Uticaj mikrotalasnog zagrevanja na kinetiku hemijskih reakcija i fizičkohemijskih procesa

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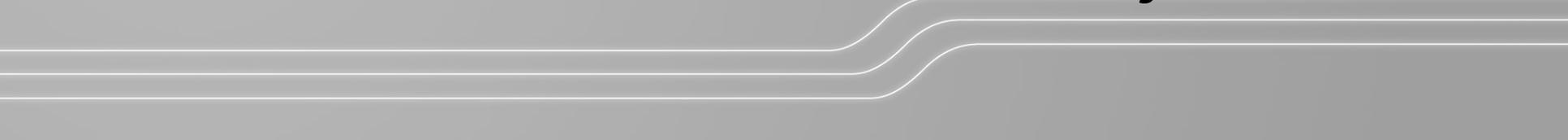
- Microwave heating is a widely accepted, non-conventional energy source which is now applied in numerous fields.

- Dramatically reduces reaction times
- Increases product yields
- Enhance product purities by reducing unwanted side reactions

The effect of microwave irradiation:
- thermal effects - overheating (Baghurst & Mingos, 1992),
- hot-spots (Zhang et. al., 1999),
- selected heating (Raner et. al., 1993),
- specific microwave effects (Hoz et. al., 2005).

- The thermal effects are connected with the different characteristics of microwave dielectric heating and conventional heating

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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

Table 1. The basic characteristics of microwave and conventional heating

Microwave heating (MWH) significantly:

- accelerates the rate of chemical reactions and physico-chemical processes,
- gives higher yields and improve properties of the products.

Microwave heating is a widely accepted, non-conventional energy source for organic synthesis and different physico-chemical processes:

- sintering, nucleation and crystallization,
- combustion synthesis,
- calcination,
- solvent-free reactions,
- heterogeneous catalysis and
- combinatorial chemistry

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

- Berlan et al., 1998, observed the acceleration of a cycloaddition reaction under isothermal microwave reaction conditions and explained the change in entropy of the reaction systems.

- Microwave enhanced the imidization reaction of a sulfone and ketone group-containing polyamic acid, which Lewis et al., 1992, 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.

- Rybakov and Semenov, 1994, 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.

- The ability of microwave radiation to excite rotational transitions and thus enhance the internal energy of a system was used by Strauss and Trainor, 1995, to explain the effects of microwave fields on the kinetics of chemical reactions.

- Binner et al., 1995, 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 the increasing value of Arrhenius pre-exponential factor which further causes an acceleration of the synthesis of titanium carbide.

- Stuerga and Gaillard, 1996, explained the acceleration of the reaction rate in condensed states under microwave reaction conditions in comparison to conventional reacting conditions by the enhanced rate of collisions in condensed phases, which induces transfer between rotational and vibrational energy levels and reaction acceleration.

- Booske et al., 1997, used the existence of non-thermal energy distributions to explain microwave-enhanced solid-state transport.

- Based on the experimentally confirmed decrease in the values of the activation energy of sodium bicarbonate decomposition under microwave reaction conditions, Shibata et al., 1996, 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.

- Perreux and Loupy, 2000, studied and classified the nature of the microwave effects considering the reaction medium and reaction mechanism, *i.e*., the polarity of the transition state and the position of the transition state along with the reaction coordinate.

- Blanco and Auerbach, 2003, theoretically proved that the energy of a microwave field is initially transferred to select molecular modes (transition, vibration and/or rotation) and used this information to explain the inverse desorption of benzene and methanol from zeolite, compared to thermal desorption.

- Conner and Tumpsett, 2008, explained specific microwave effects with the capability of microwaves to change the relative energies of rotation of intermediates in a given sequences.

The aim:

- Presents the results of investigations of the kinetics of
  - under conventional and microwave conditions for

- a) <u>chemical reactions</u>: isothermal PAA hydrogel formation, fullerole formation, and sucrose hydrolyses
- b) <u>physicochemical process</u>: ethanol adsorption and PAM hydrogel dehydration;

  - present the effects of microwave reaction conditions on:
- -kinetics model,
- -values of kinetic parameters,
- -the complexity of the kinetics of the investigated processes

- To explain the effects of a microwave field on the kinetics of chemical reaction and physico-chemical processes.

The Microwave instrument

Commercially available monomode microwave unit
- Discover, CEM Corporation, Matthews, North Carolina, USA

Methods used to evaluate the kinetic model and kinetic parameters

- Model-Fitting Metod

- Differential isoconversion method (Friedman's method)

Model-Fitting Metod

According to the model-fitting method the kinetic reaction model 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.

Model-Fitting Metod

The model-fitting method is based on the following. The experimentally determined conversion curve $\alpha exp = f(t)T$ has to be transformed into the experimentally normalized conversion curve $\alpha exp = f(tN)T$, where tN is the so-called normalized time. The normalized time, tN, was defined by the equation:

Model-Fitting Metod

$$t_N = \frac{t}{t0.9}$$

where t0.9 is the moment in time at which α=0.9.

The kinetics model of the investigated process was determined by analytically comparing the normalized experimentally conversion urves 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 one gives minimal values.

Table 2.
The set of kinetics models used to determine the kinetics model of ethanol adsorption

Model	Reaction mechanism	General expression of the kinetics model, $f(\alpha)$	Integral form of the kinetics model, $g(\alpha)$
P1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
P2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
R1	Zero-order (Polany-Winger equation)	1	α
R2	Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
R3	Phase-boundary controlled reaction (contracting volume, i.e., tridimensional shape)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
F1	First-order (Mampel)	$(1-\alpha)$	$-\ln(1-\alpha)$
F2	Second-order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
F3	Third-order	$(1-\alpha)^3$	$0.5[(1-\alpha)^{-2}-1]$
A2	Avrami-Erofe'ev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3	Avrami-Erofe'ev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A4	Avrami-Erofe'ev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
D1	One-dimensional diffusion	$1/2\alpha$	α^2
D2	Two-dimensional diffusion (bidimensional particle shape)	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha) + \alpha$
D3	Three-dimensional diffusion (tridimensional particle shape) Jander equation	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
D4	Three-dimensional diffusion (tridimensional particle shape) Ginstling-Brounshtein	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
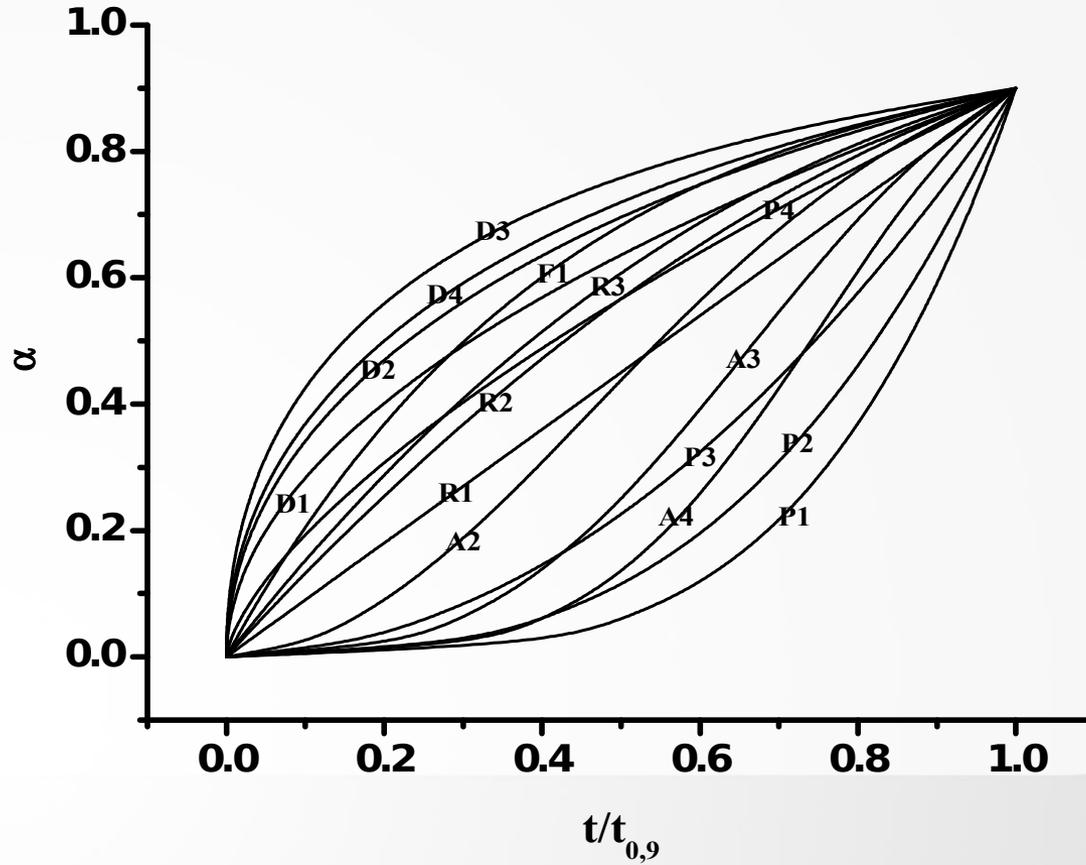
Fig 2: Modelne krive

Differential isoconversion method

The activation energy of the investigated adsorption process for various degrees of conversion was established by the Friedman method-based on the follows.

The rate of the process in condensed state is generally a function of temperature and conversion:

$$\frac{d\alpha}{dt} = \phi(T, \alpha)$$

(4)

i.e.

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

(5)

Differential isoconversion method

Where *dα/dt* is the reaction rate, is function of *α* and *T*, α is the conversion degree, the rate constant *t* the time, *T* the temperature, and is the reaction model associated with a certain reaction mechanism. The dependence of the rate constant on temperature is ordinary described by the Arrhenius law:

$$k = A \exp(-\frac{Ea}{RT})$$

(6)

where *Ea* is the activation energy, *A* is the pre-exponential factor and *R* is the gas constant

Differential isoconversion method

Then we get the following equation:

$$\frac{d\alpha}{dt} = A\exp(-\frac{Ea}{RT}) \cdot f(\alpha)$$

(7)

Accepting that the reaction rate constant is an extent of conversion and is only function of temperature, which is known as the iso-conversional principle of Friedman, the equation is easily transformed to:

$$\ln \cdot (\frac{d\alpha}{dt})_\alpha = \ln(A(f(\alpha))) - \frac{Ea \cdot \alpha}{RT}$$

(8)

That allows the evaluation of the activation energy for particular degree of conversion:

Isothermal kinetics of acrylic acid polymerization and crosslinking
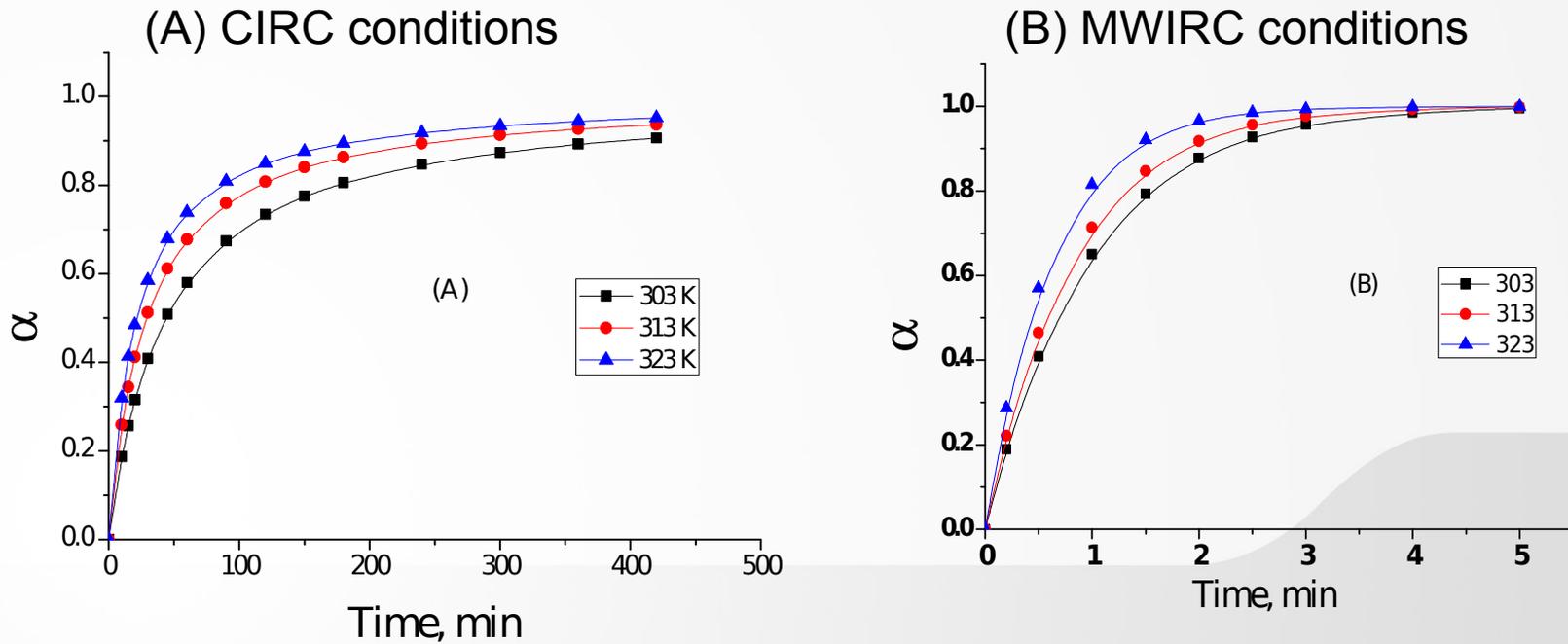
Fig 3: Conversion curves for the formation of PAA hydrogel

Dependence of *dα/dt* on the degree of PAA hydrogel formation under (A) conventional conditions and (B) microwave conditions

T, K	Conventional process		Microwave process	
	$(dα/dt)_{max}$, [min^{-1}]	Kinetic parameters	$(dα/dt)_{max}$, [min^{-1}]	Kinetic parameters
303	0.019	$E_a=22\pm0.2$ kJ/mol ln A = 5±0.1	0.947	$E_a=17\pm0.3$ kJ/mol ln A=7±0.1
313	0.023		1.105	
323	0.032		1.433	

Kinetic model of :

second-order chemical reaction (CH)
first-order chemical reaction (MWH)
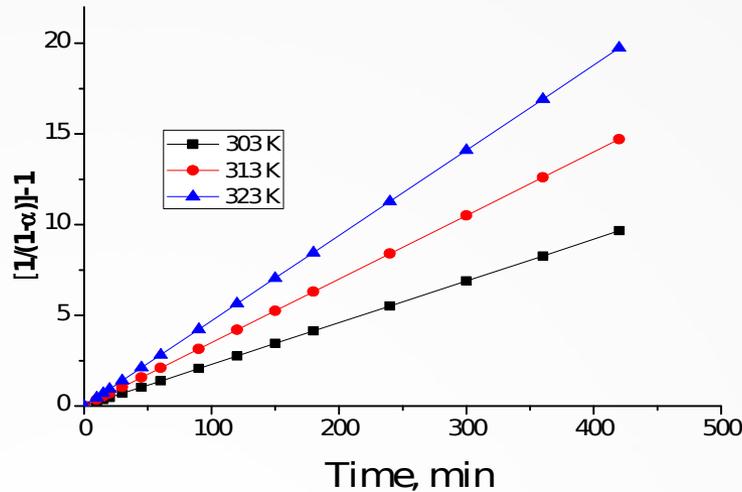
Fig 4. Isothermal dependence of [[1/(1- α)] -1] on reaction time for PAA hydrogel formation under the CH
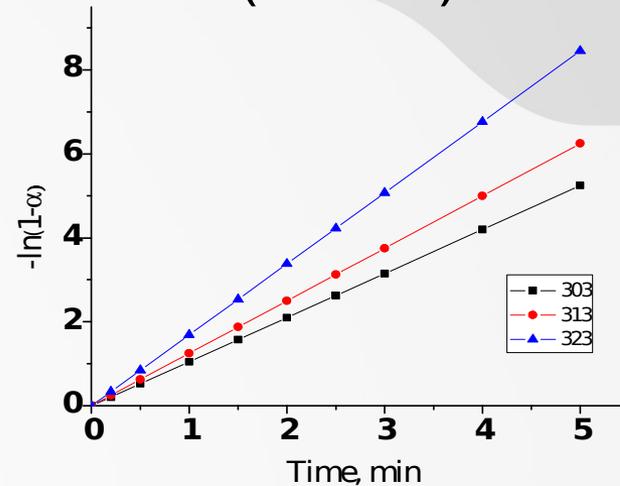
Fig 5. Isothermal dependence of [–ln(1-α)] on reaction time for PAA hydrogel formation under MWH

T, K	Conventional process		Microwave process	
	k, min^{-1}	Kinetic parameters	K, min^{-1}	Kinetic parameters
303	0.023	$E_{a,M}$=21±1 kJ/mol ln (A_M/min^{-1})= 9.4±0.2	1.008	$E_{a,M}$=17±1 kJ/mol ln (A_M/min^{-1})=8.6±0.2
313	0.035		1.180	
323	0.047		1.590	

$\ln A_f = 5.23 \pm 0.195\, E_{a,f}$
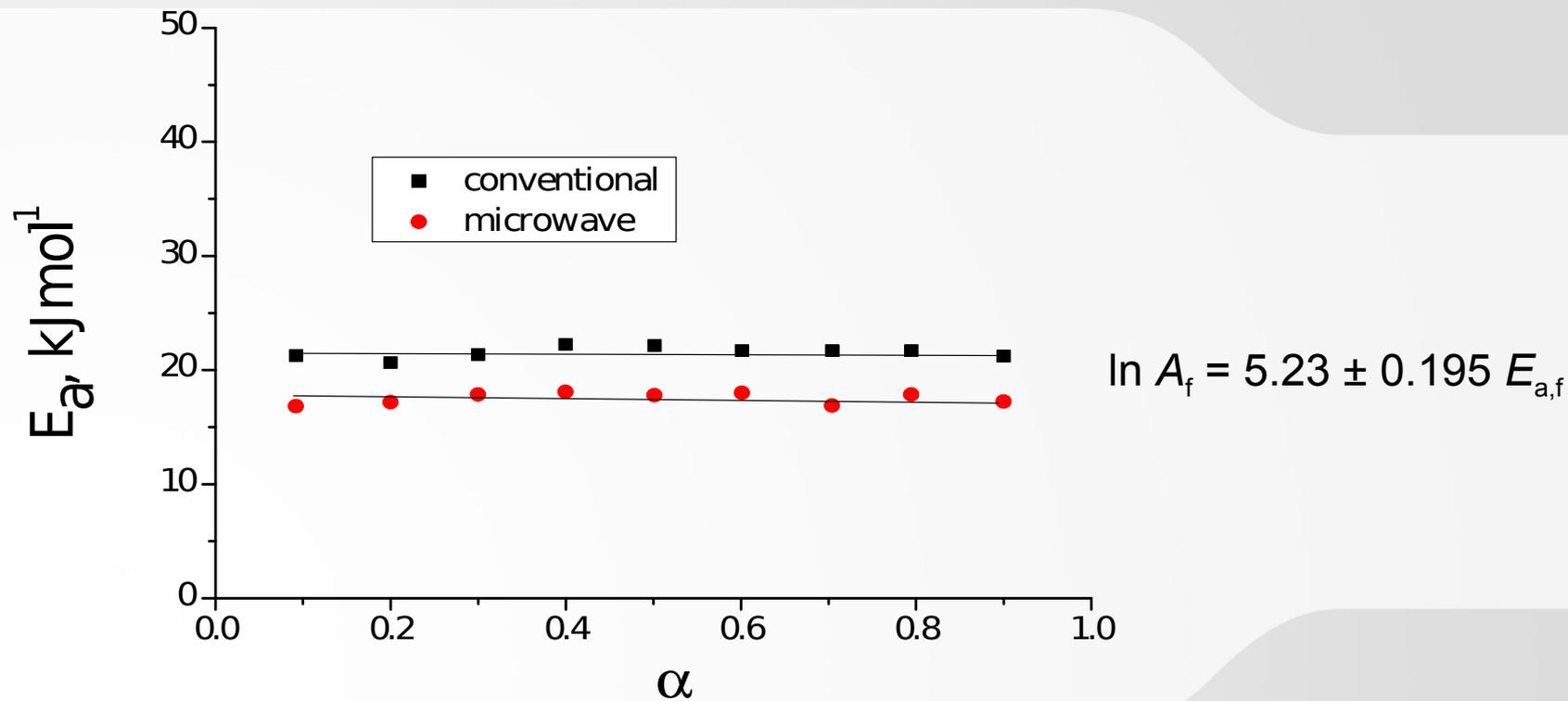
Fig 6. The dependence of $E_{a,\alpha}$ on the degree of conversion for PAA hydrogel formation

Larsson Model of selective energy

- During the interaction of a catalyst with reacting molecules, the existence of a compensation effect and the formation of an "active complex" (Larson, 1989) is explained as the consequence of transfer of the necessary amount of vibrational energy from an energetic reservoir onto the reacting molecule, which is aimed at "active complex" formation.

- The established changes in the kinetics parameters (decrease) can be explained with the decrease in: required amount of vibration energy necessary for "active complex" formation and in resonance frequency of the energetic transfer the between the oscillators under MWIRC in comparison to CIRC.

Larsson Model of selective energy

- It can be assumed that a reacting molecule can be modeled as a sum of normal oscillators and that that molecule convert into an "active complex" anytime when it accepts the necessary amount of energy (energy of activation) and that during the formation of such an "active complex", vibrational changes occur which are in relation with changes connected with the localization of the energy on a defined bond (normal oscillator).

Larsson Model of selective energy

Then, in accordance with the Larsson Model the wave number of the resonant oscillation (v) and the energy of activation (Ea) of the reaction can be calculated. The wave number of the resonant oscillation is given by:

$$v = \frac{0.715}{R \cdot b}$$
(9)

where b is the energetic parameter of the compensation effect equation, while the values of the activation energy is quantized and given as:

$$Ea = (nv + n^2 vx) + RT$$
(10)

where n is the number of quantum of vibrational energy transferred from one to another oscillator or from an energy reservoir („heat bath") to the resonant oscillator, which are necessary to overcome the energetic barrier (activation energy) and x is the anharmonicity constant of the oscillator.

Table 3: The values of v, n and x under CIRC and MWIRC

Variable	CIRC	MWIRC
v (cm^{-1})	429	429
n	4	3
x	−0.022	−0.0017

2. Isothermal kinetics of fullerol formation

Fig 7. The isothermal conversion curves for fullerol formation under (A) CIRC and (B) MWIRC
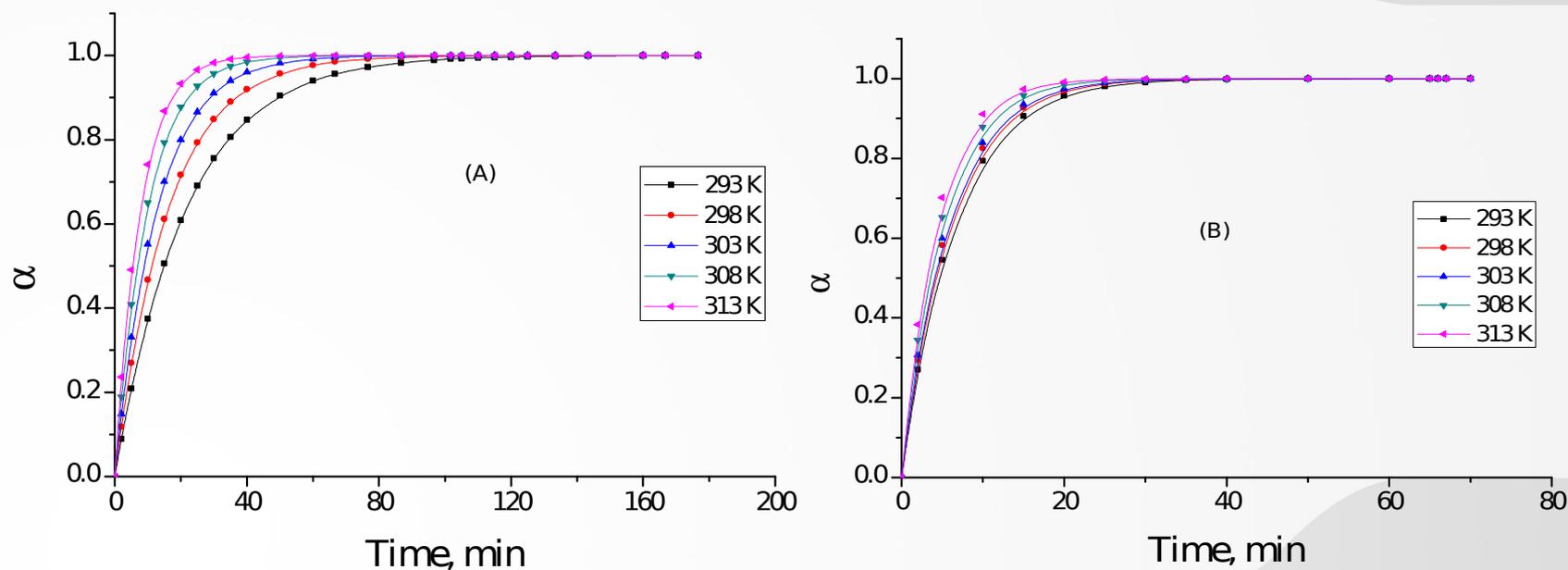
$$\alpha = 1 - \exp\left(-k_M \cdot t\right)$$

Figure 7.
The dependence of [–ln(1-α)] on reaction time for fullerol formation for (A) CIRC and (B) MWIRC
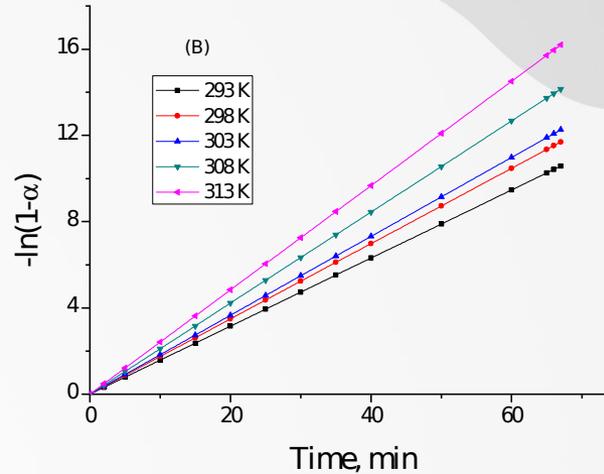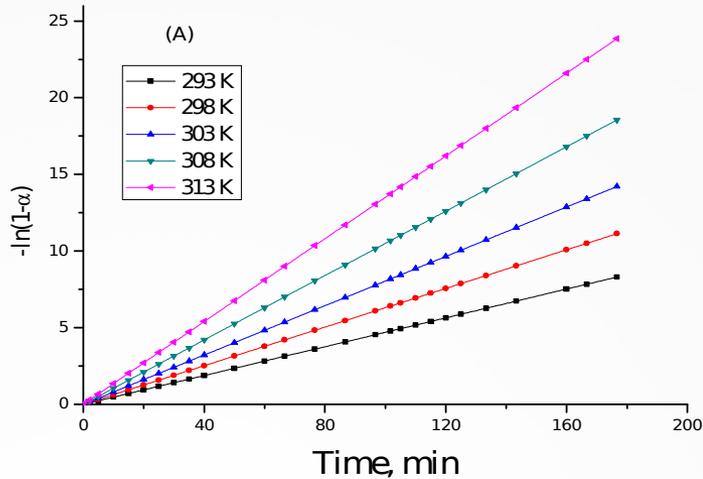
Table 4. The temperature influence on the model's reaction rate constants and the kinetics parameters for fullerol formation, for the conventional and the microwave reacting conditions

T, K	Conventional process		Microwave process	
	k, min^{-1}	Kinetics parameters	k, min^{-1}	Kinetics parameters
293	0.047	$E_{a,M}$=38±2 kJ/mol $\ln(A_M/\text{min}^{-1})=$ 12.6±0.5	0.101	$E_{a,M}$=10.5±0.5 kJ/mol $\ln(A_M/\text{min}^{-1})$=2.44±0.04
298	0.066		0.175	
303	0.080		0.186	
308	0.106		0.192	
313	0.135		0.211	

Fig 8.
Dependence of the *Ea* on the degree of fullerol formation
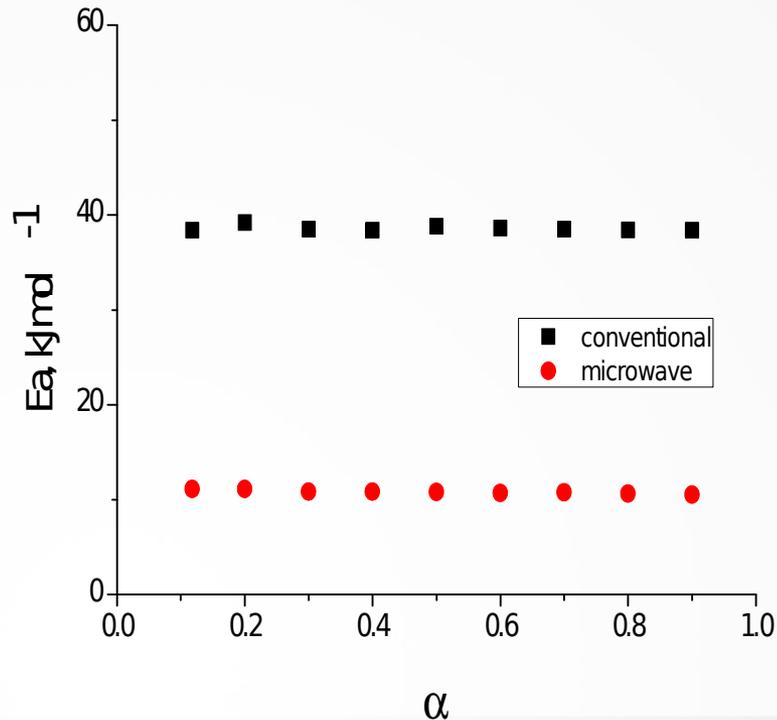
compensation effect equation:

$$\ln A_F = -1.440 + 0.368 E_{a,F}$$

Table 5. The values of the *ν, n* and, *x* under the CIRC and MWIRC

Parameter	CIRC	MWIRC
ν (cm⁻¹)	233	233
n	14	3
x	-0.004	-0.0013

Isothermal kinetics of acid catalysed sucrose hydrolyses under the CIRC and MWIRC
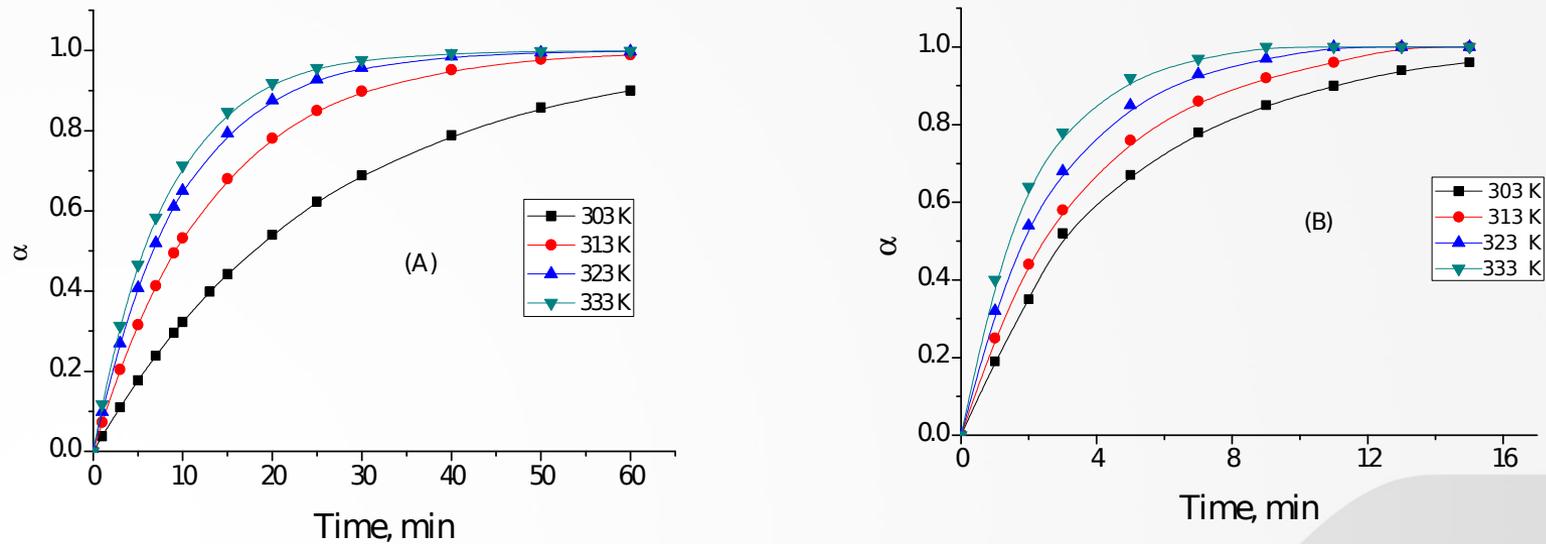
Fig 7. The isothermal conversion curves for sucrose hydrolyses

Isothermal kinetics of acid catalysed sucrose hydrolyses under the CIRC and MWIRC
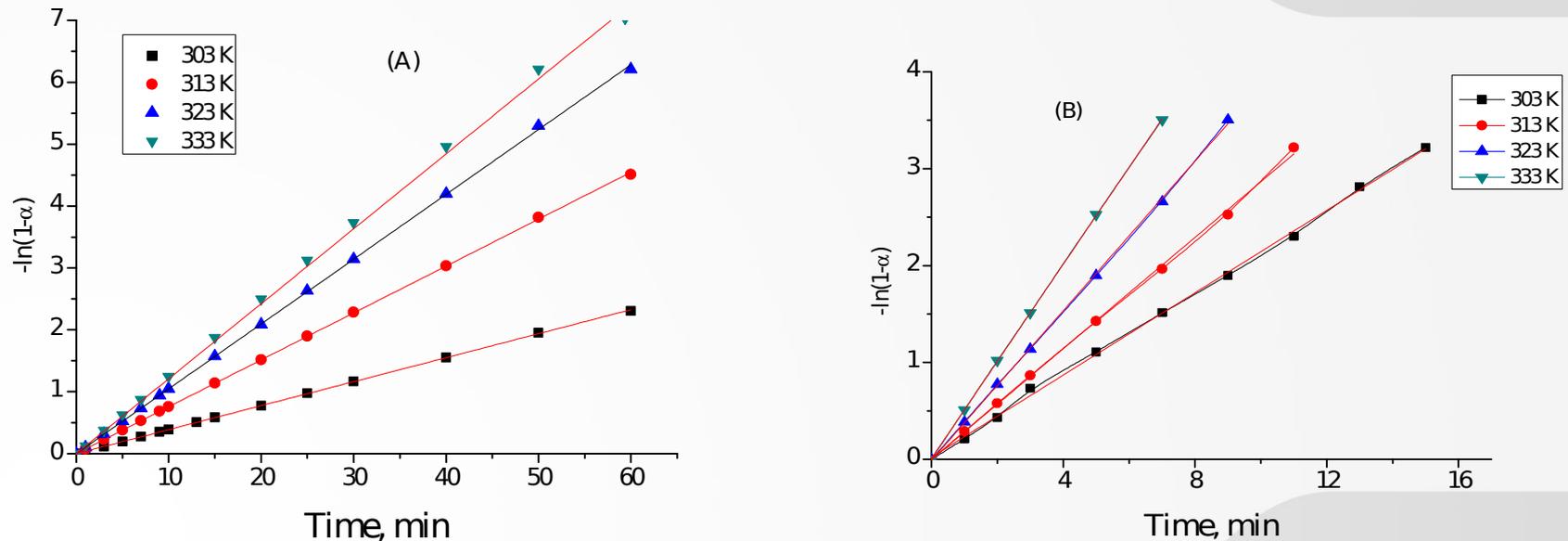
Fig 8. Dependence of [–ln(1-α)] on reaction time

$$\alpha = 1 - \exp\left(-k_M \cdot t\right)$$

Table 6. The temperature influence on the k_M and the kinetic parameters for sucrose hydrolyses under the conventional and the microwave reacting conditions

T, K	Conventional process		Microwave process	
	k, min^{-1}	Kinetics parameters	k, min^{-1}	Kinetics parameters
303	0.024	$E_{a,M}=32\pm2$ kJ/mol $\ln(A_M/\text{min}^{-1})= 9\pm1$	0.204	$E_{a,M}=25.15\pm1$ kJ/mol $\ln(A_M/\text{min}^{-1})=8.4\pm0.1$
313	0.039		0.287	
323	0.076		0.386	
333	0.105		0.510	
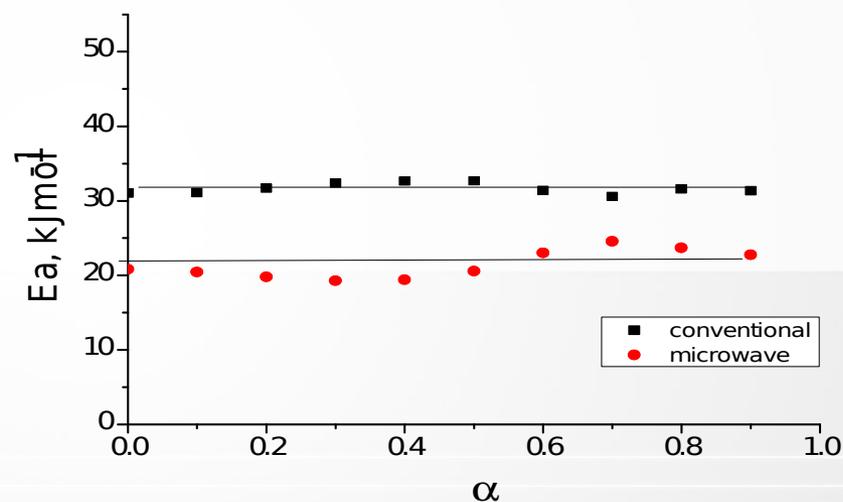
Table 7. The values of the ν, n, x for sucrose hydrolyses, under the CIRC and MWIRC		
Variable	**CIRC**	**MWIRC**
ν **(cm⁻¹)**	723	723
n	4	3
x	-0.035	-0.042

$$\ln A_F = 5.407 + 0.119 E_{a,F}$$

Isothermal kinetics of ethanol adsorption from aqueous solutions onto carbon molecular sieve under the CH and MWH
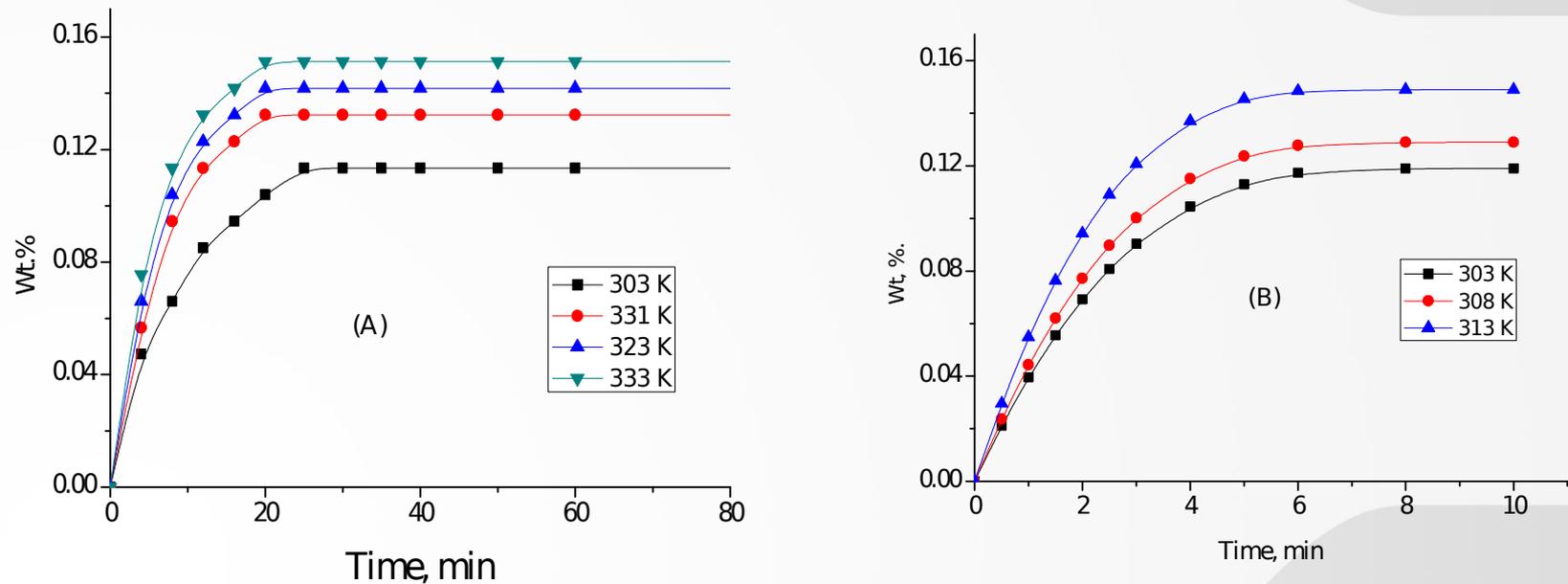
Figure 9. The kinetic curves of ethanol adsorption on CMS-3A for (A) CH and (B) MWH

Isothermal kinetics of ethanol adsorption from aqueous solutions onto carbon molecular sieve under the CH and MWH
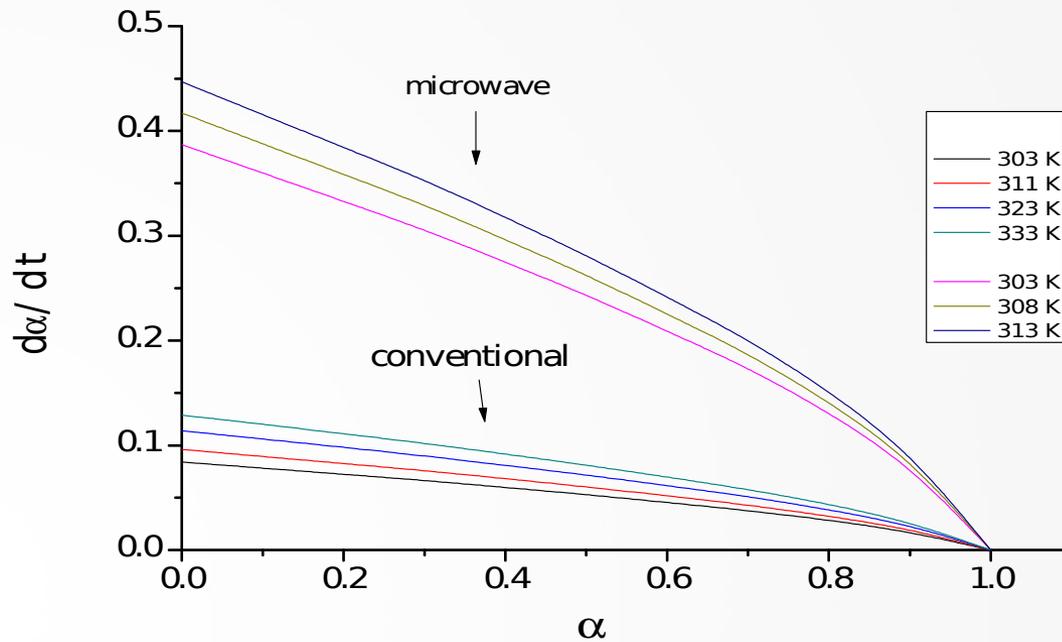
Figure 10. Dependence of *dα/dt* on the degree of ethanol adsorption

Fig 11. Dependence of *dα/dt* on the degree of ethanol adsorption
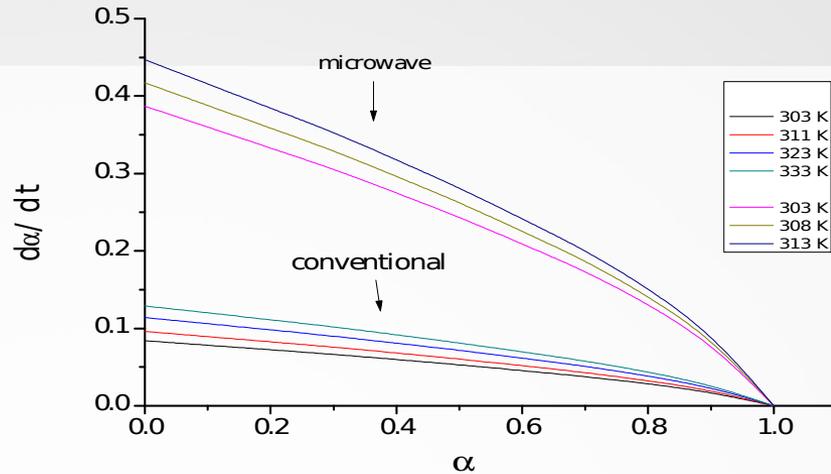
Table 8. Temperature influence on (*dα/dt*)*max* for adsorption of ethanol and kinetic parameters, for the CIRC and MWIRC processes

Conventional process			Microwave process		
T, K	(*dα/dt*)$_{max}$, [min^{-1}]	Kinetics parameters	T, K	(*dα/dt*)$_{ma}$ [min^{-1}]	Kinetics parameters
303	0.084	E_a=11.9±0.2 kJ/mol lnA = 2.2±0.1	303	0.387	E_a=10.9±0.2 kJ/mol lnA=2.6±0.1
311	0.094		308	0.417	
323	0.114		313	0.447	
333	0.129				

Model fitting method :

$$\alpha = 1 - \left(1 - k_M \cdot t\right)^3$$
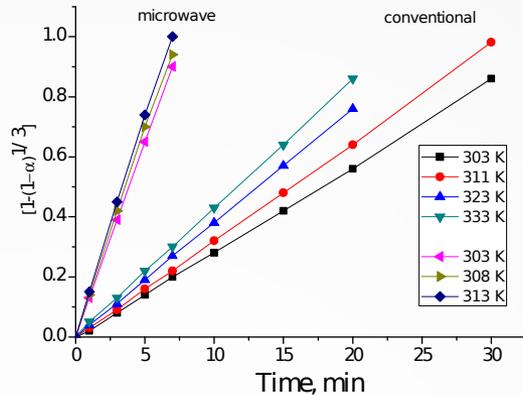
Fig 12. Dependence of *dα/dt* on the degree of ethanol adsorption
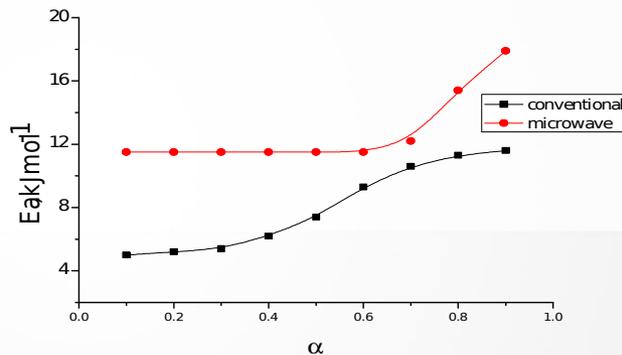
$$\ln A_\alpha^{conv} = -1.907 + 0.295 E_{a,\alpha}$$

$$\ln A_\alpha^{mw} = -1.937 + 0.223 E_{a,\alpha}$$

Table 9. The influence of temperature on model's kinetic constants of the ethanol adsorption rate and kinetic parameters, for the CIRC and MWIRC processes

Conventional process			Microwave process		
T, K	[min⁻¹]	Kinetics parameters	T, K	[min⁻¹]	Kinetics parameters
303	0.028	E_a=12±0.5 kJ/mol lnA=1.15±0.05	303	0.129	E_a=11.2±0.5 kJ/mol lnA=2.4±0.1
311	0.032		308	0.139	
323	0.038		313	0.149	
333	0.043				

Table 10. The values of the *v, n and , x* under the CIRC and MWIRC of ethanol adsorption process

Variable	CIRC	MWIRC
v (cm⁻¹)	292	386
n	3	2
x	-0.025	-0.0016

Isothermal dehydration of poly(acrylic -*co*-methacrylic acid) hydrogels

Fig 13. The conversion curves for dehydration process of the hydrogel
(A) conventional and (B) microwave
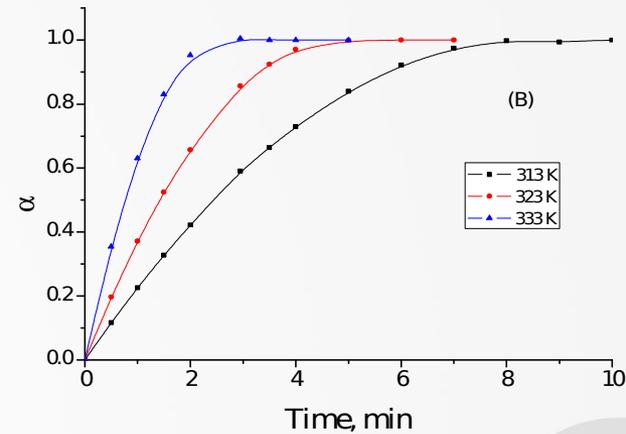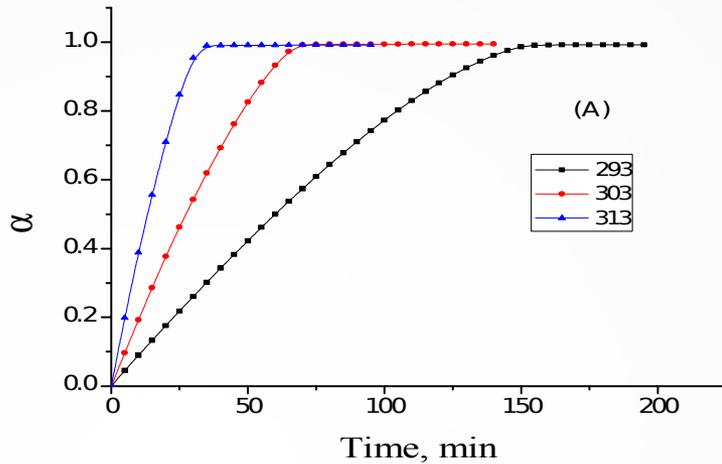
A phase-boundary controlled reaction model (contracting area) : $\left[1-\left(1-\alpha\right)^{1/2}\right] = k_M \times t$

Fig 14. The dependence of on time for dehydration process of the hydrogel (A) CH and (B) MW
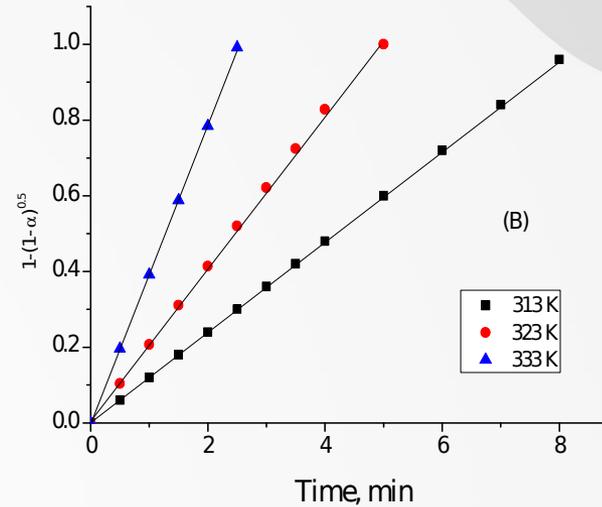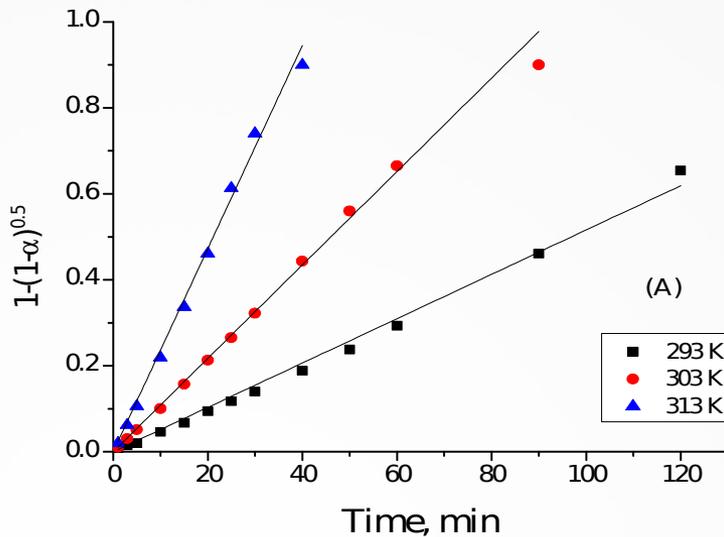
T, K	Conventional process		T, K	Microwave process	
	k_M [min^{-1}]	Kinetics parameters		k_M [min^{-1}]	Kinetics parameters
293	0.0052	E_a=58.5±0.5 kJ/mol ln A = 18.5±0.2	313	0.120	E_a=51.6±0.5 kJ/mol ln A=17.7±0.2
303	0.0109		323	0.207	
313	0.0236		333	0.393	

Table 11. The effect of temperature on the *kM* values and kinetic parameters of the isothermal dehydration of the PAM hydrogel by the CH and the MWH

Fig 15.
The dependence of the *Ea* on the dehydration degree of the hydrogel
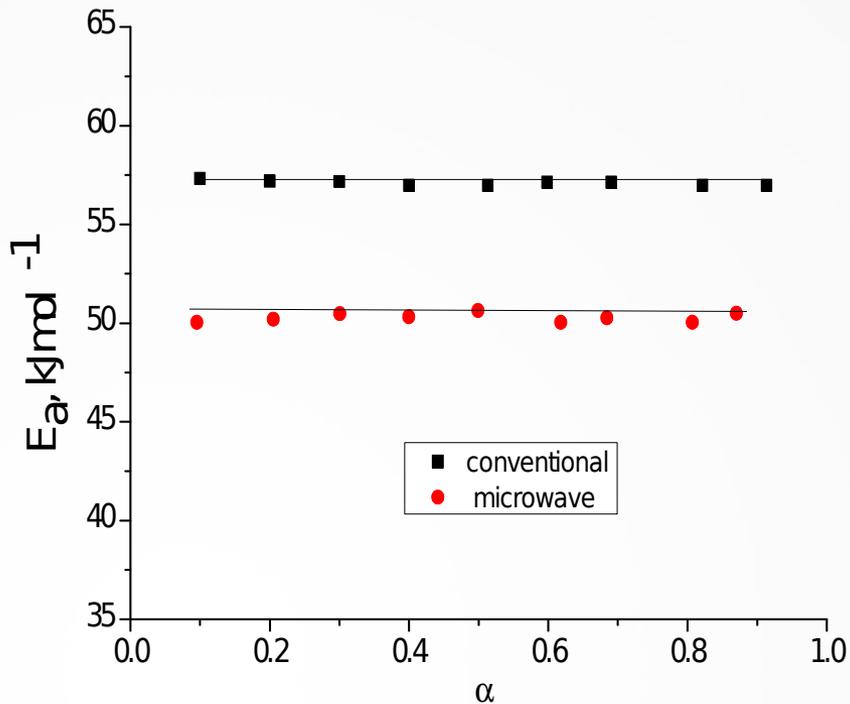
Table 12. The values of v, n, and χ under conventional and microwave conditions

Variable	CIPC	MWIPC
v	726	726
n	7	6
χ	−0.011	−0.015

$$\ln A_{\mathrm{F}} = 11.71 + 0.116 \times E_{a,\mathrm{F}}$$