Journal of Thermal Analysis, Vol. 43 (1995) 123-132

THERMAL DEHYDRATION OF SOME FOOD PRODUCTS AND KINETIC PARAMETERS OF THIS PROCESS

J. Masłowska and M. Więdłocha*

Institute of Fundamental Food Chemistry, Technical University, Łódź, Poland

Abstract

The derivatographic method was used for the quantitative determination of water content in selected flour and fat products. Weight losses and thermal effects taking place in the examined products under the influence of heat were read from the obtained derivatograms. Percentage water contents were calculated from TG curves within the range from 5.6% (rice cereal) to 16.0% (potato flour), based on the diagrams recorded within the temperature range 20–1000°C, narrower temperature ranges of dehydration and decomposition processes were determined. In addition, the number of stages of thermal decomposition of the examined products was determined and appropriate kinetic parameters were calculated.

The values of the activation energy (E_a) of dehydration, frequency factor (A) and reaction order (n) were calculated from TG, DTG and T curves within the temperature range from 20 to 90°C. For potato flour the following values were obtained: E_a=27.825 kJ/mol, $A=1.05\times10^5$ 1/s and $n=2.97\times10^{-3}$, for the remaining samples under investigation the activation energy E_a is several dozen kJ/mol and the reaction order n is very low. The obtained data show that the dehydration process under study is mainly associated with evaporation of water adsorbed on products and to less extent with chemical processes.

Keywords: food products, kinetic parameter, thermal dehydration

Introduction

Water is one of the fundamental component of food. Water content determines the physical and chemical properties of food products, their texture, processing procedures, preservation, storage stability and assimilation by the human organism. The water content of the typical food products is from about 3% (oil seeds) to 96% (vegetables such as lettuce, melon, water melon and cucumber).

Water content in food products is determined by various methods such as gravimetric, distillation, chemical, refractometric, measurement of density of

* To whom all correspondence should be addressed.

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

aqueous solutions and others. Each of the mentioned procedure is used for the determination of water content only in specified food products [1, 2].

The present study was aimed at developing a fast derivatographic method for the determination of water content in flour and fat products and finding kinetic parameters of dehydration of selected flour products.

Experimental

Thermal curves were recorded by means of a Paulik-Paulik-Erdey 100/1500 derivatograph of MOM (Hungary). Weighed portions of products under investigation were from 250 to 500 mg depending on density. Samples were heated up to 1000°C under a static atmosphere of air at a rate of 10 deg·min^{-1} in corundum crucibles, using α-Al_2O_3 as reference.

For purposes of comparison, water content of the same samples was determined also by the gravimetric method. In this case samples were dried at a temperature of 105°C to a constant weight in a universal SUP-4 drier, which took 7–8 h.

Samples used for the investigation

The following food products were used for the study: wheaten flour 'Poznanska' (PPZM Gorzów Wielkopolski), cake flour (Flour Mills at Stoisław), potato flour (Potato Processing Mill, Luboń n.Poznań), corn flour (PPH 'Denim' Łódż), wheaten cereal, rice cereal with oranges, buckwheat and rice cereal (Kalisz Food Concentrates Plant in Kalisz and Ovita Nitricia-Opole) as well as fat products such as: butter 'Extra' (Co-operative Creamery, Pabianice), sunflower oil (Hungary), soybean oil, vegetable butter and margarine (Fatty Products Plant, Warsaw).

Calculation of the kinetic parameters

Based on the obtained TG, DTG and T curves, the following kinetic parameters of dehydration were determined: the activation energy (E_a), frequency factor (A) and reaction order (n). The calculations were carried out, assuming that deviations from Arrhenius equation can be correlated linearly only in the initial phase of decomposition of the examined samples [3–6].

Arrhenius equation in the logarithmic form (Eq. 1) was solved graphically.

$$\log \frac{dm}{dt} = \log A + n \log c - E/RT \log e \qquad (1)$$

The thermoanalytical curves were used to read temperature T, the value of dm/dt as a distance between curve DTG and its base line [mm], and the value of Δm as a weight loss of the sample [mg]. The value of c was calculated from Eq. 2:

$$c = \frac{\Delta m_\infty - \Delta m}{\Delta m_\infty} \tag{2}$$

where Δm_∞-maximum weight loss at the given stage.

In order to calculate the activation energy E_a, the plot of function $\log dm/dt = f(1/T)$ was made as shown in Fig. 4.

The linear part of the curve makes it possible to calculate the activation energy E_a from its slope (tgα), using the following relationship:

$$E_a = 2.303\, R\, \mathrm{tg}\alpha \tag{3}$$

Knowing the value of E_a, function (4) was plotted:

$$\log \frac{dm}{dt} - \frac{E_a}{RT} = f(\log c) \tag{4}$$

as shown in Fig. 5. The slope of the obtained straight line corresponds to the order of reaction $n (n = \mathrm{tg}\beta)$.

The value pointed out by the straight line on the axis of ordinates is equal to $\log A$. The values found for the kinetic parameters of dehydration of the flour products under study are given in Table 3.

Results and discussion

Figure 1 shows the sets of derivatographic curves obtained for 'Poznańska' wheaten flour (1a), cake flour (1b) and potato flour (1c). The number of decomposition stages for the given sample can be read up from its DTG curve. The examined samples of flour products decompose in two stages as shown by two peaks on all the DTG curves. The dehydration of potato flour proceeds at the highest rate at a temperature 110°C. In the case of wheaten flour samples, the highest rate of the dehydration process takes place at a temperature of 95°C. The weight loss of a sample due to dehydration was calculated from the inflexion of TG curve. The water content of wheaten flour ranges from 11.0% to 13.0%, while that in potato flour is 16.0%. The results of calculations for this group of the products examined are given in Table 1.

The second group of the examined products consisted of cereals. Figure 2 shows derivatographic curves obtained for wheaten cereal, buckwheat-rice cereal and rice cereal. The results of calculations are given in Table 2. The de-

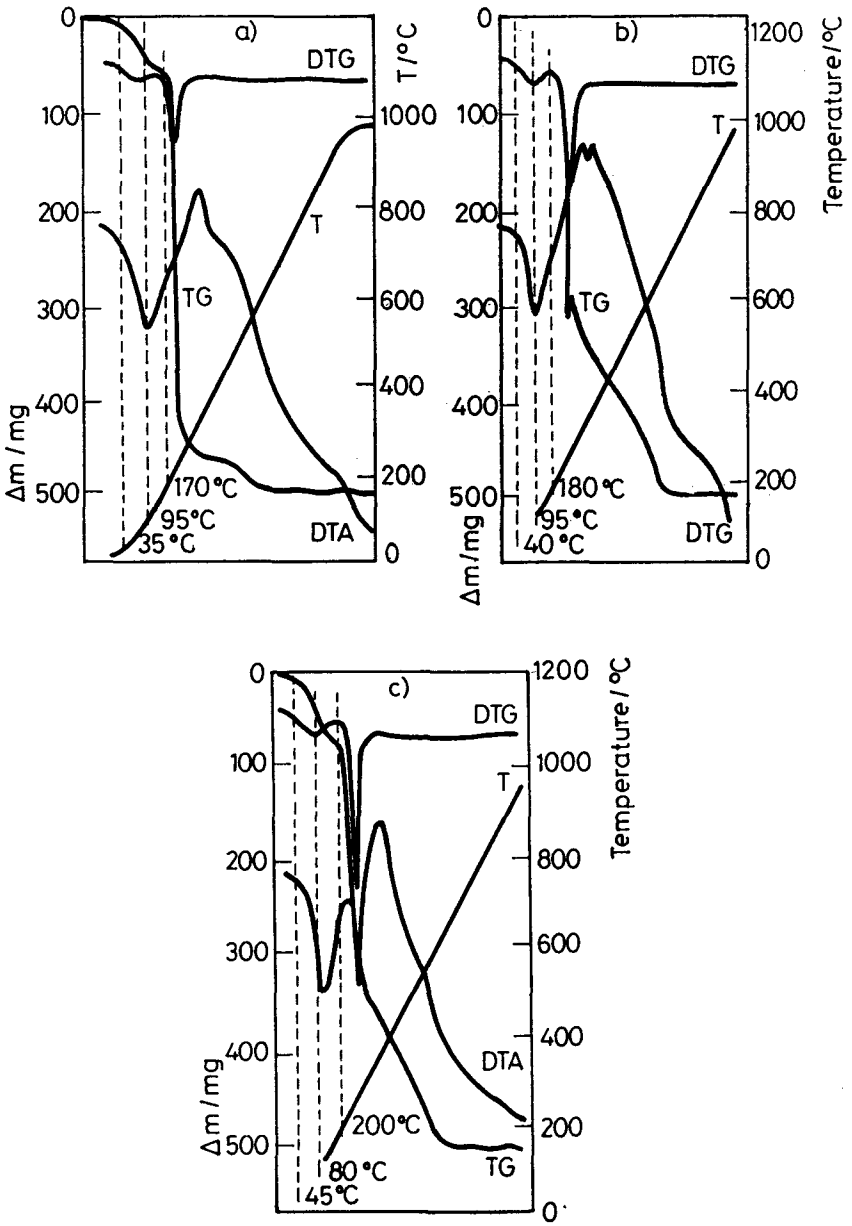

Fig. 1 Thermal curves of flour products: a) wheaten flour 'Poznańska' (m_o=498 mg); b) cake flour (m_o=499 mg); c) potato flour (m_o=500 mg). TG=500 mg, β=10 deg·min^{-1}

composition of the cereals proceeds also in two stages, except for the rice cereal containing orange, whose DTG curve shows three peaks. The third peak is prob-

Table 1 Data based on thermoanalytical curves of the dehydration process of flour products

No.	Name of product	Percentage water contents/%	Range temperature of dehydration process/°C	Temperature the highest rate the dehydration/°C	Number of decomposition stage
1	Wheaten flour "Poznańska"	12.0	35–170	95	2
2	Wheaten flour "Szymanowska"	11.4	40–180	105	2
3	Wheaten flour "500"	11.0	40–160	85	2
4	Corn flour	11.5	40–160	100	2
5	Cake flour	12.0	40–180	95	2
6	Wheaten flour	12.0	30–150	90	2
7	Potato flour	16.0	45–200	110	2
8	Rice	14.0	40–180	100	2

Table 2 Data based on thermoanalytical curves of the dehydration process of cereal

No.	Name of product	Percentage water contents/ %	Range temperature of dehydration process/°C	Temperature the highest rate the dehydration/°C	Number of decomposition stage
1	Rice cereal	5.6	40–160	90	2
2	Wheaten cereal	5.8	50–140	90	2
3	Buckwheat and rice cereal	7.0	50–150	90	2
4	Rice cereal with oranges	8.3	45–155	105	3

ably associated with the added fruit. The water content of the cereals is lower than that of flours and ranges from 5.6% for rice cereal to 8.3% for the rice cereal containing orange. The dehydration of these samples proceeds within the temperature range from 40 to 160°C.

The third group of the examined products were fatty products. Figure 3 shows the derivatographic curves obtained for three of the investigated products of this group. In the case of fatty products being solids at room temperature, e.g. butter, beside the dehydration process within the temperature range from

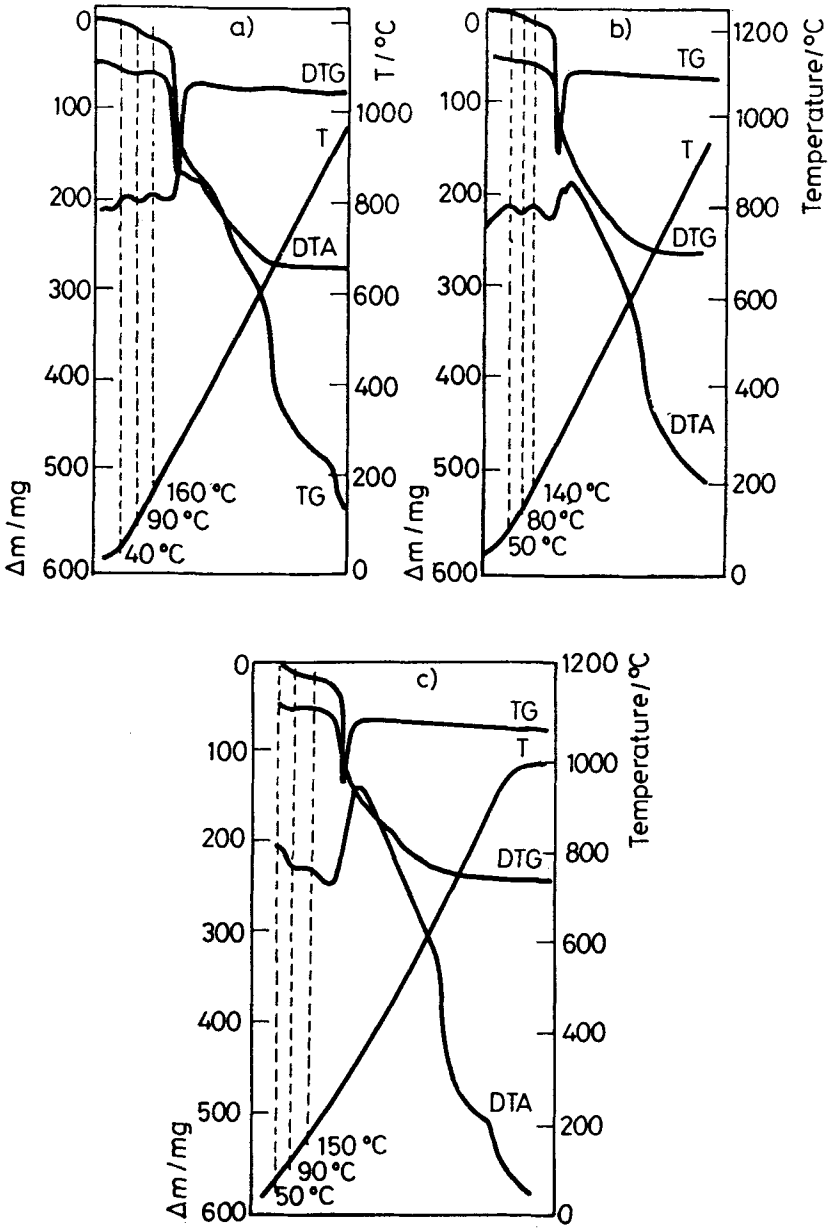

Fig. 2 Thermal curves of cereals: a) rice cereal (m_o=270 mg), b) wheaten cereal (m_o= 260 mg), c) buckwheat and rice cereal (m_o=230 mg). TG=500 mg, β=10 deg·min^{-1}

45 to 180°C, melting is also observed at about 40°C. The water content determined from the weight loss on the TG curve is 12.0% for butter 'Extra', 16.0%

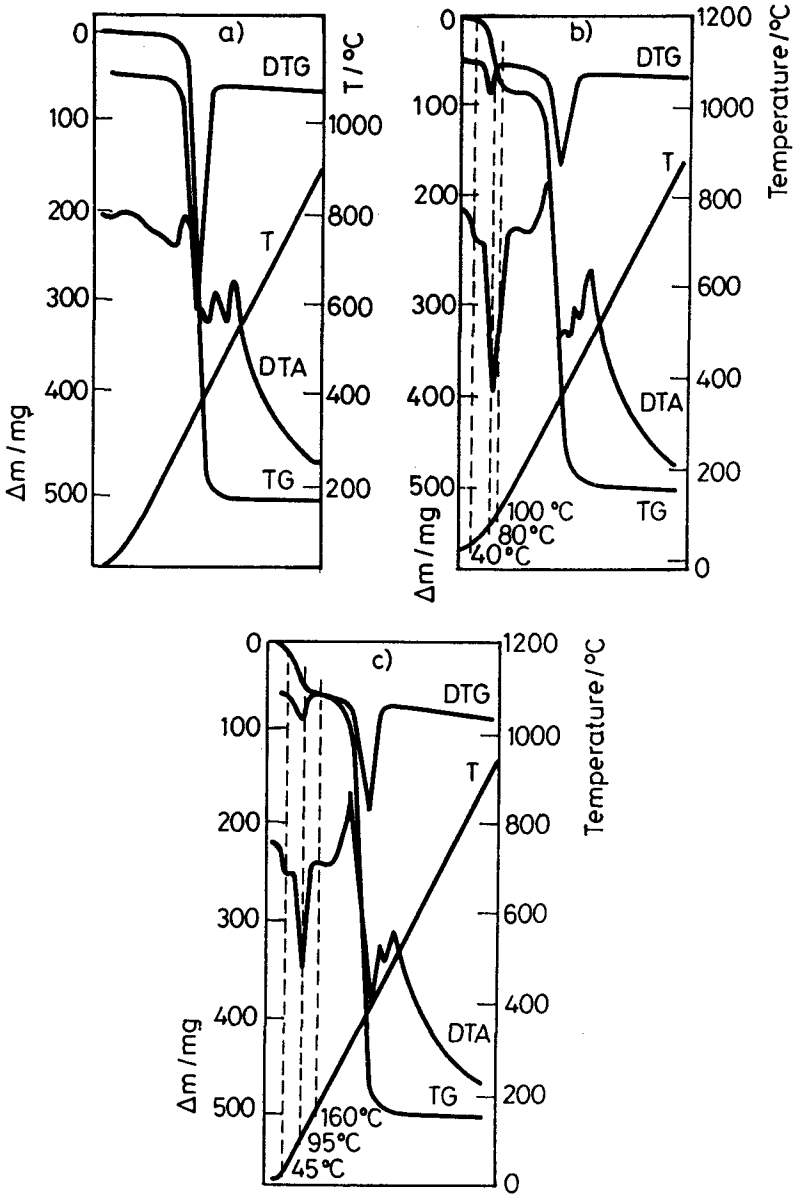

Fig. 3 Thermal curves of fat products: a) sunflower oil (m_o=500 mg), b) vegetable butter (m_o=500 mg), c) butter 'Extra' (m_o=500 mg). TG=500 mg, β=10 deg·min^{-1}

for vegetable butter and 17.4% for margarine (Table 3). The water content in soybean, sun flover and colza oils is so low that neither weight loss on the TG curve nor peak on the DTG curve is observed. It results from Fig. 3a that the

pyrolysis of the edible oils proceeds in on stage within the temperature range from 230 to 390°C. Based on many experiments, we can state that for most of

Table 3 Data based on thermoanalytical curves of the dehydration process of fat products

No.	Name of product	Percentage water contents/%	Range temperature of dehydration process/°C	Temperature the highest rate the dehydration/°C	Number of decomposition stage
1	Sunflower oil	0.0	–		1
2	Soybean oil	0.0	–		1
3	Vegetable butter	16.0	40–100	80	3
4	Butter "Extra"	12.0	45–180	95	3
5	Margarine	17.4	30–120	90	3

Table 4 A comparison of determination of water contents in food products by thermal method and scales method

No.	Name of product	Percentage water content / %	
		thermal method	classic method
1	Cake flour	12.0	11.9
2	Corn flour	11.5	11.4
3	Wheaten flour "Szymanowska"	11.4	10.9
4	Wheaten flour "Poznańska"	12.0	11.8
5	Potato flour	16.0	16.0
6	Buckwheat and rice cereal	7.0	6.8
7	Sunflower oil	0.0	0.0
8	Margarine	17.4	17.7

the products food examined by the derivatographic method, the results are somewhat higher than those obtained by the gravimetric method (Table 4). It is associated with the fact that under the conditions of derivatography (higher temperature), also the water combined chemically is partly removed from the samples.

The kinetic parameters of dehydration were calculated for the initial phase of this stage, i.e. within the range from 20 to 90°C (Figs 4, 5). The activation energy of the hydration of flour products is E_a=27.825 kJ/mol for potato flour, E_a=29.851 kJ/mol for wheaten flour and E_a=29.085 kJ/mol for wheaten cake

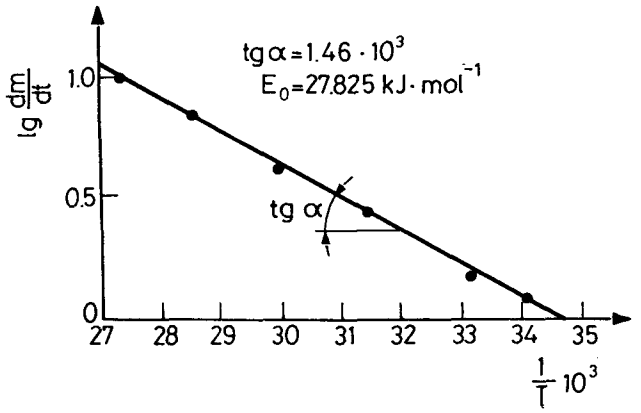

Fig. 4 Graphic dependence log $dm/dt = f(1/T)$ applied for appointing activation energy E_a of the dehydration process potato flour

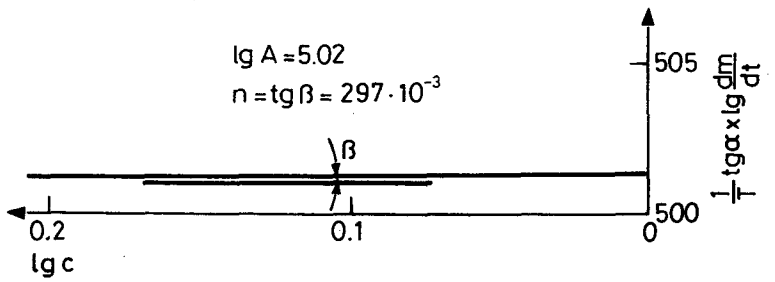

Fig. 5 Graphic dependence log $dm/dt + 1/T\,\mathrm{tg}\alpha = f(\log c)$ applied for appointing frequency factor (A) and reaction order (n) of the dehydration process potato flour

Table 5 Kinetic parameters of thermal dehydration some food products

No.	Name of product	Activation energy E_a / kJ·mol^{-1}	Value of A	Order of reaction n
1	Potato flour	27.825	1.05×10^{5}	2.97×10^{-3}
2	Wheaten flour	29.851	7.62×10^{4}	2.05×10^{-1}
3	Cake flour	29.085	9.86×10^{4}	1.01×10–1
4	Wheaten cereal	52.094	1.21×10^{5}	1.23×10^{-1}
5	Buckwheat and rice cereal	60.840	2.05×10^{5}	2.51×10^{-1}

flour. The highest value of E_a was obtained for buckwheat-rice cereal: 60.840 kJ/mol. The calculated order of reaction (n) of the dehydration process is very low for all the samples and amounts from $n=1.01\times10^{-1}$ for wheaten cake flour to $n=2.97\times10^{-3}$ for potato flour. Thus, it can be concluded that

within the temperature range 20–90°C, the predominating process is evaporation of water adsorbed by the food product under study. Probably at this stage no water is formed due to the chemical decomposition of samples, which takes place only at elevated temperatures.

Conclusions

1. It has been shown that the derivatographic method can be used for the determination of water content in typical food products within a short time (30 min) using relatively small samples from 200 to 500 mg.

2. The kinetic parameters found (E_a, n, A) show that the examined dehydration process of flour products is associated mainly with evaporation of the water adsorbed by the food product. Further stages of decomposition resulting in the release of water combined chemically take place at higher temperatures.

3. The water content determined by the derivatographic method in food products such as flour, cereals and edible oils is comparable with the results obtained by the gravimetric procedure (temperature 105±0.5°C).

References

1 J. Budzisławski and Z. Drabent, Metody analizy żywności, WNT, Warszawa, 1972.
2 B. Kowalski, Przem. Spoż., 2–3 (1990) 41; 11 (1990) 263.
3 J. Masłowska, J. Thermal Anal., 29 (1984) 895.
4 J. Masłowska and A. Baranowska, J. Thermal Anal., 29 (1984) 309.
5 J. Masłowska and M. Malicka, J. Thermal Anal., 32 (1984) 1323.
6 J. Masłowska and R. Krupa, Zeszyty Naukowe P. Ł., Chem. i Techn. Spoż., 39 (1985) 71.

Zusammenfassung — Die Derivatographie wurde zur quantitativen Bestimmung des Wassergehaltes in ausgewählten Mehl- und Fettprodukten verwendet. Anhand der erhaltenen Derivatogramme wurden infolge von Hitzeeinwirkung auftretende Gewichtsverluste und thermische Effekte in den untersuchten Produkten beobachtet. Der prozentuelle Wassergehalt wurde anhand der TG-Kurven innerhalb eines Bereiches von 5,6% (Reisflocken) bis zu 16,0% (Kartoffelmehl) bestimmt. Aufgrund der aufgezeichneten Diagramme innerhalb der Temperaturen von 20 bis 1000°C wurden schmale Temperaturbereiche von Dehydratations- und Zersetzungsprozessen festgestellt. Außerdem wurde die Anzahl der Schritte innerhalb der thermischen Zersetzung der untersuchten Produkte ermittelt und entsprechende kinetische Parameter berechnet.
Anhand der TG-, DTG- und T-Kurven wurden für den Temperaturbereich 20 bis 90°C die Werte für die Aktivierungsenergie (E_a) der Dehydratation, den Frequenzfaktor (A) und die Reaktionsordnung (n) bestimmt. Für Kartoffelmehl wurden nachstehende Werte erhalten: E_a= 27.825 kJ/mol, $A=1.05\times10^5$ 1/s und $n=2.97\times10^{-3}$, für die übrigen untersuchten Proben beträgt die Aktivierungsenergie E_a einige Dutzend kJ/mol und die Reaktionsordnung n ist sehr klein. Die erhaltenen Resultate zeigen, daß der untersuchte Dehydratationsprozeß hauptsächlich mit der Verdampfung von Wasser verbunden ist, welches an den Produkten adsorbiert ist, und nur in geringerem Umfange von chemischen Prozessen.