

PSEUDO ISO-CONVERSION NON-ISOTHERMAL APPROACHES FOR STUDY OF KINETIC OF DEGRADATION OF CHITIN FROM BLACK SEA MARINE CRABS

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ABSTRACT

On the basis of the general kinetics equation of solid-state reaction pseudo iso-conversion (PIC) non-isothermal approaches are applied for investigation of the kinetic model app parameters of degradation of chitin. The approaches are based on differential and integral iso-conversion method and allow determining the most adequacy kinetic model.

By means of simultaneous thermal analysis, with the use of STA 449 F3 Jupiter (Netzsch – Germany), an investigation of the kinetics of chitin dynamic decomposition has been conducted. The results are compared with those obtained by other methods, which indicates the correct approach of investigation and the desired accuracy of results.

Key words: pseudo iso-conversion non-isothermal kinetic analysis, velocity of conversion, thermogravimetry, chitin

INTRODUCTION

About 45% of processed seafood consists of shrimp, the waste of which is composed of exoskeleton and cephalothoraxes, the latter has become a problem for the environment. This waste represents 50–70% of the weight of the raw material; however it contains valuable components such as protein and chitin. Chitin, next to cellulose, is the second most common polysaccharide on earth, with a yearly production of approximately 10^{10} – 10^{12} tons [10]. This polymer consists of a linear chain of linked 2-acetoamido-2-deoxy-b-D-glucopyranose units (Fig. 1).

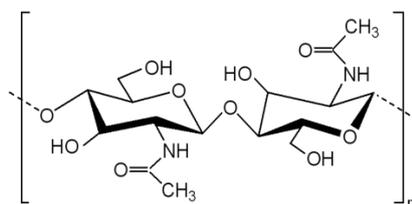
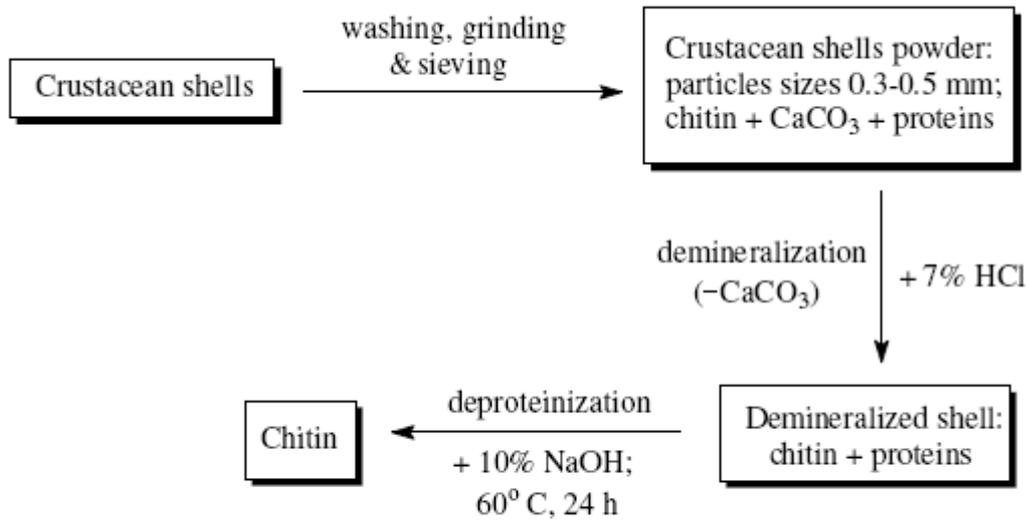


Fig. 1 Structure of chitin

Chitin is usually isolated from the exoskeletons of crustacean, mollusks, insects and certain fungi. Three different polymorphs of chitin are found in nature; the α -chitin, being the most common structure and corresponding to tightly compacted orthorhombic cells formed by alternated sheets of antiparallel chains; the β -chitin, adopts a monoclinic unit cell where the polysaccharide chains are disposed in parallel fashion; and γ -chitin, however it has not been completely identified, an arrangement of two parallel and one antiparallel sheet has

been proposed. Roberts [10] has suggested that c-chitin can be a combination of α and β structures rather than as a different polymorph. α -Chitin is usually isolated from the exoskeleton of crustaceans and more particularly from shrimps and crabs. β -Chitin can be obtained from squid pens, while c-chitin exists in fungi and yeast. Because chitin has a compact structure, it is insoluble in most solvents. These polymer have antimicrobial activity, besides being biocompatible and biodegradable. They display a wide range of applications in different fields, e.g. in cosmetics, agriculture, food, pharmacy, biomedical, paper industry and also as absorbent materials for wastewater treatment. Isolation of chitin from marine sources as shown on scheme 1.



Scheme 1. Isolation of chitin from marine sources

EXPERIMENTS

TG, DTG and DSC curves of the samples were taken in the temperature interval of 20-600°C and heating degree of 6-15/deg min⁻¹, initial sample weight about 3.5 mg in a of synthetic air at rate of 20 ml min⁻¹ in platinum crucible for analysis equipped with a lid with opening. The DSC curves were calibrated by enthalpy using the melting enthalpies of 6 pure (In, Sn, Bi, Zn, Al, Au). From the DSC curves, the temperatures (T_m) and heats ($\Delta H/ J g^{-1}$), as well as the temperatures of the thermal effects by destruction were calculated. Using the TG and DTG curves, the temperature intervals and amounts of the volatile and basic substances produced by the destruction, the maximal rates of main destruction were determined.

For the kinetic analyses, sample of chitin were studied at heating rates $\beta= 6.0, 9.0, 12.0$ and $15.0 \text{ deg min}^{-1}$ in artificial air.

METHODS

The values of the effective kinetic parameters were obtained on the basis of a new approach involving mathematical apparatus described in detail by the author [4, 6, 9] and named as *Pseudo iso-conversion* (PIC) method. The method includes preliminary smoothing the TG-experimental data by two-way filter.

$$m_i^{f, fw} = (1 - K_{f,i})m_{i-1}^{f, fw} + K_{f,i}m_i^{exp}; \quad (1.a)$$

$$m_i^{f, bw} = (1 - K_{f,i})m_{i+1}^{f, bw} + K_{f,i}m_i^{exp}; \quad (1.b)$$

$$m_i^{f, avg} = \frac{m_i^{f, fw} + m_i^{f, bw}}{2}, \quad (2)$$

where the indices (^f), (^{fw}), (^{bw}), (^{exp}) and (^{work}) denote the filtered value, forward, backward, experimentally obtained and working value, respectively.

The filter coefficient K_i^f is defined by the formula

$$K_i^f = \frac{\Delta t_i}{\tau_f + \Delta t_i}, \quad (3)$$

where Δt_i is the filtering step:

$$\Delta t_i = \begin{cases} t_i - t_{i-1} & \text{at fw - filtration ;} \\ t_{i+1} - t_i & \text{at bw - filtration ;} \end{cases} \quad (4)$$

τ_f is the time constant of the filter.

In filtration TG, DTG and the destruction rate the curves are smoothed by high-frequency interference without significantly changing of their initial profile. The studies with model and real data showed that $K^f \geq 0.15$, the kinetic parameters of the error does not exceed $\pm 1.8\%$.

The calculation of the conversion speed $d\alpha/dt$ is done by displaying of the polynomial $\alpha = M t^2 + N t + P$ for each point with inclusion of the neighboring points and subsequent differentiation. As a result, there are obtained high precision $d\alpha/dt$ -curves.

Instead of known iso-conversion sections at values of α_j , the method provides to be included the points in the area $\alpha_j \pm \Delta\alpha_j$. It can be performed using a differential or integral form of the kinetic equations [14]. In this work the kinetic evaluation was conducted by regressive analyze of the basic kinetic equation:

$$v_\alpha = \frac{d\alpha}{d\tau} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) h(P) \quad (5)$$

where α represents the degree of conversion of the process studied which is calculated by the formula

$$\alpha_\tau = \frac{m_i - m_\tau}{m_i - m_f} \quad (6)$$

where m_i , m_f and m_τ are the initial, final and current sample mass at moment τ , respectively, for the process studied;

$f(\alpha)$ is a so called *differential kinetic function* involved in the kinetic model and its general formula is represented by the function of Šesták and Berggren (SB) [12]

$$f(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \quad (7)$$

Depending on the values of coefficients n , m and p (if some coefficients are zero or not) seven variants of the kinetic function are available. The best studied are kinetic functions with one or two with a strongly limited of a second factor.

Friedman [3] suggested eq. (5) for the determination of the activation energy. The analysis is based on the logarithmic form of eq. (5):

$$\ln(v_{\alpha,i}) = \left\{ \ln(A) + \ln[f(\alpha_i)] \right\} - \frac{E}{RT_{\alpha,i}} \quad (8)$$

Several practical integrated method for iso-conversion analysis have been developed:

-Kissinger-Akahira-Sinose (KAS) [5], based on the relationship:

$$\ln\left(\frac{\beta_j}{T^2}\right) = \ln\left(\frac{AR}{g(\alpha)E_\alpha}\right) - \frac{E_\alpha}{RT} \quad (9)$$

- Flynn-Wall-Ozawa (FWO) [7]:

$$\ln(\beta_j) = C_{KAS}(\alpha) - 1.0516 \frac{E_\alpha}{RT_{\alpha,i}} \quad (10)$$

- Tang et al. [14]:

$$\ln\left(\frac{\beta_j}{T_{\alpha,i}^{1.89466100}}\right) = \ln\frac{AE_a}{g(\alpha)R} + 3.63504095 - 1.89466100 \ln E_\alpha - 1.00145033 \frac{E_\alpha}{RT_{\alpha,i}} \quad (11)$$

where

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (12)$$

is so called *integral kinetic function*; $\beta = dT/d\tau$.

The results of the calculation are direct obtaining the kinetic models and kinetic parameters (E_a kJ mol⁻¹; A min⁻¹ and coefficient of linear regression R^2 , S_r^2 etc.), as well as the most probable partial reaction mechanism of thermal destruction of the samples were determined.

RESULTS AND DISCUSION

TG, DTG and DSC curves of chitin obtained at heating rate of 12 deg min⁻¹ are shown on Fig. 2. Very less marked endothermic peak was observed between 50 and 120°C, with a minimum at 86°C. A mass loss of 9.92% was associated with this effect and it can be attributed to the evaporation of absorbed water in the internal chitin. The main thermal effect was observed within the range of 200 - 600°C, with two exothermic peaks at 324.8 and 486°C. It was associated also with the mass loss (69.6%) and 28.64 %, which corresponded to thermal degradation of the polymeric chain chitin.

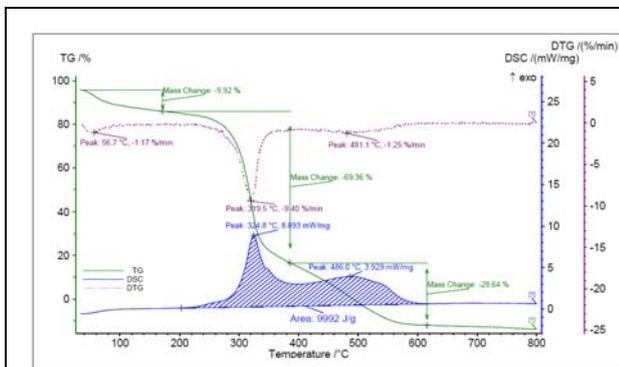


Fig. 2. TG, DTG and DSC curves of chitin obtained at $\beta = 12$ deg min⁻¹

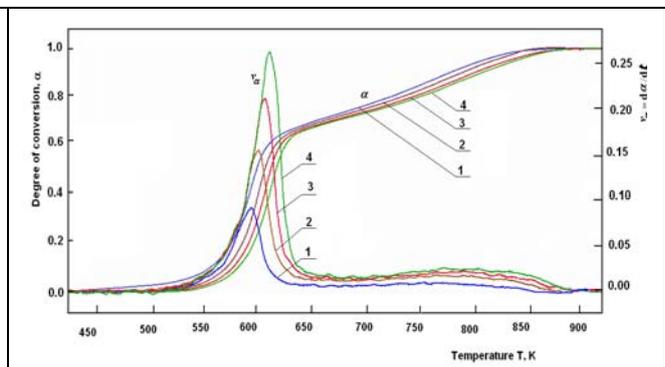


Fig.3. Degree of conversion α and reaction rate v_α at four heating rates 1 - 6; 2 - 9; 3 -12; 4 - 15 deg min⁻¹

DSC and DTG curves show that the process of decomposition cannot be strictly divided into separate stages. Conditional boundary between the two steps in the range 370-390°C.

The lines of degree of conversion α and reaction rate v_α at four heating rates are shown in Fig.3. As shown in Fig. 3, reaction rate $v_\alpha > 0$ between the two conditional steps, and α -lines has no horizontal portion, which is a criterion for a completed stage of the process. These lines are most strongly near to 645 K (372°C). The second peak is very fuzzy.

Character of TG, DTG, DSC, α and $v \alpha$ curves allow kinetic studies on the process of degradation of chitin at temperature range of 200-600°C to be considered as integrated stage. Using classical iso-conversion methods, the value of α and type of kinetic model does not affect the determined activation energy E . In the proposed PIC-methods of research we used sufficiently narrow field $\alpha_0 \pm \Delta\alpha$, to eliminate the influence of α on E and wide enough field $\pm\Delta\alpha$, which the kinetic model $f(\alpha)$ or $g(\alpha)$, pre-exponential factor A to be determined uniquely with sufficient accuracy. The whole reaction range ($0.000 \leq \alpha \leq 1.000$) is divided into N sub-ranges:

$$\alpha_{0,i} = i/(N+1); \Delta\alpha = 0.5/(N+1). \quad i - 1, 2, \dots, N. \quad (13)$$

We recommend $N=20$.

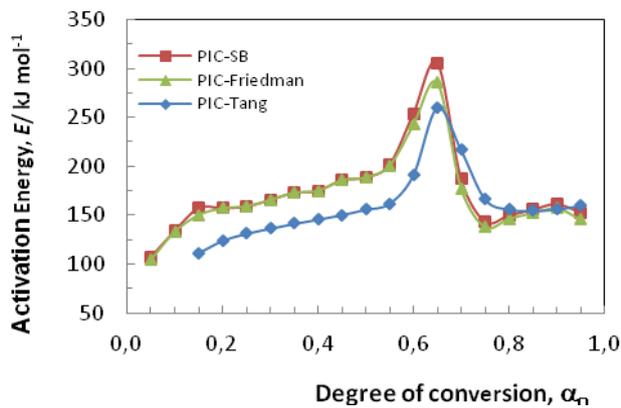


Fig.4. Dependences of the activation energies on the degree of conversion α_0

Fig.4 shows graphically the dependences of the activation energies on the degree of conversion α_0 , determined by different PIC methods. It is shown that E is changing continuously, reaching a maximum value $\alpha_0 \approx 0.65$. Both of the present PIC differential methods - direct PIC-SB, (solving the linearized model Šesták and Bergman) and Friedman PIC-method - obtained approximately equal values E . The figure shows the dependence of E on α_0 obtained by applying the PIC-approach and Tang's equation. Similar values are obtained when applying the PIC-approach to the equations of FWO, KAS etc. The results show that PIC-Tang E is amended as smooth as the

maximum value before they are lower by $\Delta E = 30-50 \text{ kJ mol}^{-1}$, and after then they are higher. Typical of this particular survey is that $\alpha_0 < 0.15$ E cannot be determined.

Preliminary studies on the kinetics of thermal destruction of chitin showed that the full process is described by the kinetic function

Since $s_r^2 = F(n)$ is unimodal, then the most appropriate approach for the determination of n is The Method of Golden section.

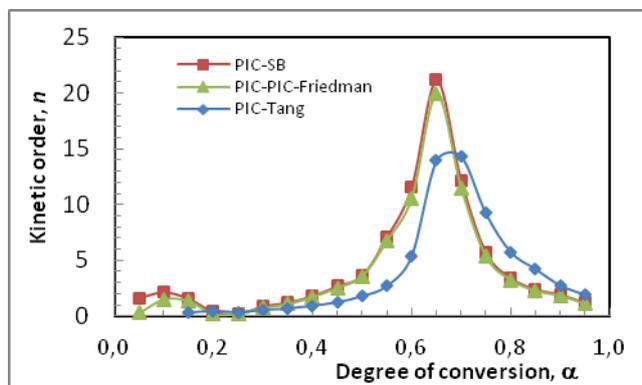


Fig.5. Dependences of the kinetic order n on the degree of conversion α_0

$$f(\alpha) = K(1-\alpha)^n; \quad K = \left| \frac{1}{n-1} \right| \quad (14a)$$

or

$$g(a) = \frac{(1-\alpha)^{(1-n)} - 1}{K(n-1)}. \quad (14b)$$

Criterion for determination of n is a minimum of residual variance s_r^2 which for $f(\alpha)$ can be calculated by the formula

$$s_r^2 = \frac{\sum_{i=1}^l (v_{\alpha,i} - \hat{v}_{\alpha,i})^2}{l_r}, \quad (15)$$

where l_r is the number of degree of freedom.

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