# Non–isothermal kinetics of degradation of chitin and chitosan

Dilyana Zvezdova, Velyana Georgieva, Lyubomir Vlaev

***Abstract:*** *Thermogravimetric studies of chitin and chitosan in air atmosphere were carried out at six rates of linear increase of the temperature. The kinetics and mechanism of the thermal decomposition reaction were evaluated from the TG data using recommended from ICTAC kinetics committee iso-conversional calculation procedure of Kissinger-Akahira-Sunose, as well as 27 mechanism functions. The values of the apparent activation energy E, pre-exponential factor A in Arrhenius equation, as well as the changes of entropy ΔS≠, enthalpy ΔH≠ and Gibbs free energy ΔG≠ for the formation of the activated complex from the reagent are calculated.*

***Key words:*** *Chitin and Chitosan, Thermal Degradation, Non-isothermal Kinetics, Kinetics Triplet*

## INTRODUCTION

A number of reviews [12,13,15,16] and articles [6,9,10,11] have been dedicated to chitin and the products obtained from its chemical treatment at different conditions.

Beside of cellulose, chitin is the second most popular polysaccharide. It is estimated that annually $10^{11}$ ton of this biopolymer is synthesized [14]. It forms a linear biopolymer with highly crystalline microfibers and characterized by a higher degree of polymerization than cellulose. Chitin as polysaccharide consist of $\beta$-(1-4)-linked 2-acetamido-2-deoxy-D-glucopyranose units [1,16] and is structurally similar to cellulose. Chitosan is linear polysaccharide composed of randomly distributed $\beta$-(1-4)-linked D-glucosamine (deacetylated unit) and *N*-acetyl-D-glucosamine (acetylated unit) and generally is obtained by extensive deacetylation of chitin [10]. The structures of cellulose, chitin and chitosan are shown in Fig.1.
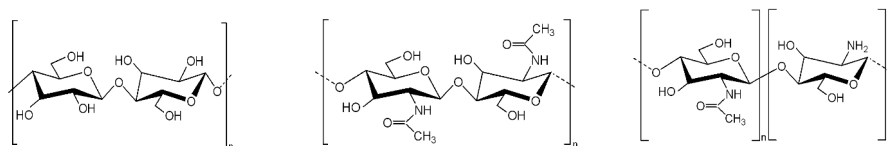


Fig. 1. Structures of cellulose, chitin and chitosan.

Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.89%) compare to synthetically substituted cellulose (1.25%). In this respect, chitin and chitosan are recommended as suitable functional materials, because these natural polymers have excellent properties such as hydrophilicity, biocompatibility, biodegradability, antibacterial, non-toxicity, adsorption properties, and remarkable affinity for many biomacromolecules. Chitosan has been widely studied for biosensors, tissue engineering, separation membrane, waste water treatment and so one, because of its multiple functional groups. The knowledge of their thermal stability and pyrolysis may help to better understand and plan their industrial processing.

The study on the mechanism and kinetics of reactions involving solid compounds is challenging and difficult task with complexity results from the great variety of factors with diverse effects. Recently, the methods of thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are quite useful, since they provide reliable information on the physico-chemical parameters, characterizing the processes of transformation of solids or participation of solids in processes of isothermal or non-isothermal heating [2,3,7,19,20]. The kinetic triplet (i.e., *E*, *A* and *f*($\alpha$)) is typical outcome of the regular kinetic analysis. The results, obtained on this basis can be directly applied in materials science for the preparation of various metals and alloys, cements,

ceramics glasses, enamels, glazes, synthetic or natural polymers and composite materials [20].

The aim of this paper is to assess the kinetic models of chitin and chitosan pyrolysis and to estimate the kinetics triplet ($E$, $A$ and the shape of the most appropriate $f(\alpha)$-function) of this process by means of thermogravimetric data, using different calculation procedures.

## 2. Methods
### 2.1. Materials
The used for thermal degradation chitin and chitosan were commercially obtained from crab shells from SIGMA-ALDRICH (Cat. No. C3646) and SIGMA (Cat. No. 28191), deacetylated with ≥75 and were used without further purification. Before using, chitin and chitosan were vigorously grounded in agate mortar and dried in air at $60^{\circ}$C for 4 hours.

### 2.2. Thermal analysis
The thermogravimetrical measurements (TG-DTG-DTA) were carried out in a flow of synthetic air at a rate of 25 cm$^3$ min$^{-1}$ under non-isothermal conditions on an instrument STA 449 F3 Jupiter (Nietzsch, Germany) with its high temperature furnace. Samples of about 7±0.1 mg mass were used for the experiments varied out at hearing rates of 3, 6, 9, 12, 15 and $18^{\circ}$C min$^{-1}$ up to $800^{\circ}$C. The samples were loaded without pressing into an open 6 mm diameter and 3 mm high platinum crucible, without using of a standard reference material. The TG, DTG and DSC curves were recorded simultaneously with 0.1 mg sensitivity.

### 2.3. Theoretical approach and calculation procedures
The kinetics of thermal degradation reactions is described with various equations taking into account the special features of their mechanisms. The reaction rate can be expressed through the degree of conversion $\alpha$, according to the Equation (1):

$$\alpha = \frac{m_i - m_t}{m_i - m_f}, \tag{1}$$

where: $m_i$, $m_f$ and $m_t$ are the initial, final and current sample mass at the moment $t$, respectively. The rate of many condensed phase reactions can be conveniently parameterized as a function of the temperature $T$, and the extent of the reaction conversion $\alpha$. In non-isothermal kinetics of heterogeneous condensed phase reactions, it is usually accepted that the reaction rate is given by [2,19,20]:

$$\int_0^\alpha \frac{d\alpha}{\alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p} = \frac{A}{q} \int_0^T \exp\left(-\frac{E}{RT}\right) dT, \tag{2}$$

where: $\alpha$ is the degree of conversion, $m$, $n$ and $p$ are empirically obtained exponent factors, one of them always being zero, $T$ – absolute temperature, $t$ – time, $R$ – the gas constant (8.314 Jmol$^{-1}$K$^{-1}$), $q$ is the linear constant heating rate $q = dT/dt$ and $A$ and $E$ are the pre-exponential factor or frequency factor and the activation energy respectively, given by the Arrhenius equation. The solution of left-hand side integral are denoted as $g(\alpha)$. The formal expression of the function $g(\alpha)$ depend on the conversion mechanism and its algebraic expression. The algebraic expression of functions of the most common reaction mechanisms operating in solid-state reactions are presented in some papers [2,4,19-21].

The right-hand side integral or so called "temperature integral" in Eq. (2) has no exact analytical solution. Several author [5,18,24] suggested different ways to solve this integral.

### 2.3.1. Iso-conversional method
Iso-conversional methodology in non-isothermal experiments is recommended from ICTAC kinetics committee [22]. Iso-conversional methodology in non-isothermal experiments assumes that for a given degree of conversion $\alpha$, the reaction mechanism does not depend on the heating rate. In this respect Kissinger-Akahira-Sunose [7,8] proposed own model-free method and the next linear equation:

$$\ln\left(\frac{q}{T^2}\right) = \ln\left[\frac{AR}{g(\alpha)E}\right] - \frac{E}{RT}, \tag{3}$$

For each conversion degree $\alpha$, the linear plot of $\ln(q/T^2)$ versus $1/T$ enables $E$ and $\ln[AR/g(\alpha)E]$ to be determined from the slope and the intercept respectively

The change of the entropy at the formation of the activated complex from the reagent may be calculated according to the formulae [2,19,20]:

$$\Delta S^{\neq} = R \ln \frac{Ah}{e \chi k_B T_p} \tag{4}$$

Since

$$\Delta H^{\neq} = E - RT_p, \tag{5}$$

the changes of the enthalpy $\Delta H^{\neq}$ and Gibbs free energy $\Delta G^{\neq}$ for the activated complex formation can be calculated, using well known thermodynamic equation:

$$\Delta G^{\neq} = \Delta H^{\neq} - T_p \Delta S^{\neq}. \tag{6}$$

The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ were calculated at $T = T_p$ ($T_p$ is the peak temperature at the corresponding stage), since this temperature characterizes the highest rate of the process, and therefore, is its important parameter [2,19,20].

### RESULTS AND DISCUSSION

The TG and DTA curves, obtained by thermal degradation of chitin and chitosan at different heating rates are presented in Fig. 2.
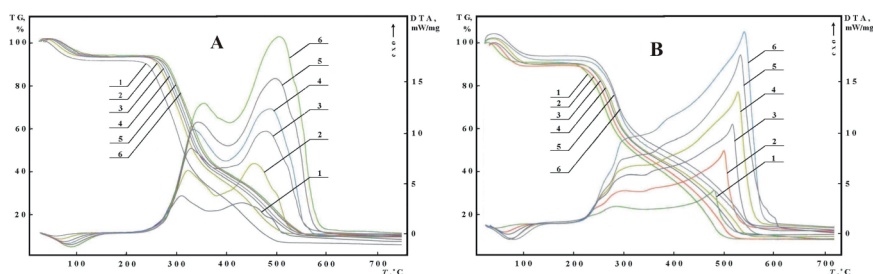


Fig. 2. TG and DTA-curves of: A – chitin and B -chitosan, obtained at different heating rates: 1 – 3; 2 – 6; 3 – 9; 4 – 12; 5 – 15 and 6 – 18$^{\circ}$C min$^{-1}$.

As can be seen from Fig. 2, the TG and DTA-curves of chitin and chitosan shifted to higher temperatures with the increase of the heating rates. Furthermore, two exo-effects were observed, one of them stronger. These effects correspond to a step which abruptly changes its course at temperatures above 380$^{\circ}$C for chitin and above 400$^{\circ}$C for chitosan.

To perform the kinetic computations on the thermal analytical data, the Kissinger-Akahira-Sunose calculation procedure was used, recommended from ICTAC kinetics committee [22]. The reaction model $g(\alpha)$ is determinate for each of stages of thermal degradation of chitin and chitosan. The thermal decomposition of two polymers was described with $F_n$ mechanism functions at different values of $n$. For the first stage of thermal degradation of chitin, it was established that $n$ is equal to 2.7 and for the second stage - to 1.5. For the first stage of thermal degradation of chitosan, it was established that $n$ is equal to 3.0 and for the second stage - to 1.0 respectively. A reaction order $n > 2$ is mathematically equivalent to Gamma distribution of frequency factor. The interpretation of the high values of reaction order has been discussed in the literature [14]. However, the reason why this parameter has such a high value in relation to the described phenomena has not been completely explained.

The values of the apparent activation energy and pre-exponential factor for both stages of thermal degradation of chitin and chitosan were calculated according KAS procedure. On Table 1 are given for comparison the kinetic parameters, characterizing thermal degradation of chitin and chitosan.

Table 1. Comparison of the kinetic parameters obtained with the most probable mechanism function $g(\alpha)$ for non-isothermal degradation of chitin and chitosan.

| Parameter | Chitin | | Chitosan | |
|---|---|---|---|---|
| | First stage | Second stage | First stage | Second stage |
| $E$, kJ mol$^{-1}$ | 154.0 | 114.8 | 126.0 | 99.1 |
| $A$, min$^{-1}$ | $2.51\times10^{14}$ | $5.36\times10^{7}$ | $2.01\times10^{12}$ | $1.47\times10^{6}$ |
| $-\Delta S^{\neq}$, J mol$^{-1}$K$^{-1}$ | 29.7 | 148.3 | 69.1 | 183.4 |
| $\Delta H^{\neq}$, kJ mol$^{-1}$ | 149.7 | 108.5 | 121.9 | 92.7 |
| $\Delta G^{\neq}$, kJ mol$^{-1}$ | 165.0 | 220.6 | 155.8 | 233.3 |

As can be seen from Table 1 chitin is more stable than chitosan. The values of the apparent activation energy and pre-exponential factor for both stages of thermal degradation of chitin are higher than these of chitosan. The same tendency was established from other authors [14,24]. The negative values of $\Delta S^{\neq}$ for both compounds showed that the formation of the activated complex from the reagents is connected with a decreasing of entropy, i.e. the activated complex is "more organized" structure and the formation process can be classified as "slow" [20].

**CONCLUSIONS**

Chitin and chitosan have excellent properties such as hydrophilicity, biocompatibility, biodegradability, antibacterial, non-toxicity, adsorption properties. The kinetics and mechanism of the thermal decomposition reaction were established using iso-conversional calculation procedure. The determination of the most probable mechanism function is very important. In this respect the iso-conversional calculation procedure turned out to be the most appropriate. In the present work, the values of the apparent activation energy $E$, pre-exponential factor $A$ in Arrhenius equation, as well as the changes of entropy $\Delta S^{\neq}$, enthalpy $\Delta H^{\neq}$ and free Gibbs energy $\Delta G^{\neq}$ for the formation of the activated complex from the reagent are calculated. All calculations were performed using programs compiled by ourselves.

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**Докладът е рецензиран**

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" Non-isothermal kinetics of degradation
of chitin and chitosan"**

# D I P L O M A

**The Programme Committee of
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" Non-isothermal kinetics of degradation
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