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A comparative kinetics study on the isothermal heterogeneous acid-catalyzed hydrolysis of sucrose under conventional and microwave heating

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ABSTRACT

The isothermal kinetics of sucrose hydrolysis at the acidic ion-exchange resin type IR-120 H under conventional (CH) and microwave heating (MWH) was investigated. Isothermal kinetics curves in the temperature range from 303 to 343 K for both CH and MWH were determined. By application the model-fitting method, it was recognized that the kinetics of sucrose hydrolysis can be described by a first-order chemical reaction for both heating modes. The values of the activation energy (E_a) and pre-exponential factor ($\ln A$) for sucrose hydrolysis were found to be lower under MWH than under CH. Application of the differential isoconversional method showed that sucrose hydrolysis was kinetically an elementary reaction. It is found that the increased rate of hydrolysis observed under MWH was not a consequence of overheating. A new explanation of the established effects of microwave heating based on a model of selective energy transfer during the chemical reaction is suggested. The established decreases in the activation energy and in the pre-exponential factor under MWH in comparison to CH is explained by an increase in the energy of the ground vibrational level of the –OH out-of-plane deformation in the sucrose molecule and with a decrease in the anharmonicity factor, which is caused by the selective resonant transfer of energy from the catalyst to the –OH oscillators in the sucrose molecules.

1. Introduction

Ethanol production from biomass presents now one of the most attractive alternative resources for the promising economic production of novel fuels and chemicals [1]. Hydrolysis of polysaccharides, celluloses, and hemicelluloses to monosaccharide presents one of the most important reactions in the process of biomass conversion to bioethanol.

The kinetics of heterogeneous acid-catalyzed sucrose hydrolysis by application of cationic exchange resins in the H^+-form was investigated in numerous publications. Reed et al. [2] and Gilliland et al. [3] investigated the effects of temperature and particle size on the kinetics of sucrose inversion on different ion-exchange resins, Amberlit IR-120, Dowex 50W-X8 and Amberlist IR-15. Siegers et al. considered the effects of the degree of crosslinking and particle size of an ion-exchange resin, the reaction temperature and the sucrose concentration [4]. Buttersack et al. [5] investigated the kinetics of hydrolysis of sucrose at a concentration of 100 g/L in the temperature range from 303 to 343 K on de-aluminated Y-zeolites. Examinations of the kinetics of hydrolysis of sucrose and starch on water-tolerant sulfonated mesoporous silicas at 353 K and 403 K are presented in the work of Daphea et al. [6]. Nasef et al. investigated the kinetics of sucrose hydrolysis to glucose and fructose by radiation grafted sulfonic acid membranes and established that the catalytic activity of a membrane depended on the reaction temperature and the concentration of sulfonic acid groups on the membranes [7]. Kinetics of hydrolysis of sucrose at a concentration of 0.6 M at 353 K using sulfonated poly(vinyl alcohol) as the catalyst was investigated in the work of Pito et al. [8]. Plazl et al. [9] studied sucrose hydrolysis under conventional and microwave conditions (sucrose: 90 g/L, catalyst: Amberlite 200C in the H^+ form, 160 g/L, temperature: 313–773 K) and found that isothermal microwave heating did not lead to rate enhancement or reaction time reduction.

However, it is widely accepted that microwave heating (MWH) significantly accelerates the rate of chemical reactions and physico-chemical processes, gives higher yields and improves the properties of the products; for these reasons, the use of microwaves is attracting more and more attention. Microwave heating is a widely accepted, non-conventional energy source for organic synthesis [10] and different physico-chemical processes, such as sintering [11], nucleation and crystallization [12], combustion synthesis [13], calcination [14], solvent-free reactions [15], heterogeneous catalysis [16] and combinatorial chemistry [17].

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Table 1
The basic properties of microwave and conventional heating.

Microwave heating	Conventional heating
Energetic coupling	Conduction/convection
Coupling at the molecular level	Superficial heating
Rapid	Slow
Volumetric	Super ficial
Selective	Non-selective
Dependant on the properties of the materials	Less dependant on the properties of the materials

The effect of microwave irradiation in chemical reactions and physico-chemical processes is a combination of thermal effects (overheating [18], hot-spots [19], selected heating [20]), as well as specific microwave effects [21]. The thermal effects are connected with the different characteristics of microwave dielectric heating and conventional heating. Table 1 presents the basic characteristics of microwave and conventional heating.

Microwave heating is based on the ability of some components of a material to transform electromagnetic energy into heat, whereby the magnitude of the heating depends on the dielectric properties of the molecules. Energy transmission is produced by dielectric losses, which is in contrast to the conduction and convection processes observed in conventional heating. Microwave heating is rapid and volumetric, with the whole material being heated simultaneously. In contrast, conventional heating is slow and is introduced into the sample from the surface.

The thermal effects observed under microwave heating are a consequence of the inverted heat transfer, the inhomogeneties of the microwave field within the sample and the selective absorption of the radiation by polar compounds. These effects can be used efficiently to improve processes, modify selectivity or even to perform reactions that do not occur under conventional heating.

The issue of specific microwave effects is still a controversial matter. Several hypotheses have been postulated and also some predicted models have been published.

Berlan et al. observed the acceleration of a cyclo-addition reaction under isothermal microwave reaction conditions and explained it by a change in the entropy of the reaction system [22].

Microwave enhanced the imidization reaction of a sulfone and ketone group-containing polyamic acid, which Lewis et al., elucidated with a mechanism based on “excess dipole energy”, in which it was proposed that the localized energy (temperature) of the dipole groups was higher compared to the non-polar bonds within these systems [23]. Rybakov and Semenov, explained the effect of microwave reaction conditions on the kinetics of reactions in the solid state with the formation of a ponderomotive force, which influences the time-average motion of charged particles and enhances ionic transport in the solid state [24].

The ability of microwave radiation to excite rotational transitions and thus enhance the internal energy of a system was used by Strauss and Trainor to explain the effects of microwave fields on the kinetics of chemical reactions [25]. Binner et al., investigating the effect of a microwave field on the kinetics of titanium carbide formation, concluded that in the presence of a microwave field, the molecular mobility increases which leads to increasing values of the Arrhenius pre-exponential factor, which further causes an acceleration of the synthesis of titanium carbide [26]. Stuerga et al. explained the acceleration of the reaction rate in condensed states under microwave reaction conditions in comparison to conventional reacting conditions by enhanced rates of collisions in condensed phases, which induces transfer between rotational and vibrational energy levels and reaction acceleration [27]. Booske et al. used the existence of non-thermal energy distributions to elucidate microwave-enhanced solid-state transport [28].

Based on the experimentally confirmed decrease in the values of the activation energy of sodium bicarbonate decomposition under microwave reaction conditions, Shibata et al. concluded that the effect of a microwave field on dielectric materials is to induce rapid rotation of the polarized dipoles in the molecules. This generates heat due to friction while simultaneously increasing the probability of contact between the molecules, thus enhancing the reaction rate and reducing the activation energy [29]. Conner and Tumpsett, explained specific microwave effects with the capability of microwaves to change the relative energies of rotation of intermediates in given sequences [30].

Aimed at finding an explanation for the effects of microwave heating on the kinetics of chemical reactions, in this investigation, a comparative analysis of the kinetics of the heterogeneous acid hydrolysis of sucrose under conventional and microwave conditions was performed in depth. For this purpose, kinetics models, kinetics parameters and kinetics complexity were investigated and based on them, a new explanation of the effects of microwave heating on the kinetics of chemical reactions is suggested.

2. Materials and methods

2.1. Materials

The following materials were used: Sucrose, *p.a.*, was purchased from Merck, Germany. Strong acid cation-exchange resin, Amberlite IR-120H, with a total capacity of 1.8 mmol/mL and a particle size distribution in the range from 0.3 mm to 1.1 mm for >90%, was purchased from Rohm & Haas, USA. Distilled water was used throughout the investigation.

2.2. Hydrolysis of sucrose

The hydrolysis of sucrose, both conventional and microwave, was performed in the batch mode in a glass reactor ($V \sim 150$ mL) which was supplied by the manufacturer for the microwave reactor. To a 100 mL of aqueous solution of sucrose with an initial concentration $C_s = 57$ g/L was added a 15 g of acid cation-exchange resin. The temperature ranged from 303 to 343 K (±1 K).

During the conventional heating experiments, the reactor was placed in a thermostated controlled water bath. The contents were agitated by means of a magnetic stirrer at a stirring rate of 400 rpm to eliminate mass transport resistance and to ensure a thermally homogeneous suspension. The temperature was monitored with a thermocouple which was placed in the center of gravity of the reactor.

The microwave-assisted reactions were conducted using a commercially available monomode microwave unit, Discover, CEM Corporation, Matthews, North Carolina, USA. The microwave reactor consists of a continuously focused microwave power delivery system with an operator selectable power output from 0 to 300 W. All the reactions were realized in a microwave field of 2.45 GHz. The temperature of the reaction mixture was controlled by simultaneously varying of the input power of the microwave field and cooling of the reaction mixture with dry nitrogen. The temperature was monitored by means of a calibrated fiber-optic probe inserted into the center of gravity of the reactor. The content of reactor was continuously stirred by means of a rotating magnetic plate at a stirring rate of 400 rpm located below the floor of the microwave cavity and a teflon-coated magnetic stirrer bar in the reactor.

The samples (free of ion-exchange resin) were taken from the reacting systems at regular time intervals.

2.3. Glucose concentration

The glucose concentration in the reaction mixture was determined by the DNS method [31]. The UV spectra were recorded using a UV-visible spectrometer Cintra 10e, GBC Scientific Equipment, UK.

2.4. The degree of sucrose conversion

The degree of sucrose conversion (α) at a given temperature after certain reaction period was calculated from the equation:

$$\alpha = \frac{C_i}{C_{\max}} \tag{1}$$

where C_i is glucose concentration at the reaction time (t_i) and $C_{\max}$ is the theoretical maximal value of glucose in the reaction system.

3. Methods used to evaluate the kinetic model and kinetic parameters

The kinetic model and kinetic parameters were evaluated applying the following methods.

3.1. The stationary point (SP) method

In isothermal heterogeneous chemical reaction kinetics, the function $\mathrm{d}\alpha/\mathrm{d}t = f(t)$ (where $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of the process and t is the reaction time), can be observed as a function with a local maximum. This maximum appears at the so-called stationary point, where the reaction system under the given conditions has the maximal reaction rate ($(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$) [32], which can be expressed by the following equation:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\max} = k(T, p_j) f(\alpha_{\max}) \tag{2}$$

In Eq. (2), α_{max} represents the degree of conversion at $t = t_{\max}$, $f(\alpha_{\max})$ is a function of the reaction mechanism at the value of $\alpha_{\max}$ ($f(\alpha_{\max}) = f(\alpha = \alpha_{\max})$), and $k(T, p_j)$ is the rate constant at temperature T, where p_j denotes the partial pressure of the gaseous species. Commonly, if the Arrhenius dependence of $k(T, p_j)$ on temperature is assumed, Eq. (2) can be transformed into the following form:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\max} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha_{\max}) \tag{3}$$

where E_a is the apparent activation energy of the overall process, whereas A and R are the pre-exponential factor and gas constant, respectively. The logarithmic form of Eq. (3) is:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\max} = \ln[A \cdot f(\alpha_{\max})] - \frac{E_a}{RT} \tag{4}$$

The apparent activation energy (E_a) of the investigated process was determined from the slope of the dependence of $\ln(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$ *vs.* $1/T$.

3.2. Model-fitting method [33,34]

According to the model-fitting method, the kinetics reaction models in solid state are classified in 5 groups depending on the reaction mechanism: (1) power law reaction, (2) phase-boundary controlled reaction, (3) reaction order, (4) reaction described by the Avrami equation and, (5) diffusion controlled reactions. The model-fitting method is based on the following. The experimentally determined conversion curve $\alpha_{\exp} = f(t)_T$ must be transformed to the experimentally normalized conversion curve $\alpha_{\exp} = f(t_N)_T$, where t_N is the so-called normalized time. The normalized time, t_N, was defined by the equation:

$$t_N = \frac{t}{t_{0.9}} \tag{5}$$

where $t_{0.9}$ is the moment in time at which $\alpha = 0.9$ [33,34]. The kinetics model of the investigated process was determined by analytically comparing the normalized experimentally conversion curves with the normalized model's conversion curves. The kinetics model of the investigated process corresponds to the one for which the sum of squares of the deviation of its normalized conversional curve from the experimental normalized conversional curve gives minimal values.

3.3. Differential isoconversion method

The activation energy of the investigated adsorption process for various adsorption degrees was established by the method of Friedman [35] which is based on the follows. The rate of the process in condensed state is generally a function of temperature and conversion:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \Phi(T, \alpha) \tag{6}$$

i.e.,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T) \cdot f(\alpha) \tag{7}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the reaction rate, $\Phi(T, \alpha)$ is function of α and T, α is the degree of conversion, $k(T)$ the rate constant, t the time, T the temperature, and $f(\alpha)$ is the reaction model associated with a certain reaction mechanism. The dependence of the rate constant on temperature is ordinarily described by the Arrhenius law:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \tag{8}$$

where E_a is the activation energy, A the pre-exponential factor and R is the gas constant.

We then get the following equation:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = A \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \tag{9}$$

Accepting that the reaction rate constant is an extent of conversion and is only function of temperature, which is known as the isoconversional principle of Friedman (Eq. (9)) is easily transformed to:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha} = \ln[A \cdot f(\alpha)] - \frac{E_{a,\alpha}}{RT} \tag{10}$$

That allows the evaluation of the activation energy for particular degree of sucrose hydrolysis.

4. Results and discussion

The experimentally obtained isothermal conversion curves of the acid catalyzed hydrolysis of sucrose under conventional and microwave heating at different temperatures are shown in Fig. 1.

The conversion curves of sucrose hydrolysis have same shape at all the investigated temperatures for both conventional and microwave heating. Initially, the degree of sucrose conversion increases significantly and linearly with time, then gradually slows down until equilibrium is attained. With increasing hydrolysis temperature, the period of linear change of the sucrose hydrolysis with time became shorter and the duration of both the linear and nonlinear changes decreased for each heating mode, while the maximal value of the degree of sucrose conversion (α) increased. It is clear from Fig. 1 that microwave heating had a pronounced effect on

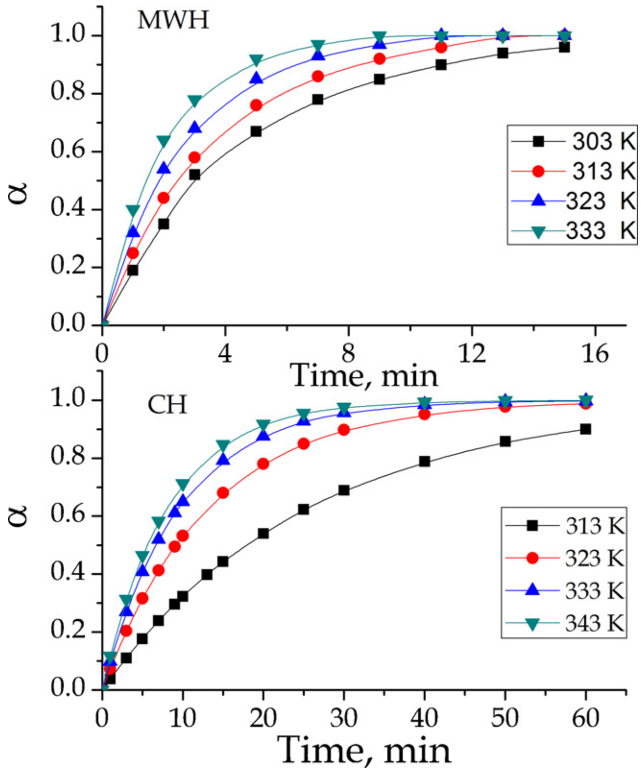

Fig. 1. The isothermal conversion curves for sucrose hydrolysis under conventional and microwave reaction conditions.

sucrose hydrolysis, *i.e.*, the sucrose conversion was significantly increased compared to that obtained by CH at the same temperature.

With the purpose of finding a preliminary kinetic model for sucrose hydrolysis, the dependences of $d\alpha/dt$ on the degree of sucrose conversion for conventional and microwave heating were analyzed and are presented in Fig. 2.

The changes in $d\alpha/dt$ on the degree of sucrose conversion are of identical shape – linearly decreasing for each heating mode at all the investigated temperatures. The identical shapes of the changes in $d\alpha/dt$ on α imply a unique kinetic model under conventional and microwave conditions [36]. As can be seen, for the each heating mode, the maximal rate of hydrolysis was achieved at the beginning of the process, *i.e.*, when $\alpha \to 0$. The influence of temperature on $(d\alpha/dt)_{max}$ and kinetics parameters under the conventional and microwave heating are presented in Table 2.

The maximal rates of the isothermal acid catalyzed hydrolysis of sucrose were approximately 4–7 times higher for the microwave heating compared to the conventional heating. With the increasing temperature, the maximal hydrolysis rates exponentially increased for both modes of heating. Based on this, by using the Arrhenius equation, the kinetic parameters of sucrose hydrolysis ($E_{a,s}$ and $\ln[A_s \cdot f(\alpha)_{max}]$) were determined by application of the stationary point method and are also given in Table 2.

The stationary activation energy for hydrolysis under the microwave heating was ≈37% lower than that for conventionally heated sucrose hydrolysis.

Based on the shape of the dependence of rate of hydrolysis on the degree of sucrose conversion, it can be assumed that the rate of hydrolysis could be modeled with the equation of a first order chemical reaction. To ensure that the kinetics of sucrose hydrolysis could be modeled by the kinetics of a first order chemical reaction, the model-fitting method was used to determine kinetics model. For this purpose, the normalized experimental conversion curves of sucrose hydrolysis for conventional and microwave heating at the investigated temperatures were determined and are presented in Fig. 3.

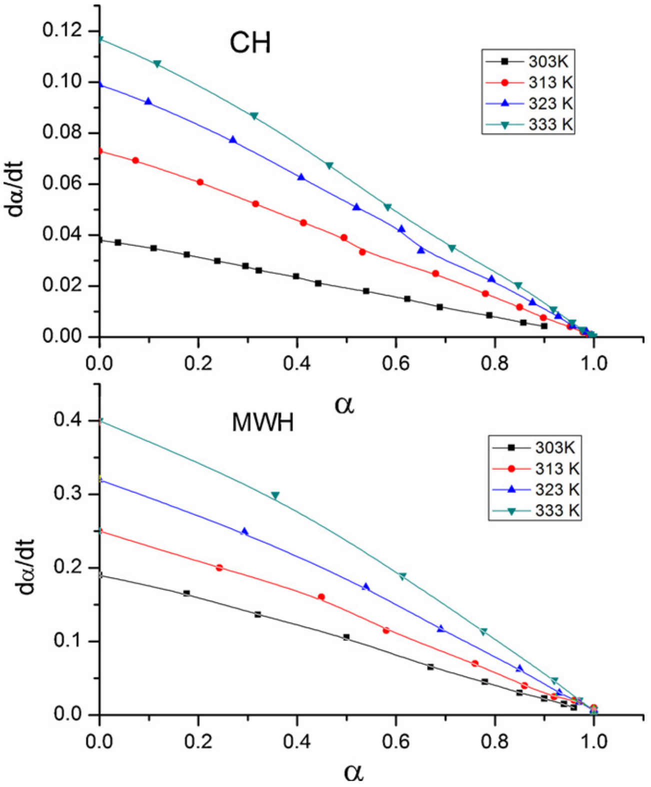

Fig. 2. The dependence of $d\alpha/dt$ on the degree of sucrose hydrolysis for CH and MWH.

It is obviously that the normalized experimental conversion curves of sucrose hydrolysis attained at conventional and microwave heating are mutually identical at all the investigated temperatures, which indicates the kinetic model of sucrose hydrolysis is the same and is independent of temperature within the investigated experimental conditions. By analytically comparing the $\alpha_{exp} = f(t_N)$ with normalized conversion curves $\alpha = f(t_N)$ for different solid state reaction models, it was established that the kinetics of acid catalyzed sucrose hydrolysis under all reaction conditions can be modeled with the equation characteristic for the kinetics of a first order chemical reaction:

$$\alpha = 1 - \exp(-k_M \cdot t) \tag{11}$$

where the k_M is a model constant for the first-order chemical reaction rate.

If the kinetics of hydrolysis occur in accordance with Eq. (11), then the dependences of $[-\ln(1-\alpha)]$ on reaction time should give straight lines. The dependences of $[-\ln(1-\alpha)]$ on reaction time for sucrose hydrolysis at different temperatures for microwave and conventional reaction conditions are shown in Fig. 4.

As can be observed from Fig. 4, the dependences of $[-\ln(1-\alpha)]$ on the time of hydrolysis are straight lines over the entire range of degrees of hydrolysis at all the investigated temperatures for both heating mode, thereby the validity of the selected kinetics model was confirmed, which enabled the calculation of the rate constant of the hydrolysis model. The effects of temperature for acid catalyzed sucrose hydrolysis on the k_M values and the kinetic parameters of the hydrolysis are given in Table 3.

The k_M values under the microwave reaction conditions were ≈5–7 times higher than the corresponding values under the conventional reaction conditions. The increasing the temperature of

Table 2
The effect of temperature on the $(d\alpha/dt)_{max}$ and kinetic parameters of sucrose hydrolysis for CH and MWH.

T, K	Conventional heating		Microwave heating	
	$(d\alpha/dt)_{max}$, min^{-1}	Kinetics parameters	$(d\alpha/dt)_{max}$, min^{-1}	Kinetics parameters
303		$E_{a,s} = 33.3 \pm 0.5$ kJ/mol $\ln[Af(\alpha_{max}/\text{min}^{-1})] = 9.6 \pm 0.2$	0.19	$E_{a,s} = 20.8 \pm 0.5$ kJ/mol $\ln A[Af(\alpha_{max}/\text{min}^{-1})] = 6.6 \pm 0.2$
313	0.038		0.25	
323	0.073		0.32	
333	0.099		0.4	
343	0.117			

Table 3
The influence of temperature on k_M and the kinetic parameters for sucrose hydrolysis under conventional and microwave reaction conditions.

T, K	Conventional process		Microwave process	
	k_M^{conv}, min^{-1}	Kinetics parameters	k_M^{mw}, min^{-1}	Kinetics parameters
303		$E_{a,M} = 41.5 \pm 2$ kJ/mol $\ln(A_M/\text{min}^{-1}) = 12.8 \pm 1$	0.204	$E_{a,M} = 25.15 \pm 1$ kJ/mol $\ln(A_M/\text{min}^{-1}) = 8.4 \pm 0.1$
313	0.039		0.287	
323	0.076		0.386	
333	0.105		0.510	
343	0.172			

the hydrolysis reaction led to an exponential increase in the k_M values for both types of reaction heating. The kinetic parameters of sucrose hydrolysis, activation energy and pre-exponential factor, were calculated by application of the Arrhenius equation and they are presented in Table 3.

The activation energy of sucrose hydrolysis under the conventional reaction conditions was ≈1.6 times higher than that for the microwave reaction conditions, while the value of ln *A* for the conventional hydrolysis process was ≈1.5 times higher than the corresponding value for the microwave process.

The increase in the rate of some chemical reactions and physico-chemical processes under the influence of microwave heating is most frequently explained by the existence of local overheating, *i.e.*, by the presence of “hot-spot” points [18–20].

The established values of the rate constants of the model and their changes with temperature under conventional and microwave reaction conditions enabled the effects of so-called “hot-spots” on the kinetics of the investigated process to be objectively evaluated. In fact, if it is assumed that the values of the activation energy and the pre-exponential factor obtained under the microwave reaction conditions were identical to the values for the conventional reaction conditions, then, based on the

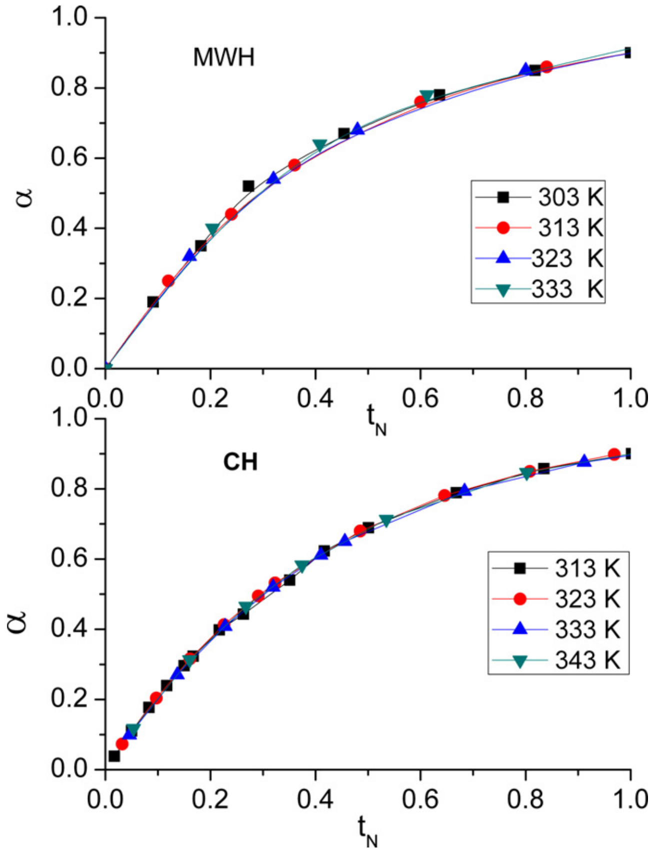

Fig. 3. The normalized experimental conversion curves for CH and MWH sucrose hydrolysis.

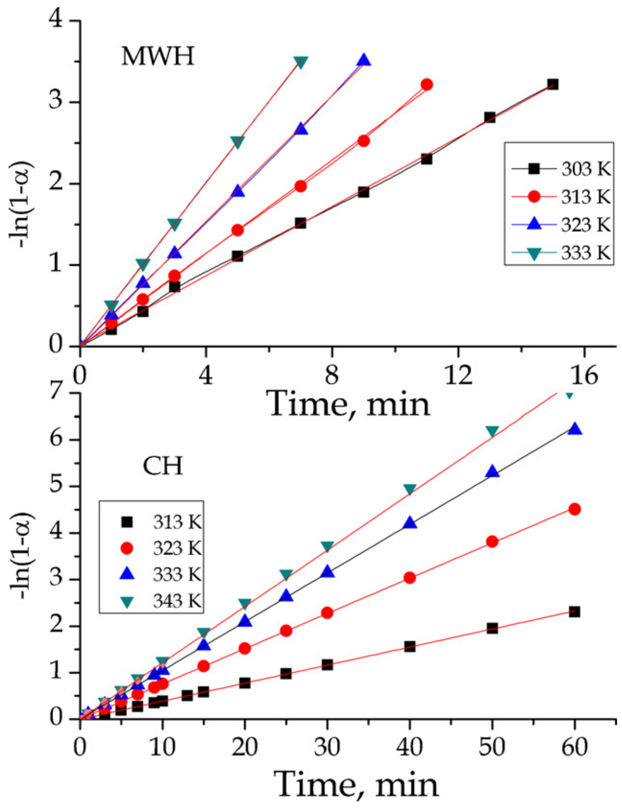

Fig. 4. The dependence of $[-\ln(1-\alpha)]$ on reaction time for CH and MWH sucrose hydrolysis.

Table 4
The values of the calculated microwave temperatures.

T, K	303	313	323	333
T^*, K	347	355	363	370

experimentally determined values of the rate constants of the model under the microwave reacting conditions (k_M^{mw}), it is possible to calculate the temperature of the reacting system under microwave reacting conditions – the calculated microwave temperature (T^*) using the following equation:

$$T^* = \frac{E^c_{a,M}}{R(\ln A^c_M - \ln k^T_{mw})} \tag{12}$$

where $E^c_{a,M}$ is the activation energy under conventional conditions, R is the universal gas constant, $\ln A^c_M$ is the pre-exponential factor for CH and k^T_{mw} is the reaction rate constant for MWH at a defined temperate. The values of the calculated microwave temperature T^* are given in Table 4.

As the calculated values of the temperatures of the reaction system are significantly higher than the real macroscopic values, it can be stated that the acceleration of sucrose hydrolysis under microwave condition was not the consequence of the existence of "hot spots" in the reaction system.

With the aim of assessing the possible complexity of the kinetics of the investigated reaction, the method of Vyazovkin was applied to examine the complexity of the kinetics of this process [37]. In order to apply the method of Vyazovkin, the dependences of $E_{a,\alpha}$ on the degree of conversion were established by the Friedman differential isoconversional method.

By using this method, the values of $E_{a,\alpha}$ were determined for different degrees of conversion. The dependences of $\ln(\mathrm{d}\alpha/\mathrm{d}t)_\alpha$ on $1/T$ are given in Fig. 5 for different degrees of hydrolysis.

As the dependences of $\ln(\mathrm{d}\alpha/\mathrm{d}t)_\alpha$ on $1/T$ for all degrees of sucrose hydrolysis gave straight lines, based on their slopes and intercepts, the kinetic parameters sucrose hydrolysis ($E_{a,\alpha}$ and $\ln A_\alpha$) were determined. The dependences of $E_{a,\alpha}$ as a function of the degree of sucrose hydrolysis for microwave and conventional reaction conditions are presented in Fig. 6.

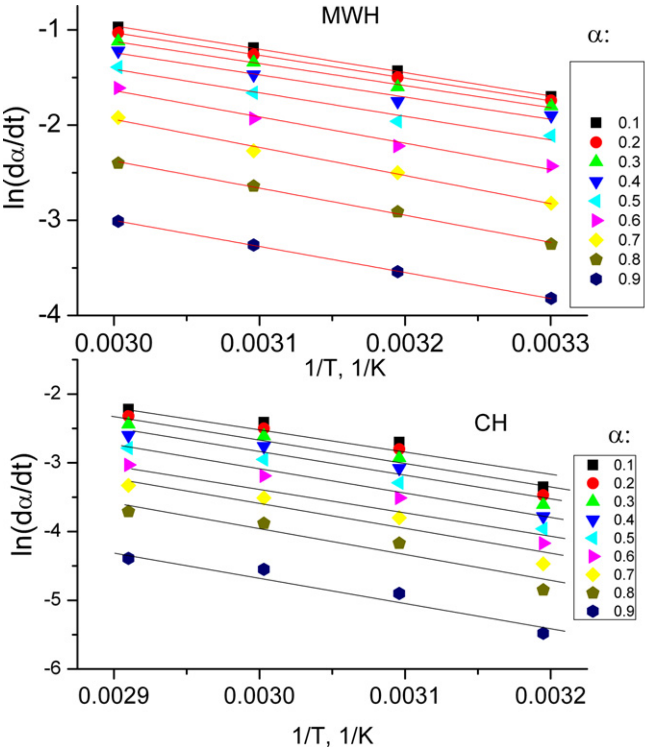

Fig. 5. The dependences of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ on $1/T$ for different degrees of sucrose hydrolysis.

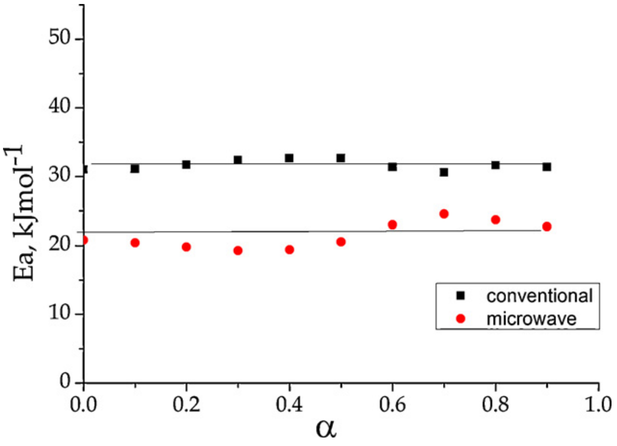

Fig. 6. The dependence of $E_{a,\alpha}$ on the degree of sucrose hydrolysis.

It is obvious that the activation energy is practically independent of the degree of sucrose hydrolysis for both heating modes and that the values of E_a for microwave heating were lower over all degrees of sucrose hydrolysis than those for the conventional heating hydrolysis. Therefore, as the independence of $E_{a,\alpha}$ on the degree of sucrose hydrolysis is characteristic for an elementary (single-stage) processes [38], it may be concluded that the investigated process of acid catalyzed sucrose hydrolysis on an ion-exchange resin presents an elementary chemical reaction with a unique kinetic model and mechanism and that the microwave field does not lead to changes in the mechanism of the process.

The established decrease in the values of activation energy and $\ln A$ under microwave heating compared to the conventional heating permit the possibility of an entirely new explanation for the influence of microwave heating on the kinetics of chemical reactions. The essence of this novel approach is the existence of a functional relationship between the values of the kinetic parameters of sucrose hydrolysis for conventional and microwave reacting conditions, which is expressed as:

$$\ln A_F = 1.646 + 0.268 E_{a,F} \tag{13}$$

where $E_{a,F}$ and $\ln A_F$ are the activation energy and pre-exponential factor in a defined physical field (thermal or microwave). The form of Eq. (18) is recognized as the equation of the compensation effect, which is in relation to distinct changes in the conditions of a reaction or process [39].

In accordance with the model of selective energy transfer, the existence of a compensation effect is explained as a consequence of resonant transfer of the necessary amount of vibrational energy from an energetic reservoir (catalyst) onto a reacting molecule. The main idea of the model of selective energy transfer is a state of resonance between a vibrational mode of the catalyst (ω) and a vibrational mode of a reacting molecule (ν), which is most likely to carry the reactant towards the shape and form of the "activated complex". This activation requires a transfer of resonance energy from the catalyst to the reactant and when the reactant has received a suitable number of vibrational quanta, the reaction proceeds [40]. Treating this resonance system as a classical forced, damped harmonic oscillator, an empirical Arrhenius equation can be obtained:

$$\ln k = \ln A + \frac{\omega}{\nu^2 - \omega^2}\left[\pm\frac{\pi}{2} - \mathrm{arctg}\frac{\nu\omega}{2(\nu^2 - \omega^2)}\right]\frac{\sum_i \Delta E_i}{hc} - \frac{E_a}{RT} \tag{14}$$

where $\Delta E_i = hc\nu_i$ is the energy increment between the two levers n_i and n_{i+1}, h is the Planck constant and c is the velocity of light.

As $n\sum_i \Delta E_i = E_a$, Eq. (14) can be rewritten in the following form:

$$\ln k = \ln A + \frac{E_a}{R}\left(\frac{1}{T_{ic}} - \frac{1}{T}\right) \tag{15}$$

where

$$T_{ic} = \frac{Nhc}{R}\,\frac{\nu^2-\omega^2}{\omega}\,\frac{1}{\pm(\pi/2) - \mathrm{arctg}(\nu\omega/(2(\nu^2-\omega^2)))} \tag{16}$$

For resonance conditions, Eq. (16) can be transformed to:

$$T_{ic} = \frac{Nhc\nu}{2R} = 0.715\nu \tag{17}$$

which ν is given in cm^{-1} and T_{ic} is in K.

According to Linert [41], the isokinetic temperature (T_{ic}) is in relationship with the slope of the equation of the compensation effect (b) as follows:

$$T_{ic} = \frac{1}{R\cdot b} \tag{18}$$

Therefore, by combining Eqs. (17) and (18), it is possible to get the expression for wave number of resonant frequency:

$$\nu = \frac{1}{0.719R\cdot b} \tag{19}$$

According to the model of selective energy transfer (SET) model, the E_a of reacting molecule equals to the change of its vibration energy level which is caused with resonant absorption of energy, which is given with the following expression:

$$E_a = Go(n) + RT \tag{20}$$

where $Go(n)$ is the vibration energy of the molecule in excess of the zero energy vibrational level, n is the vibrational quantum number.

Since the values of energetic terms of an anharmonic vibrator (reacting molecule) are defined with the expression (21) given by Herzberg [42]:

$$Go(n) = n\nu + n^2\nu x \tag{21}$$

then:

$$E_a - RT = n\nu + n^2\nu x \tag{22}$$

where x is the anharmonicity constant.

It is easy to transform Eq. (22) to (23):

$$E_a - RT = n\nu(1+nx) \tag{23}$$

Because the numeric value of x is small it can be neglected in first approximation and then, we can calculate approximate value of vibration quantum number n^* by using Eq. (23) as follows:

$$n^* = \frac{E_a - RT\,(\mathrm{J/mol})}{\nu\,(\mathrm{J/mol})} \tag{24}$$

As the value of the vibration quantum number has to be the whole number, we can rounded number of n^* to the whole number, where x is a negative number, we get the value of n.

Based on knowing values of E_a, ν and n, the x is calculated according to the expression:

$$x = \frac{((E_a - RT)/n\nu) - 1}{n} \tag{25}$$

Based on the parameters of the interactive compensation effect, the values of ν, n and x for microwave and conventional reacting conditions were calculated and the results are presented in Table 5.

Table 5
The values of ν, n and x for sucrose hydrolysis under CH and MWH.

Variable	CH	MWH
ν (cm^{-1})	625	625
n	6	4
x	−0.021	−0.056

The formation of "activated complex" for the reaction of sucrose hydrolysis under conventional and microwave reacting conditions, takes places due to the resonance between the oscillators of sucrose molecules and the ion-exchange resin which have the same values of wave number ($\omega = \nu = 625\,\mathrm{cm}^{-1}$). As the wave number of the resonant frequency corresponds to the so-called –OH out-of-plane deformation vibration [43] of the sucrose molecule, it may be concluded that activation of sucrose molecule for hydrolysis begins with the intensification of that vibration, which is in the following stage accompanied with the breakage of the glycoside bond. The presence of microwave field leads to a decreasing number of vibrational quanta which should be accepted from the sucrose molecule in order to form the "activated complex". That decreases, as in the previously given examples, is a consequence of the increased energy of the ground vibration level of the resonant oscillator of sucrose molecules due to the absorption of microwave energy. The decreased value of the pre-exponential factor and the enhanced values of the anharmonicity factor under microwave reaction conditions in comparison to conventional conditions are caused by the decreasing frequency of energy transfer from one to another oscillator which is provoked by the increase in vibrational energetic level of the oscillators.

5. Conclusions

The rates of isothermal heterogeneous sucrose hydrolysis by using acid ion-exchange resin IR-120H are higher for MWH 5–7 times against the CH. The MWH does not lead to the change in the kinetics model of heterogeneous sucrose hydrolysis. The values of kinetics parameters of hydrolysis under the MWH are lower than the corresponding values under the CH.

The established decreases in the activation energy and increases in the pre-exponential factor under the MWH in comparison to the CH is explained with the increase in the energy of ground vibrational level of the –OH out-of-plane deformation in sucrose's molecule and with the decrease in its anharmonicity factor which is caused with the selective resonant transfer of energy from the energetic reservoir-heating bath to the –OH-oscillators in sucrose molecules.

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