Trade Science Inc.

July 2006 *Volume 1 Issue 1*

CHEMICAL TECHNOLOGY
An Indian Journal

Full Paper

CTAIJ, 1(1), 2006 [1-7]

Influence Of Artificial Antioxidants On Thermal And Oxidative Stability Of The Rice Bran Oils Using Thermogravimetry And Differential Scanning Calorimetry

Corresponding Author

José Carlos Oliveira Santos
Unidade Acadêmica de Educação, CES Universidade Federal de Campina Grande, UFCG, 58185-000, Cuité, Paraiba (BRAZIL)
Ph./fax: 55 83 32167441
E-mail: zecarlosuepb@yahoo.com.br

Co-Authors

Antonio Gouveia Souza[1], Shiva Prasad[2]
[1]Departamento de Química, CCEN, Universidade Federal da Paraíba, UFPB, Campus I, 58059-900, João Pessoa, Paraíba (BRAZIL)
[2]Departamento de Engenharia Química, CCT, Universidade Federal de Campina Grande, UFCG, Campus I, Bodocongó, 58109-970, Campina Grande, Paraíba, (BRAZIL)

Received: 31st March, 2006
Accepted: 26th April, 2006

Web Publication Date : 27th July, 2006

ABSTRACT

Thermal analytical characterization of rice bran oils, with and without artificial antioxidants, was evaluated using thermogravimetry and differential scanning calorimetry. Thermal decomposition of these oils occurred in three stages, related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids, respectively. DSC curves show two events that characterize the polymerization and decomposition of triglycerides. The heat capacities of the rice bran oils, obtained by DSC were dependent on the composition of fatty acids. The kinetic parameters were dependent on the antioxidant used. Increasing the frying time produced a decrease in the onset of decomposition temperature in the rice bran oils.

KEYWORDS

Rice bran oil;
Thermal analysis;
Kinetics;
DSC;
Thermogravimetry.

INTRODUCTION

Rice bran oil for food use has been commercially produced in the Brazil since 1996. Despite its similarities to other common vegetable oils, rice bran oil offers several unique properties that make it very appealing nut-like flavor and once extracted is very stable with good fry-life[1]. Only large milling operations can justify stabilization systems and extracted oil from rice bran at a scale that is economically prac-

tical, while much of the world rice crop is processed by very small mills. For this reason, it is unlikely that oil will be extracted from more than half the total rice bran production at any time in the near future.

The bran fraction, which includes the germ in most commercial milling operations, represents only about 8.0% of the paddy weight but contains about three-fourths of the total oil. Containing about 15-20% oil, rice bran is a commercially feasible feedstock for oil extraction. Besides the oil, bran contains about 12-16% protein, 7-11% crude fiber, 34-52% available carbohydrate, and 7-10% ash[2,3].

Several methods have been proposed to evaluate the quality of vegetable oils. Most of these methods submit a sample to conditions that accelerate the normal oxidation process. The older methods used to estimate the quality of vegetable oils cause deterioration by maintaining the sample at elevated temperatures in contact with air and then periodically weighing to verify the gain in mass or examining organoleptically for rancidity. The peroxides or other oxidation products formed can be determined by spectral or chemical analysis[4]. Some of the frequently used tests employed to predict the quality of vegetable oils are the periodic determination of peroxide index, the active oxygen method (AOM), the automated AOM method and the oxygen pump method[5]. Currently, thermoanalytic methods such as differential scanning calorimetry (DSC) and thermogravimetry (TG) are receiving considerable attention. TG curves can be used to estimate the quality of vegetable oil by determining the kinetic parameters[6-7], and the oxidative induction period. On the other hand, as the oxidative thermal decomposition involves exothermic and endothermic reactions, it is possible to estimate the energy involved in the determination process by thermal techniques such as DTA and DSC. Therefore, these methods are more advantageous than the conventional methods, because they are more precise and sensitive and require a smaller sample mass and results are obtained more rapidly[8].

In view of these advantages, it becomes indispensable to analyze the stability of rice bran oil during thermal treatment (frying) and storage. The thermal analytical (specific heat, stability, decomposition enthalpy) and the kinetic (activation energy, frequency factor, order of reaction) parameters were determined in this study; deterioration of rice bran oil under frying conditions was also studied with the use of differential scanning calorimetry and thermo gravimetry, in an atmosphere of nitrogen and air, respectively.

EXPERIMENTAL

Materials

Samples of edible rice bran oils with and without artificial antioxidants, acquired at a local market and produced by Brazilian industry were used in the study.

The fatty acid composition, free fatty acid level, saponification value, iodine value, peroxide value, and color value were obtained by AOCS methods[9].

Thermal analysis measurements

The non-isothermal TG/DTG curves were obtained in a Shimadzu TGA-50 thermobalance in air (30 $mLmin^{-1}$), using an alumina crucible with heating rates of 2, 5, 10 and 20°$Cmin^{-1}$ and a sample mass of 10.0±0.5mg in a temperature range of 25 to 800°C.

The DSC curves were obtained in a Shimadzu DSC-50 differential scanning calorimeter, in nitrogen (50 $mLmin^{-1}$) using an alumina crucible with heating rates of 5, 10 and 20°$Cmin^{-1}$ and a sample mass of 10.0±0.5mg in a temperature range of 25 to 500°C.

Specific heat measurements

The heat capacities of the rice bran oils were determined from the data obtained by DSC. The calculations were based on implementation of the temperature program. The oil samples were heated at a rate of 5°$Cmin^{-1}$ up to 30°C during five minutes. Then, they were heated at a rate of 10°$Cmin^{-1}$ up to 200°C during five minutes.

The following ratio was used to calculate the heat capacities:

$$c = \frac{m_0 c_0}{m} \cdot \frac{S_3 - S_1}{S_2 - S_1} \quad (1)$$

Where c_0 and c are the specific heat of the refer-

ence material and of the rice bran oil, respectively; m_0 and m refer to the mass of rice bran oil samples and of the reference material, respectively, and S_1, S_2 and S_3 are the thermal displacements of the DSC in relation to the blank, reference and sample, respectively[10].

Kinetic study

The theoretical basis for the kinetic calculations by non-isothermal Thermogravimetry is expressed in the following equation:

$$g(\alpha) = \frac{A}{\phi}\int_0^T exp\left(-\frac{E_a}{RT}\right)dT \quad (2)$$

Where A is the frequency factor, T is the temperature, R is the universal gas constant, ϕ is the heating rate and E_a is the activation energy. This mathematical equation describes the thermogravi metric curve, where $g(\alpha)$ represents the reaction mechanism and the second term in the equation can not be solved analytically; it can only be solved by approximation numerical methods. Various approximations for calculation of this integral have been proposed, giving rise to the different methods for determining kinetic parameters from thermogravi metric curves[11].

The integral methods proposed by Coats and Redfern and Madhusudanan and the approximation methods proposed by Horowitz and Metzger and Van Krevelen were used in this study[6].

Thermal degradation in frying conditions

The study of thermal degradation of rice bran oils was carried out by thermogravimetric measurement. For this purpose the oils were heated to 190°C for periods of 0.5, 4.0 and 8.0 h. The rice bran oils were heated in a 500 mL flask with a surface diameter of about 4 cm that was exposed to air.

Afterwards, TG/DTG curves were obtained in a Shimadzu TGA-50 thermobalance in air (30 $mLmin^{-1}$) at a heating rate of $5°Cmin^{-1}$ with the objective of verifying of influences the frying time and temperature on the thermal stability of rice bran oils.

RESULTS AND DISCUSSIONS

Chemical characterization

TABLE 1 compares the fatty acid composition of rice bran oil with and without artificial antioxidant. Rice bran oil is similar to peanut oil in fatty acid composition with a saturation level that is slightly higher than that of conventional soybean oil[1].

Appearance of rice bran oil ranges from cloudy to clear depending on the degree of winterization process applied. The quality characteristics of refined rice bran oil should be a maximum free fatty acid level (as oleic acid) of 0.1%, a maximum peroxide value of 1.1 meq/kg, 0.06% moisture, and iodine value of 100-110, a saponification value of 175-185, and a color value of 3.5.

Thermogravimetric behavior

The thermal decomposition profiles for the rice bran oils have similar characteristics, as can be observed in figure 1 and 2, where all the non-isothermal TG/DTG curves have three thermal decomposition steps in the range of 220 to 550°C, with no residue remaining at 800°C. Thermal decomposition of these oils occurred in three stages, related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids, respectively.

In relation to the thermal decomposition steps, it was observed that the first step (220 to 380°C) corresponds to the decomposition of the polyunsaturated fatty acids. During heating, the triglycerides, which form 96 to 98% of the edible oils, produce volatile compounds, which are constantly removed

TABLE 1: Compositions of the rice bran oils analyzed

Fatty acids	Rice bran Oil A	Rice bran Oil B
Oleic	42.5	42.0
Linoleic	38.7	39.1
Linolenic	0.9	1.0
Myristic	0.2	0.2
Palmitic	14.5	15.0
Stearic	1.5	1.7
Arachidic	0.4	0.5
Behenic	0.2	0.1
Artificial antioxidant	Citric acid	—

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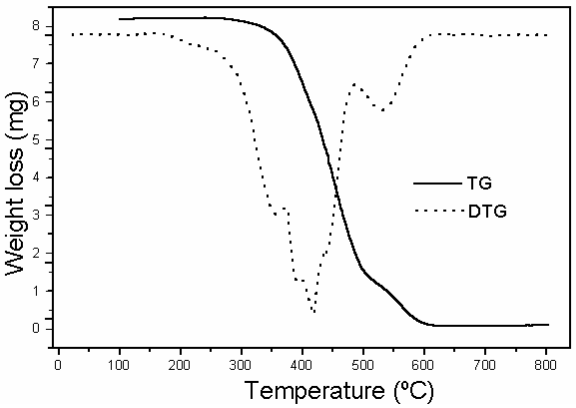

Figure 1: TG/DTG curves for rice bran oil with artificial antioxidants

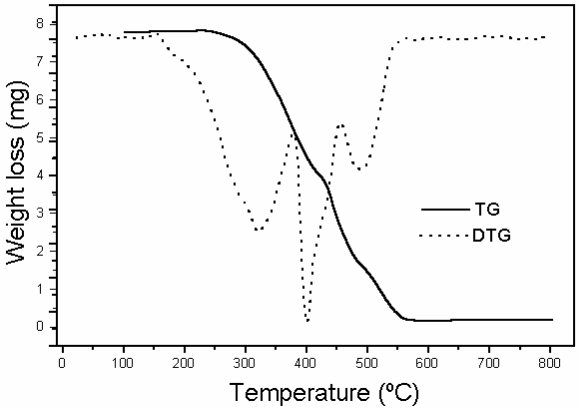

Figure 2: TG/DTG curves for rice bran oil without artificial antioxidants

by vapor generated during heating. These products (dimers, trimers, polymers) are formed principally by thermal reactions of unsaturated fatty acids, such as linoleic acid.

The first step is the most important for the thermal stability of vegetable oils, because this is the step where decomposition of the unsaturated fatty acids begins. On the basis of the temperature at the beginning of thermal decomposition, it can be established that rice bran oil A, containing the antioxidants citric acid and vitamin E, had a higher thermal stability than that observed for rice bran oil B. Thus, it can be verified that the thermal stability of rice bran oils is dependent on the composition of the fatty acids, as it is influenced by artificial antioxidants.

The beginning of oxidation in vegetable oils is characterized by absorption of oxygen through the fatty acid chain, subsequently forming the oxidation product as peroxides. This behavior is generally identified by an increase in the initial mass of the sample. For the rice bran oil samples analyzed in air, a small gain in mass in the DTG curve for oil B was observed (Figure 2), indicating that the process of thermal decomposition involved the absorption of oxygen as well as the liberation of volatiles. This was not observed for rice bran oil A, where the reaction resulted only the liberation of volatiles.

The second step in the thermal decomposition of rice bran oils (380 to 480°C) corresponds to the decomposition of monounsaturated fatty acids, such as oleic acid. During this reaction, the double bonds are broken, causing the triglyceride molecules in the vegetable oils to become saturated. The third step in the thermal decomposition, which occurs in a temperature range of around 480 to 550°C, corresponds to the thermal decomposition of saturated fatty acids, such as palmitic acid.

To verify the dependence of the thermogravi metric profile for rice bran oils on experimental factors, the heating rate was varied from 2 to 5, 10 and 20°Cmin^{-1}, as shown in figure 3. It can be observed that there is a displacement in the initial decomposition temperature with the increase in heating rate. The thermal decomposition occurred in three steps at the heating rates 2, 5 and 10°Cmin^{-1}, whereas at 20°Cmin^{-1} only two events corresponding to thermal decomposition were observed. This was probably due to the superposition of the steps.

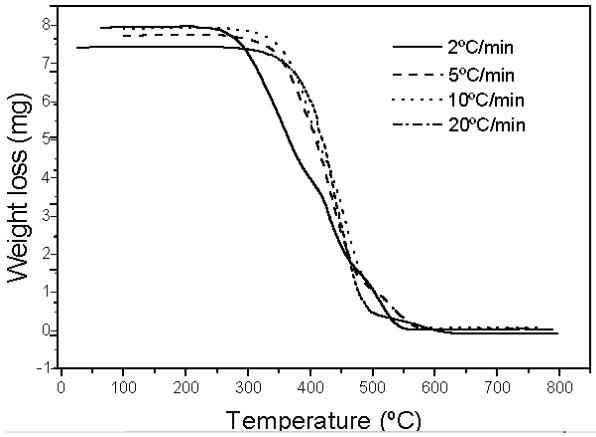

Figure 3: TG curves for rice bran oils at different heating rates

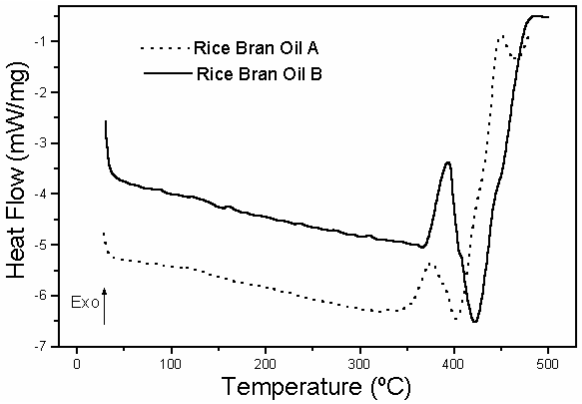

Figure 4: DSC curves for rice bran oils with and without artificial antioxidants

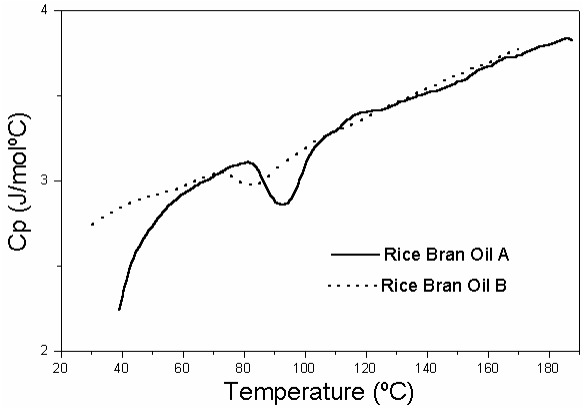

Figure 5: C_p curves for rice bran oils

Calorimetric behavior

DSC curves (Figure 4) for rice bran oils have similar profiles, verifying the endothermic and exothermic transitions. The exothermic transitions probably correspond to polymerization of a fatty acids component of the rice bran oils, occurring at around 340°C, whereas the endothermic transitions refer to thermal decomposition of saturated and unsaturated fatty acids, component of the vegetable oils, in agreement with the thermogravimetric results. The increase in heating rate produces a broadening and, consequently, an increase in the area of the peaks corresponding to the thermal decomposition of these oils. As the events observed refer to chemical processes, the increase in heating rate results in the decomposition of a larger quantity of fatty acids.

The enthalpies involved in the thermal decomposition process, observed in the DSC curves correspond to the molar enthalpies of polymerization and decomposition and have differentiated values, as shown in TABLE 2. These results indicate that the polymerization and decomposition enthalpies are directly related to the fatty acids composition of rice bran oils.

TABLE 2: Polymerization and decomposition enthalpies ($J.g^{-1}$) of rice bran oils

Rice bran oils	Heating rate (°Cmin^{-1})	ΔH_{pol}	$-\Delta H_{dec}$
A	5	15.30	32.84
	10	13.93	28.93
	20	5.74	26.90
B	5	18.76	55.26
	10	14.13	42.50
	20	6.61	28.13

Heat capacity

The specific heat capacities were determined by the method described earlier. The curves related to the heat capacities of rice bran oils are shown in figure 5.

The specific heat values for the rice bran oils analyzed do not vary substantially. The calculated C_p values are in agreement with those found in the literature for other vegetable oils[10].

Kinetic parameters

Kinetic parameters for the three steps of thermal decomposition of rice bran oils were determined by using an interval of decomposed fraction (α) of 0.10 to 0.90 and applying the thermogravimetric data in the program for determination of kinetic parameters developed in turbo basic language.

The program for determination of kinetic parameters calculates the reaction order (n), activation energy (E_a) and frequency factor (A) by the approximation and integral methods, using kinetic equations proposed by Coats and Redfern CR), Horowitz and Meltzger (HM), Madhusudanan (MD) and Van Krevelen (VK)[6]. The calculated kinetic parameters and linear correlation coefficient (r) found for all the steps in thermal decomposition of rice bran oils are summarized in TABLE 3 and 4.

The different heating rates used resulted the same

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TABLE 3: Kinetic parameters obtained for thermal decomposition of rice bran oil A

Kinetic method	Kinetic parameters	Steps		
		1	2	3
CR	n	0.98	2.01	2.07
	E_a [kJmol^{-1}]	84.76	108.39	155.95
	A [s^{-1}]	1.7E +06	1.5E +19	2.9E +21
	r	0.9998	0.9994	0.9991
MD	n	0.97	2.02	2.11
	E_a [kJmol^{-1}]	82.45	109.48	152.14
	A [s^{-1}]	1.8E +06	1.7E +19	1.5E +21
	r	0.9997	0.9994	0.9990
HM	n	1.00	2.03	2.15
	E_a [kJmol^{-1}]	87.16	109.45	162.19
	A [s^{-1}]	2.4E +06	9.9E +20	3.2E +21
	r	0.9999	0.9993	0.9994
VK	n	0.99	2.06	2.10
	E_a [kJmol^{-1}]	84.48	108.37	158.96
	A [s^{-1}]	2.7E +06	4.4E +20	3.3E +21
	r	0.9996	0.9980	1.0000

TABLE 4: Kinetic parameters obtained for thermal decomposition of rice bran oil B

Kinetic method	Kinetic parameters	Steps		
		1	2	3
CR	n	0.96	2.08	1.98
	E_a [kJmol^{-1}]	76.88	108.81	147.43
	A [s^{-1}]	1.7E +07	2.7E +13	4.5E +17
	r	0.9998	0.9990	0.9992
MD	n	0.95	2.03	1.88
	E_a [kJmol^{-1}]	77.61	105.28	146.88
	A [s^{-1}]	1.7E +07	1.5E +13	8.9E +16
	r	0.9998	0.9990	0.9991
HM	n	0.99	2.12	2.05
	E_a [kJmol^{-1}]	78.93	115.67	147.73
	A [s^{-1}]	8.5E +07	2.7E +14	1.0E +19
	r	0.9995	0.9960	0.9991
VK	n	0.97	2.06	1.96
	E_a [kJmol^{-1}]	80.28	108.88	141.74
	A [s^{-1}]	1.0E +07	1.2E +18	5.4E +18
	r	0.9948	1.0000	0.9993

mechanism, only varying the values of the kinetic parameters. Nevertheless, these was a good correlation between the kinetic parameters obtained by the integration and approximation methods, but the values obtained by the approximation methods were higher than the values obtained by the integration methods, which can be ascribed to the different mathematical treatments of the methods[12].

The results presented in TABLE 3 and 4 indicate that the first step in the thermal decomposition of rice bran oils corresponds to the first-order reaction, whereas, the second and the third steps behave as second-order reactions.

The medium activation energy from rice bran oil with artificial antioxidants was higher that from rice bran oil without artificial antioxidants, indicating that the artificial antioxidant citric acid produced an increase in thermal stability of the oils analyzed. The increase in activation energy in relation to the steps in thermal decomposition of samples occurred due to the possible break in the molecular bonds of unsaturated fatty acid, which than the molecular bonds are less stable saturated fatty acids, requiring higher activation energy for degradation.

Thermal degradation analysis

The study of oils before their cooking use in food permits data to be obtained on the influence of variables (time, temperature) on their thermal decomposition. Comparison with data obtained in earlier tests increases the amount of data available, there by allowing better conclusions to be drawn in this study.

To verify the dependence of the thermogravi metric profiles for the rice bran oils on frying time and temperature, the oils were heated to 190°C and the TG curves were obtained after 0.5, 4.0 and 8.0 h of heating. The data obtained from TG/DTG curves for the process of degradation of rice bran oils are summarized in TABLE 5.

TABLE 5: Decomposition onset temperature (T_{onset}) of rice bran oils after different frying times.

Time (h)	T_{onset} (°C)	
	Rice bran Oil A	Rice bran Oil B
0	226.67	218.78
0.5	192.80	207.78
4	186.51	177.95
8	184.66	169.60

According to the thermogravimetric curves for rice bran oil with and without antioxidants as a function of frying time, it can be verified that the onset temperature of thermal decomposition of the oils analyzed decreased with the increase in frying time, i.e., an increase in frying time led than increase in the degradation of these oils. This is caused by the decrease in unsaturation due to prior heat treatment, resulting in degradation of the samples under analysis.

The autoxidation of unsaturated fatty acids produces a decrease in the thermal stability of the rice bran oils, causing a decrease in the oxidative induction time. Factors such as change in color, increase in viscosity and unpleasant odor are observed in the process of degradation of these oils.

During the heating in the process of frying, a complex series of reactions produces numerous degradation compounds. With the occurrence of the thermal reactions, the functional, sensorial and nutritional qualities are modified. The oils repeatedly used in frying without immersion undergo degradation by oxidative reactions. In this case, as shown in TABLE 5, the loss of stability is accelerated by the increase in process time, which is responsible for changes in the physicochemical and organoleptic characteristics of the rice bran oils.

During prolonged heating, edible vegetable oils, including rice bran oils with and without artificial antioxidants, undergo the process of thermal degradation resulting in oxidative rancidity, resulting in the formation of hydroperoxides and other products of degradation that can liberate volatile compounds such as hydrocarbons, aldehydes, ketones, furans and carboxylic acids, lower the temperature of onset of thermal decomposition (T_{onset}) of the samples analyzed.

CONCLUSIONS

Thermal analytical and kinetic properties of rice bran oils are dependent on the composition of fatty acids and are influenced by artificial antioxidants. The thermoanalytic methods were considered to be versatile techniques for this work, because in addition to the study of thermal stability and of the deterioration occurring in frying, they require only a small sample mass, making it possible to obtain results more rapidly and enabling verification of presence of the artificial antioxidants.

ACKOWLEDGEMENT

The authors acknowledge CAPES and CNPq for scholarship and financial support of this work.

REFERENCES

[1] D.R.McCaskill, F.Zhang; Food Tech., **53(2)**, 50-52 **(1999)**.
[2] J.A.Amorim, J.C.O.Santos, M.F.S.Trindade, M.M. Conceição, A.G.Souza, A.S.M.Simões, S.A.Eliziário; J.Therm.Anal.Calor., **75(2)**, 393-399 **(2004)**.
[3] B.O.Juliano, D.B.Bechtel; 'Rice: Chemistry and Technology', 1st Ed., St.Paul.Am.Assn.Cereal Chemists Inc., 24-59 **(1985)**.
[4] B.Kowalski; Thermochim.Acta, **156**, 347-353 **(1989)**.
[5] S.Lee, D.B.Min; J.Agric.Food Chem., **38**, 1630-1635 **(1990)**.
[6] J.C.O.Santos, A.V.Santos, A.G.Souza, S.Prasad, I.M.G. Santos; J.Food Sci., **67(4)**, 1393-1998 **(2002)**.
[7] J.C.O.Santos, M.M.Conceição, A.G.Souza, S.Prasad, I.M.G.Santos; J.Therm.Anal.Calor., **75(2)**, 419-428 **(2004)**.
[8] A.G.Souza, M.M.Conceição, S.A.Silva; J.Therm.Anal. Calor., **75(2)**, 411-417 **(2004)**.
[9] P.Simon, L.Kolman, I.Niklová, S.Schmidt; J.Am.Oil Chem.Soc., **77(6)**, 639-642 **(2000)**.
[10] T.Kasprzycka-Guttman, M.Jarosz-Jarszewska, G. Litwinienko; Thermochim.Acta, **250**, 197-201 **(1995)**.
[11] C.D.Gamlin, N.K.Dutta, J.Matisons, D.Kehoe, N. Roy-Choudhury; Thermochim.Acta, **392**, 357-368 **(2002)**.
[12] J.Guo, A.C.Lua; J.Therm.Anal.Calor., **59**, 763-771 **(2000)**.