Several samples of edible oil were heated at various constant temperatures in oxygen atmosphere. The same conditions were used for systems: oil + lignin, oil + fraction M (fraction obtained by extraction of lignin with methanol) and oil + fraction E (obtained by extraction with a mixture of methanol and ethyl acetate). DSC data obtained allowed calculation of activation energy and induction time and consequently the antioxidant properties of lignin to be proved.

The influence of the antioxidant properties of lignin was also studied.

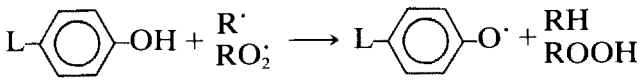
This work is a part of an investigation concerning the economic use of lignin, a waste product in furfurol production from coniferous trees.

* Corresponding author.

THEORETICAL

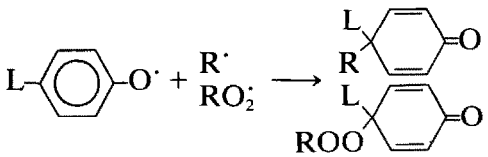
Lignin is a natural polymer and consists of phenylopropane-based monomeric units linked together by different types of bonds including alkyl–phenol, alkyl–alkyl and phenol–phenol ether bonds [2, 3].

Many phenolic substances can behave as inhibitors in auto-oxidation and polymerization reactions [4, 5]. Phenolic groups occurring in lignin can be regarded as acceptors of free radicals created in the auto-oxidation process [6]. The mechanism of lignin activity in oils is similar to that of simpler phenolic-based inhibitors such as hydroquinone, 2,6-di-t-butyl-4-methyl-phenol and 2-t-butyl-4-methoxyphenol [6]



(1)

and what is much less probable because of spherical barriers



(2)

where L is the polymeric chain of lignin.

EXPERIMENTAL

Materials

The refined edible oil derived from arachide nuts was purchased from Instytut Przemyslu Spozywczego; its fatty acid composition determined by GLC is shown in Table 1. Lignin from Instytut Prezemysłu Fermentacyjnego was initially extracted with water at room temperature by stirring a diluted suspension for 2 h. The remaining water-insoluble fraction was air

TABLE 1

Percentage contents of fatty acids in arachide oil determined by GLC

C_m^n [a]				
C_{16}^0	C_{18}^0	C_{18}^1	C_{18}^2	C_{18}^3
4.85	6.44	0.69	66.32	21.67

[a] *m*, Number of carbon atoms; *n*, number of double bonds.

TABLE 2
Elemental analysis of investigated lignin

Element	C	H	N	O
Content/%	64	6.3	0.2	31.1

dried at room temperature and used thereafter. The results of elemental analyses are gathered in Table 2.

Fractions of lignin were obtained [7] by extraction of lignin with methanol (fraction M) and afterwards a mixture of methanol and ethyl acetate (fraction E). Residual solvents were removed from extracts under reduced pressure.

Apparatus

A Du Pont 910 Differential Scanning Calorimeter was used. This model was a plug-in module connected to a Du Pont 9900 Computer/Thermal Analyzer to control the progress of the experiment and which afterwards was used for data analysis. The DSC module was equipped with a pressure cell (calibrated by the use of pure indium) in order to carry out experiments in purging gas flow (oxygen, $6\,l\,h^{-1}$), under pressure of 2 atm. All the measurements were made in isothermal conditions.

Measurements of induction time (onset point of the peak) and maximum point of the peak

An oil sample (18 mg) was placed in an aluminium pan. An empty pan served as the reference. The oil was heated at constant temperature and the thermal effects recorded during experiments are similar to those in Fig. 1.

This experiment was run at three different temperatures. To avoid poor reproducibility of DSC data [1] samples were of the approximate mass (18 mg).

The same conditions were used for systems with the following components: oil + lignin; oil + fraction M; oil + fraction E. These mixtures were prepared in 10 ml flasks and the additive was at 10%. Uniformity of the suspension was provided by electromagnetic stirrers.

Total mass of samples used in DSC expriments was 18 mg, as in experiments with pure oil. Each measurement was reproduced three times. Induction time (t_{on}) and maximum point (t_{max}) values presented in Table 3 are average values.

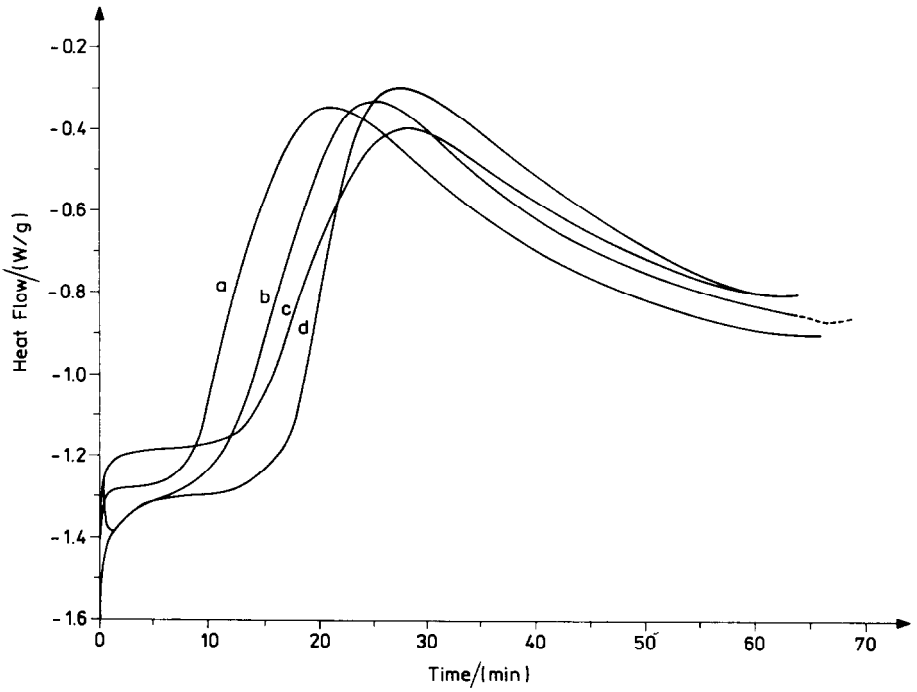


Fig. 1. Thermal effects obtained during heating of archide oil under isothermal conditions: curve a, 144°C; curve b, 142°C; curve c, 140°C; curve d, 144°C with addition of fraction M.

Experiments carried out for other arachide oils purchased from other sources proved that values of t_{on} and t_{max} differed within the range of 10%.

The influence of antioxidant concentration upon t_{on} and t_{max} was tested at 140°C (oxygen flow as in previous experiments) for several concentrations of lignin (Table 4).

To investigate the antioxidant properties of lignin, measurements were carried out under the same conditions using the inhibitor BHT (Table 3, Fig. 2).

Enthalpy measurements

The differential heat flow versus time recorded under isothermal conditions allowed a determination of the enthalpy of the process by calculation of the area under the peak. Because of heat capacity changes of samples during experiments [8], a sigmoidal baseline was used for this purpose. This type of baseline was calculated by the use of a special computer program which compensated for the above mentioned changes (Fig. 3).

TABLE 3

t_i and t_{max} values for inhibited and uninhibited arachide oil at several temperatures

Temp./°C	t_i/min	t_{max}/min
Arachide oil		
140	11.0	24.2
142	10.1	23.8
144	8.6	21.0
Oil and lignin		
140	22.3	38.2
142	18.1	33.5
144	14.7	27.6
Oil and fraction M		
140	22.1	39.0
142	17.9	33.4
144	15.0	27.9
Oil and fraction E		
140	22.5	37.9
142	18.4	33.4
144	14.3	27.6
Oil and BHT [a]		
140	19.1	34.7
142	16.3	31.0
144	11.5	25.1

[a] BHT is 2,6-di-*tert*-butyl-4-methylphenol.

TABLE 4

Values of t_{on} and t_{max} for different concentrations of lignin at 140°C

Concentration of lignin/%	t_{on}/min	t_{max}/min
0	11.2	24.3
2.5	16.9	34.2
4.5	19.4	36.0
6.4	21.8	37.1
8.4	22.3	37.7
10.5	22.5	38.0
12.5	22.5	38.1

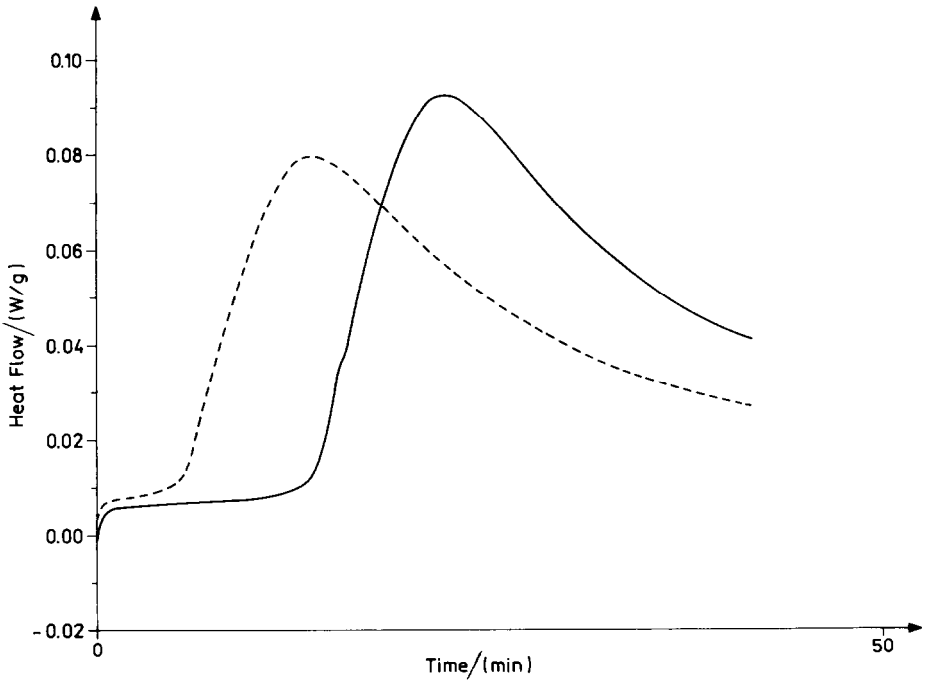


Fig. 2. Thermal effects for pure arachide oil (broken line) and arachide oil + BHT (solid line).

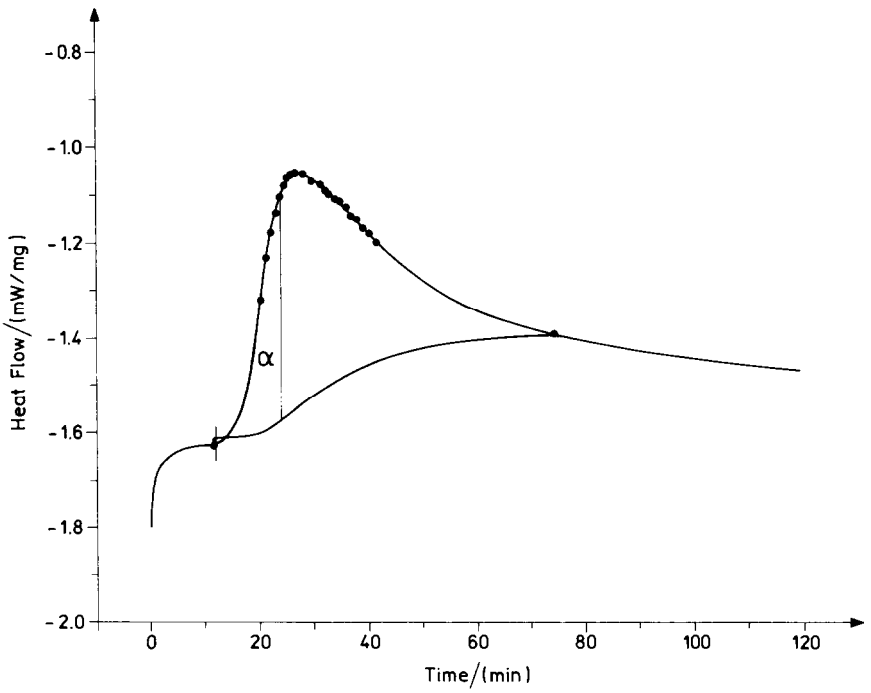


Fig. 3. Signoidal baseline used in enthalpy measurements: the conversion ratio is α; see text for explanation.

Activation energy calculations

In DSC measurements the ratio of heat liberated in a certain period of time (proportional to the partial area under the peak) to the total heat evolved during the reaction (proportional to the total area of the peak) is assumed to be the conversion ratio (Fig. 3). Taking into account the auto-oxidative character of the reaction, the following kinetic equation can be used to describe the investigated process:

$$d\alpha/dt = k\alpha^n(1-\alpha)^m \quad (3)$$

In this equation α denotes a conversion ratio (Fig. 3), k is the rate constant, and n and m are parameters indicating reaction order. Typical data used for calculations of k, m and n for a constant temperature (144°C) are listed in Table 5. Calculations (each for a different temperature) made with the use of eqn. (3) allowed calculation of the activation energy (E) by means of a logarithmic form of the Arrhenius equation

$$\ln k = -E/RT + \ln A \quad (4)$$

where R is the gas constant and A is the pre-exponential factor.

TABLE 5

Typical data for calculation of k, m and n

Time/min	α	$d\alpha/dt$ in min^{-1}	Time/min	α	$d\alpha/dt$ in min^{-1}
7.683	0.0507	0.0240	15.187	0.3143	0.0442
8.733	0.0795	0.0307	15.763	0.3461	0.0437
9.677	0.1112	0.0362	16.467	0.3110	0.0427
10.480	0.1417	0.0398	17.200	0.4009	0.0421
11.130	0.1682	0.0416	17.987	0.4311	0.0400
11.783	0.1960	0.0430	18.723	0.4626	0.0396
12.473	0.2262	0.0439	19.443	0.4912	0.0383
13.900	0.2549	0.0448	20.363	0.5182	0.0363
14.460	0.2894	0.0441	21.140	0.5514	0.0353
			21.913	0.5785	0.0339

RESULTS AND DISCUSSION

Comparing data from Table 3 it is clear that the addition of lignin and its fractions to oil inhibited auto-oxidation. This effect was similar to that observed for BHT (Table 3) whose antioxidant properties were obvious.

TABLE 6

Activation energy (in kJ mol^{-1}) or arachide oil auto-oxidation

Pure oil	Oil and lignin	Oil and fraction M	Oil and fraction E
68.2	71.9 ± 7	70.5 ± 11	69.4 ± 6

Lignin and all its fractions had very similar effects, probably because they were of similar chemical composition.

The activation energy E was calculated using the logarithmic form of eqn. (3) for different temperatures

$$\log(d\alpha/dt) = \log k + n \log[(1-\alpha)\alpha^{m/n}] \quad (5)$$

Values of E seemed to be similar (Table 6) for inhibited and uninhibited auto-oxidation. The same relation was observed for the enthalpy which in both cases was equal to about 0.8 kJ g^{-1} of pure oil. This proves that the inhibitors investigated cause only delay of the process without affecting its rate after the induction time when inhibitor was consumed.

According to some literature reports [9, 10], relatively high concentrations of some phenolic-type antioxidants can cause pro-oxidation. In this work such an action was not observed, although at concentrations of about 10% lowering of the antioxidant efficiency of the inhibitors studied was found.

Lignin, because of its chemical composition, is active both in its whole form and as different fractions. The antioxidant properties are associated with the free radical acceptor character of phenolic groups occurring in the lignin investigated.

REFERENCES

1 L. Batch and C.W. Macosco, Thermochim. Acta, 166 (1990) 185.
2 R.L. Cranford, D.L. Cranford and G.L. Dikes, Appl. Environ. Microbiol., 41 (1981) 1112.
3 Z. Klin, Lignina Chemia i Wykorzystanie, WET, Warszawa, 1971 (in Polish).
4 P. Mastalerz, Chemical Organics. PWM, Warszawa, 1986 (in Polish).
5 W.O. Launder (Ed.). Auto-oxidation and Antioxidants, Vol. 1, John Wiley, New York, 1961.
6 T.A. Pereira and N.P. Das, Thermochim. Acta, 165 (1990) 129.
7 R.W. Thring, E. Chornet, J. Bouchared and P.V. Viol, Ind. Eng. Chem. Res., 30 (1991) 232.
8 T. Kasprzycka-Guttman and D. Odzeniak, Thermochim. Acta. 191 (1991) 41.
9 B. Kowalski, Progress in Development of Food Production Technology, Proc. 19th Scientific Session, Polish Academy of Science, Szczecin, 1988, p. 45.
10 C. Pietrzyk, Wpływ Stężenia Inhibitorów na Szybkość Autooxydacji, Zesz. Nauk. Politech. Szczeciń., Pr. Monogr., 37 (1962) 50 (in Polish).