



Kinetic investigations on the modified chitosan catalyzed solvent-free synthesis of jasminaldehyde

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ABSTRACT

Kinetic investigations were performed for the modified chitosan catalyzed solvent-free synthesis of jasminaldehyde. The rates of formation for both jasminaldehyde and 2-pentyl nonenal were calculated. Kinetic investigations were performed as a function of the amount of the catalyst, heptanal, benzaldehyde and temperature. The rate of formation of jasminaldehyde was first order with respect to the lower amount of catalyst and showed saturation at higher amounts. A critical amount of heptanal was needed for the formation of jasminaldehyde. The maximum rate was showed for heptanal–benzaldehyde ratio of 1:4. The Langmuir–Hinshelwood rate model used for the formation of jasminaldehyde was found to fit with R^2 value of 0.95. The computational studies were indicative for the rate determining steps, as the reaction of benzaldehyde with deprotonated heptanal on surface for jasminaldehyde, and proton abstraction for the formation of 2-pentyl nonenal. Mass transfer effects for the condensation reaction were studied.

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1. Introduction

α -Pentyl cinnamaldehyde is a perfumery chemical of jasmine odor with commercial name jasminaldehyde [1]. It is synthesized by the condensation of heptanal with benzaldehyde in the presence of a catalyst. The used catalysts are liquid alkalis like NaOH and KOH [2]. The liquid alkalis have drawbacks of environmental pollution due to alkali wastes, lack of catalyst recycling and post reaction treatment of the spent catalyst. Thus the development of heterogeneous solid catalysts can be a substitute for overcoming these drawbacks.

There are few reports where the heterogeneous solid catalysts like H-beta zeolites, Al-MCM-41, ALPO, Na-ALPO [3], magnesium organo silicate [4] and hydrotalcite [5] have been investigated for the synthesis of jasminaldehyde. Development of a heterogeneous catalyst based on biopolymer can gain a much attraction towards the synthesis of jasminaldehyde. Chitosan, a biopolymer derived from naturally occurring chitin have the potential to act as a solid base catalyst. However the research in this regard is very scanty [6–9]. Chitosan were extensively studied for its bio-activity related to drug delivery and medical applications [10–12]. The investigations on chitosan, a biopolymer, have promising potential to develop eco-friendly catalyst for condensation reactions. A chitosan based solid base catalyst [6] was recently reported to be an efficient

catalyst for the condensation of heptanal and benzaldehyde. The catalyst was active by giving >99% conversion with major selectivity (84%) to jasminaldehyde by cross condensation along with small formation of the self condensation product.

Kinetics of such reactions play an important role to address the extent of the contribution of the catalyst towards the cross and self condensation products. The kinetics of condensation reactions were reported for the both self and cross condensations. The kinetics of self condensation of acetaldehyde using NaOH as catalyst was investigated by Bell and McTigue [13,14] and Guthrie [15]. Casale et al. have reported the kinetics of C_2 – C_8 aliphatic aldehydes [16]. Cross condensation of benzaldehyde–acetone [17,18], benzaldehyde–propanal [19], citral–acetone [20,21] and butyraldehyde–formaldehyde [22] are kinetically investigated.

Detail kinetic investigations are paid less attention for the synthesis of jasminaldehyde by condensation of benzaldehyde and heptanal. The possible products during the condensation are the cross and self aldol products, jasminaldehyde and 2-pentyl nonenal respectively. The endeavor of the present study is to investigate the reaction kinetics and mechanism of the synthesis of jasminaldehyde using heterogeneous chitosan a biopolymer as catalyst.

2. Experimental

2.1. Materials and methods

Benzaldehyde and heptanal were procured from Sigma–Aldrich and used without further purifications. NaOH and HCl were pur-

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Table 1
Physical properties of the catalyst.

Physical parameter	Value	Dimension
BET surface area	1.04	m ² g ⁻¹
Accessible amine group	45%	
Particle size	0.411 × 10 ⁻³	m

chased from s.d. Fine Chemicals, India for the synthesis of catalyst. The double distilled milli-pore water was used during the synthesis of the catalyst. The catalyst was synthesized according to the method available in literature [6]. The physical properties of the synthesized catalyst are given in Table 1.

2.2. Aldol condensation and kinetic measurements

Benzaldehyde and heptanal were taken in the desired molar ratio with the required amount of the chitosan catalyst, in a two neck round bottom flask and 0.01 g decane was added to this mixture as an internal standard. One neck of the flask was connected with a condenser through which water at 18 °C was circulated. Other neck was blocked with silicon rubber septum. The flask was kept in an oil bath equipped with temperature controller and a magnetic stirring unit. The reaction was conducted under inert atmosphere (N₂) to inhibit the formation of corresponding acids from aldehyde. The product mixture was cooled down to room temperature after completion of the reaction and was filtered. The analysis of product mixture was carried out by GC (Shimadzu 17A, Japan) and GC-MS (Schimadzu QP-2010, Japan). The GC has 5% diphenyl and 95% dimethyl siloxane universal capillary column and flame ionization detector (FID). Repeated experiments were carried out under identical reaction conditions to ensure the reproducibility of the reaction.

For kinetic measurements, a series of kinetic experiments were carried out for the determination of the rates. Aliquots were withdrawn from the reaction mixture at different intervals and were analyzed by GC.

3. Results and discussion

3.1. Kinetic profile

The kinetic profiles in term of the consumption of heptanal and formations of condensation products are given in Fig. 1. With time

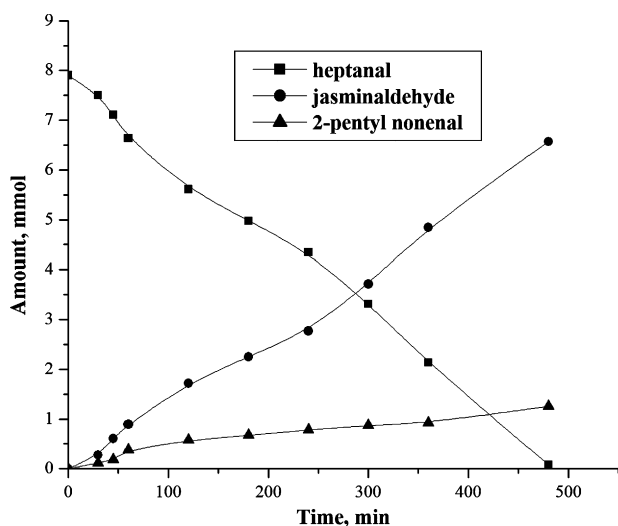


Fig. 1. Kinetic profile: catalyst = 100 mg, heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol and temperature = 140 °C.

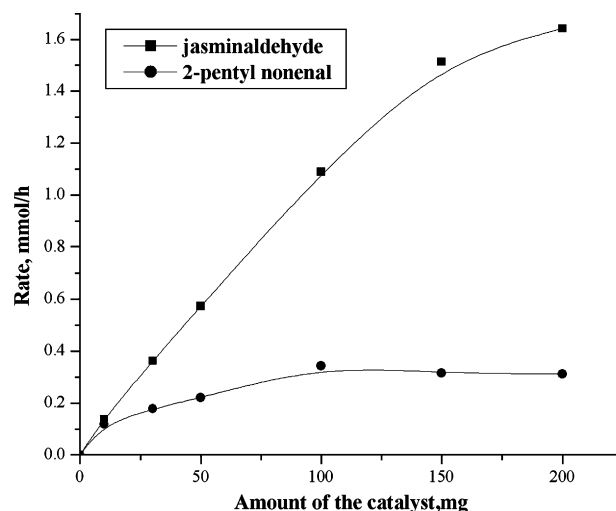


Fig. 2. Dependence of rate on the amount of catalyst: heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, temperature = 140 °C and 600 rpm.

almost linear decrease in the amount of heptanal and the formation of jasminaldehyde and self condensation product 2-pentyl nonenal were observed. Similar types of kinetic profile plots were made for all parametric variations and the rates were calculated from the slopes of early linear portions of the corresponding plots.

Kinetic investigations were performed as a function of the amount of the catalyst, heptanal, benzaldehyde and temperature by varying these parameters in a wide range. While varying a parameter, other parameters were kept constant under identical conditions. The effects of these parameters were investigated on the rates of the formation of jasminaldehyde and 2-pentyl nonenal. The rates of the formation of jasminaldehyde (Eq. (1)) and 2-pentyl nonenal (Eq. (2)) were calculated from the plots (Fig. 1) of their increasing concentration with time.

$$\text{Rate}_{\text{jasminaldehyde}}, \nu_1 = \frac{d[\text{jasminaldehyde}]}{dt} \quad (1)$$

$$\text{Rate}_{\text{2-pentyl nonenal}}, \nu_2 = \frac{d[\text{2-pentyl nonenal}]}{dt} \quad (2)$$

The rate was expressed in terms of mmol of product per unit time per gram of the catalyst [23].

3.2. Dependence of the rate on catalyst amount

The effect of the catalyst amount on rates of aldol condensation was studied between 10 and 200 mg of the catalyst and the corresponding results are given in Fig. 2. The rate of formation of jasminaldehyde was increased linearly indicating first order dependence with the catalyst amount. The increase in the amount of the catalyst increases the total available active sites and thus will increase the rate of reaction. When the amount of the catalyst was increased to higher amounts the rate tends to attain saturation. On the other hand the rate of formation of self condensation product, 2-pentyl nonenal, was increased slowly upto 100 mg of the catalyst and further the rate showed a saturation kinetics.

3.3. Dependence of the rate on heptanal

The dependence of rate on heptanal was studied between heptanal amounts of 0 and 31.6 mmol and was shown in Fig. 3. It was observed that the rate of formation of jasminaldehyde was very low at lower heptanal concentration and also a critical amount of the heptanal is needed for the cross aldol condensation to yield jasminaldehyde. The rate of formation of jasminaldehyde

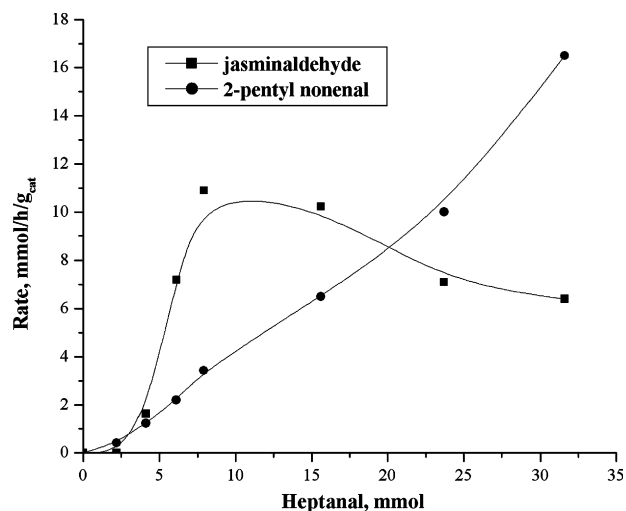


Fig. 3. Dependence of rate on heptanal: catalyst = 100 mg, benzaldehyde = 39.5 mmol, temperature = 140 °C and 600 rpm.

was increased after this critical amount and reaches a maximum and then decreased. Heptanal showed inhibition kinetics towards higher amounts. At higher amounts of the heptanal the self condensation was highly favored due to more availability of heptanal on the catalytic sites leading to the self condensation. The rate of formation of 2-pentyl nonenal was linearly increased with increase in the amount of heptanal.

3.4. Dependence of the rate on benzaldehyde

The dependence of rate on benzaldehyde was studied between benzaldehyde amounts of 0 and 79 mmol, and the result was shown in Fig. 4. The rate of formation of jasminaldehyde was increased with increase in the amount of the benzaldehyde. The highest rate was observed for heptanal to benzaldehyde ratio of 1:4, i.e. heptanal 7.9 mmol and benzaldehyde 31.6 mmol. The rate of formation of 2-pentyl nonenal was decreased with increase in the amount of benzaldehyde. The inhibition kinetics shown for formation of jasminaldehyde at higher benzaldehyde amount was due to higher adsorption of benzaldehyde onto the active sites of the catalyst leading to lower availability of the same for heptanal. This results in the formation of lower amount of carbanion from heptanal thus

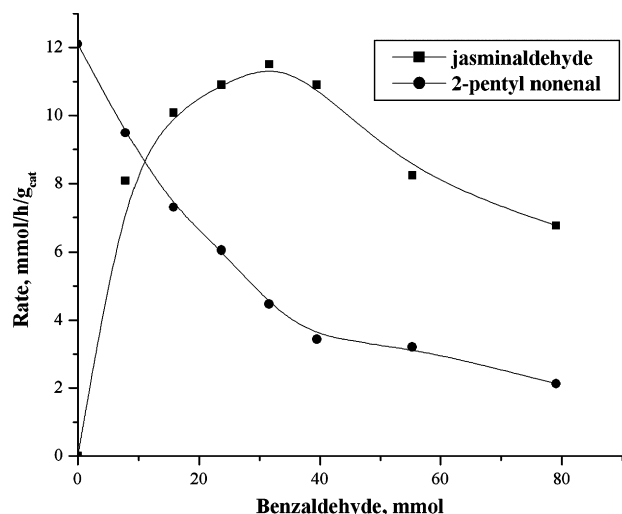


Fig. 4. Dependence of rate on benzaldehyde: catalyst = 100 mg, heptanal = 7.9 mmol, temperature = 140 °C and 600 rpm.

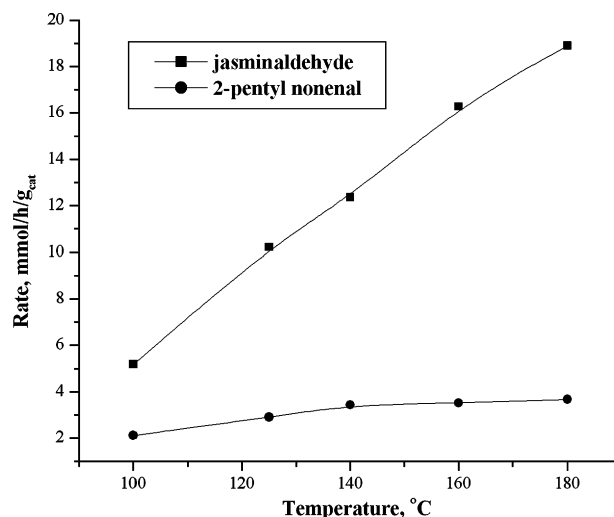


Fig. 5. Dependence of rate on temperature: catalyst = 100 mg, heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol and 600 rpm.

decreasing the rate of formation of both jasminaldehyde and 2-pentyl nonenal.

3.5. Dependence of rate on the temperature

The dependence of rate on the temperature was studied between 100 and 180 °C, and was shown in Fig. 5. The rate of formation of jasminaldehyde was increased with temperature. The rate of self condensation product was not much affected by the temperature. The activation energy was calculated from the Arrhenius plot and found to be 20.1 kJ/mol for the formation of jasminaldehyde.

3.6. Dependence of rate on the particle size and stirring speed

The catalytic experiments on the effects of the variation of particle size (0.211–0.853 mm) and stirring speed (200–800 rpm) were conducted and the corresponding results are given in Figs. 6 and 7 respectively. The particle size lower than 0.5 mm had no effect on the rates (Fig. 6) showing that the reactions were under kinetic regime with negligible internal mass transfer towards lower particle size. The particle size of 0.411 mm was taken for studying the effect of rate on stirring speed, Fig. 7. The rate of formation of jasm-

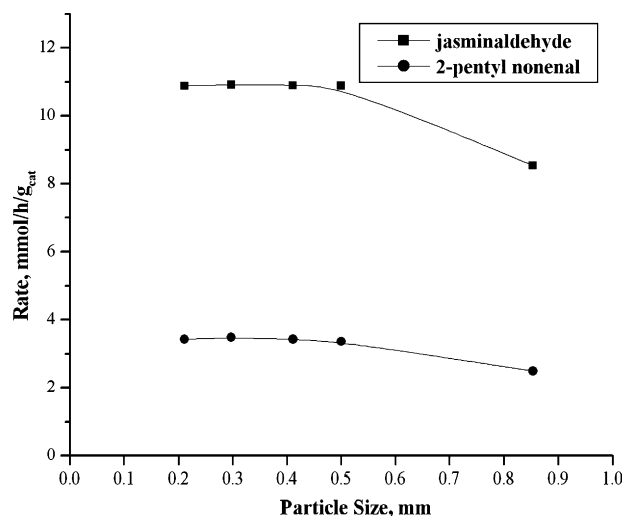


Fig. 6. Dependence of rate on particle size: catalyst = 100 mg, heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, temperature = 140 °C and 600 rpm.

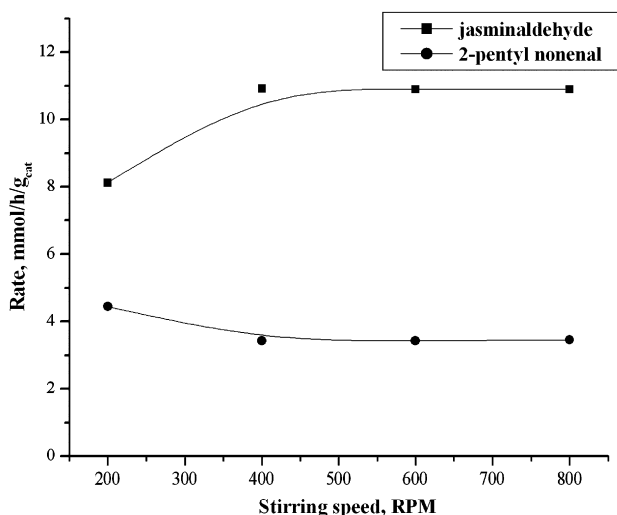


Fig. 7. Dependence of rate on stirring speed: catalyst = 100 mg, particle size = 0.411 mm, heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol and temperature = 140 °C.

naldehyde was lower at 200 rpm which increased at 400 rpm and remained almost same. The rate of formation of 2-pentyl nonenal, the self condensation product, was higher at lower stirring speed of 200 rpm and then decreased at 400 rpm and remained almost same. This shows that the aldol reactions were under kinetic regime with negligible mass transfer.

3.7. Mass transfer effects

Reaction engineering parameters have been studied for the mass transfer effects during the reaction to have an insight into external (liquid/solid interface) and internal diffusions (pore) using the Carberry number and Wheeler–Weisz criterion respectively [24].

The Carberry number (Ca) defined as the ratio of observed experimental reaction rate to mass transfer rate at liquid/solid interface is given as Eq. (3):

$$Ca = \frac{\text{Rate}_{\text{obs}} d_p \rho_p}{6k_f C_0 w} \quad (3)$$

where Rate_{obs} = total rate ($v_1 + v_2$) in mol s^{-1} , d_p = the particle diameter, ρ_p = particle density, C_0 = initial heptanal concentration, w = catalyst weight and k_f = mass transfer coefficient (obtained from Eq. (4)).

$$Sh = \frac{k_f d_p}{D} \quad (4)$$

where Sh is the Sherwood number and D is the diffusivity calculated using Wilke–Chang correlation (Eq. (5)),

$$D = \frac{7.4 \times 10^{-12} (\phi_s M_s)^{1/2} T}{\mu_s (V_A)^{0.6}} \quad (5)$$

where M_s is the molecular weight of solvent (benzaldehyde), ϕ_s is the association factor for solvent, μ_s is the viscosity of solvent at temperature T and V_A is the molar volume of solute (heptanal) at its normal boiling point. The V_A and μ_s in Eq. (5) are expressed in $\text{cm}^3 \text{mol}^{-1}$ and centi Poise respectively, to obtain D in $\text{m}^2 \text{s}^{-1}$.

Sherwood number (Eq. (6)) is obtained from the correlation,

$$Sh = 2 + 0.6Re^{1/2} Sc^{1/3} \quad (6)$$

where Re is the Reynolds number (Eq. (7)) for stirred vessel,

$$Re = \frac{\rho_s N S_d^2}{\mu_s} \quad (7)$$

Table 2
Physico-chemical data for mass transfer calculations.

Symbol	Quantity	Value	Dimension
T	Temperature	413	K
C_0	Concentration of heptanal	1580	mol m^{-3}
V_r	Reaction volume	5×10^{-6}	m^3
w	Catalyst weight	0.1×10^{-3}	kg
d_p	Particle diameter	0.411×10^{-3}	m
ρ_p	Particle density	860	kg m^{-3}
μ_s	Viscosity of benzaldehyde	7.901×10^{-4}	Pa s^{-1}
ρ_s	Density of benzaldehyde	980	kg m^{-3}
M_s	Molecular weight of benzaldehyde	106.12	g mol^{-1}
ϕ_s	Association factor for benzaldehyde	1	
N	Stirring revolutions	10	s^{-1}
S_d	Characteristic length of magnetic bead	2×10^{-2}	m
V_A	Molar volume of heptanal at normal boiling point	163.99	$\text{cm}^3 \text{mol}^{-1}$
D	Diffusivity	1.8685×10^{-9}	$\text{m}^2 \text{s}^{-1}$
Re	Reynolds number	4961.4	
Sc	Schmidt number	431.35	
Sh	Sherwood number	321.24	
k_f	Mass transfer coefficient	14.608×10^{-4}	m s^{-1}
R_{obs}	Experimental rate	0.398×10^{-6}	mol s^{-1}
Ca	Carberry number	0.01×10^{-2}	
θ	Porosity	0.0142	
τ	Tortuosity factor	4.5	
D_{eff}	Effective diffusivity	0.5895×10^{-11}	$\text{m}^2 \text{s}^{-1}$
$\eta\phi^2$	Wheeler–Weisz group	0.361	

where ρ_s is the density of solvent (benzaldehyde), N is the rotational speed (revolutions per second), S_d is the stirrer length. Sc is the Schmidt number (Eq. (8)):

$$Sc = \frac{\mu_s}{\rho_s D} \quad (8)$$

The Wheeler–Weisz criterion is given by Eq. (9):

$$\eta\phi^2 = \frac{\text{Rate}_{\text{obs}} d_p^2}{4V_r C_0 D_{\text{eff}}} \quad (9)$$

Effective diffusivity D_{eff} is given by Eq. (10):

$$D_{\text{eff}} = \frac{D\theta}{\tau} \quad (10)$$

where θ is the porosity and τ is the tortuosity factor.

The values calculated for physico-chemical data for mass transfer is listed in Table 2. The mass transfer is negligible and does not affect the reaction kinetics at $Ca < 0.05$ and $\eta\phi^2 < 1$. For present system, the calculated Ca (0.01×10^{-2}) and $\eta\phi^2$ (0.361) both being very low, indicated that the mass transfer is negligible and has no effect on reaction rate.

3.8. Reaction mechanism

The proposed reaction mechanism for the condensation of heptanal and benzaldehyde for the synthesis of jasminaldehyde on the chitosan catalyst has been shown in Fig. 8. The reaction gets initiated on the $-\text{NH}_2$ group present on the chitosan **1**. As the initiation step, heptanal loses its acidic hydrogen to the amine group forming a carbanion, benzaldehyde gets adsorbed on the other $-\text{NH}_2$ and form an imine species **2**. The carbanion of heptanal attacks on the $\text{C}=\text{N}$ species **3** and forms an unstable intermediate **4** which releases the jasminaldehyde and the active sites are again reused for the further catalytic cycles. The mechanism is equivalent to the reported [4] synthesis of jasminaldehyde over amino functionalized magnesium organosilicate. Self condensation of the heptanal is possible by the reaction between the heptanal carbanion with another molecule of heptanal to yield the product, 2-pentyl nonenal.

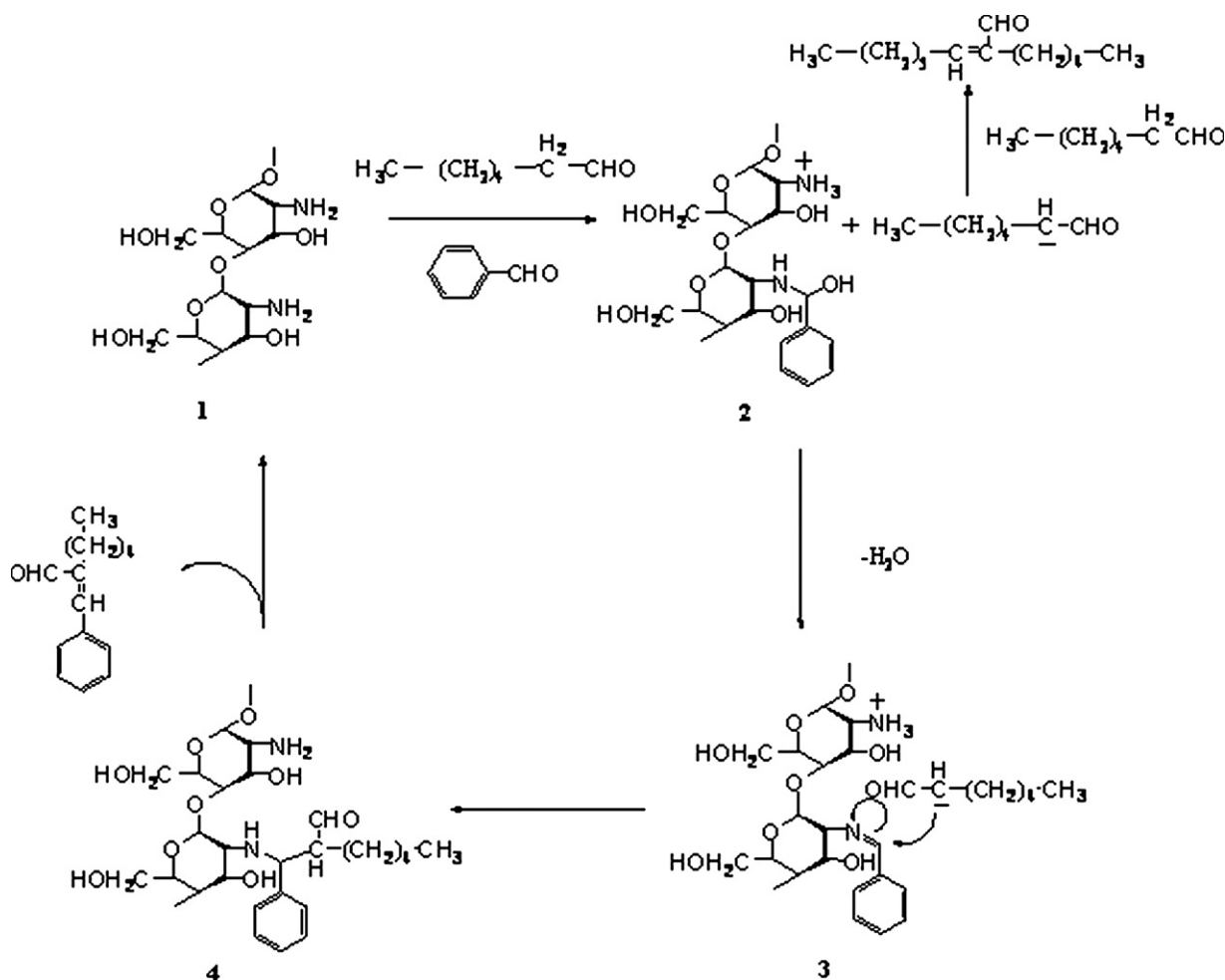


Fig. 8. Proposed reaction mechanism for the synthesis of jasminaldehyde over modified chitosan.

3.9. Kinetic modelling

The reaction steps for the condensation of heptanal with benzaldehyde are presented in Fig. 9. It is important to find the rate determining step (RDS) for the formation of aldol condensation products. The heptanal (step (1)) and benzaldehyde (step (2)) get adsorbed on the catalyst surface [●]. Heptanal carbanion forms by abstraction of proton from adsorbed heptanal in step (3). On the surface, heptanal carbanion reacts with adsorbed benzaldehyde and a proton yielding jasminaldehyde and water in step (4).

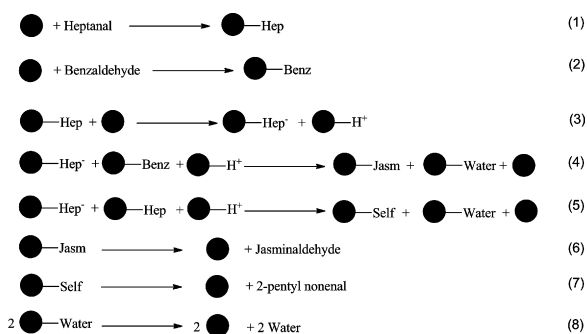


Fig. 9. The important reaction steps for the condensation of heptanal with benzaldehyde (catalyst surface [●], heptanal [Hep], benzaldehyde [Benz], jasminaldehyde [Jas], 2-pentyl nonenal [Self]).

These surface adsorbed heptanal carbanions can also undergo surface reaction with adsorbed heptanal and a proton to yield self condensed product 2-pentyl nonenal (step (5)). Finally jasminaldehyde (step (6)), 2-pentyl nonenal (step (7)) and water (step (8)) get desorbed and the catalyst surface becomes available.

The calculation of Ca and $\eta\phi^2$ showed that the reaction was not diffusion controlled. The RDS for jasminaldehyde may be proton abstraction (Fig. 9, step (3)) or the surface reaction (Fig. 9, step (4)). A kinetic model for the proton abstraction as RDS is given as Eq. (11):

$$\text{Rate}_{\text{jasminaldehyde}}, \nu_1 = \frac{k_j K_H C_H}{1 + K_H C_H + K_B C_B} \quad (11)$$

where k_j is the reaction rate constant for the formation of jasminaldehyde, C_H and C_B are the concentrations of heptanal and benzaldehyde respectively and K_H and K_B are the adsorption coefficients of heptanal and benzaldehyde, respectively. The model (Eq. (11)) did not fit with the experimental data and gave a linear trend rather than the initial increase and decrease in rates on increasing the benzaldehyde/heptanal ratio.

Hence a RDS based on surface reaction may be the model suitable for jasminaldehyde formation. The rate of formation of jasminaldehyde being dependent on the ratio of benzaldehyde to heptanal can be regarded as a reaction following typical Langmuir–Hinshelwood (L–H) mechanism [17]. The experimental rates were compared with the rates obtained from the L–H model

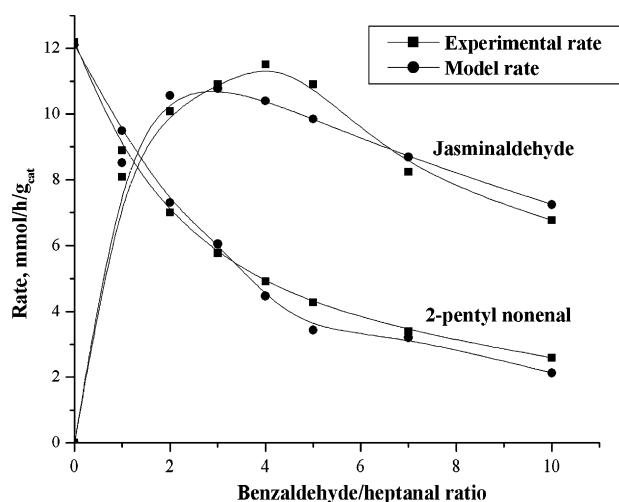


Fig. 10. Comparison of experimental and model rates vs. benzaldehyde/heptanal ratio for the formation of jasminaldehyde and 2-pentyl nonenal.

for bimolecular reaction (Eq. (12)).

$$\text{Rate}_{\text{jasminaldehyde}} \cdot \nu_1 = \frac{k_j K_H K_B C_H C_B}{(1 + K_H C_H + K_B C_B)^2} \quad (12)$$

The parameters in the model rate equation (Eq. (12)) were calculated by data regression of the experiments at different benzaldehyde/heptanal ratios using Levenberg–Marquardt nonlinear least-square method [20] and the values obtained for k_j , K_H and K_B are 43.43 mmol/h/g_{cat}, 22.94 mmol⁻¹ and 8.53 mmol⁻¹ respectively.

The experimental and model rates of formation of jasminaldehyde vs. benzaldehyde/heptanal ratio were plotted in Fig. 10. The model fits with the experimental data with in the R^2 value of 0.95. These observations indicated that the RDS for jasminaldehyde is the surface reaction of adsorbed benzaldehyde with heptanal carbanion and a proton (Fig. 9, step (4)).

For 2-pentyl nonenal also, the two possible RDS may be the proton abstraction (Fig. 9, step (3)) or surface reaction (Fig. 9, step (5)). For self condensation, the surface reaction was observed to be not RDS since it did not follow the L–H model.

The proton abstraction as RDS is given by Eq. (13):

$$\text{Rate}_{\text{2-pentyl nonenal}} \cdot \nu_2 = \frac{k_s K_H C_H}{1 + K_H C_H + K_B C_B} \quad (13)$$

where k_s is the rate constant for the formation of 2-pentyl nonenal.

By putting the K_H and K_B obtained from L–H model for jasminaldehyde (Since the K_H and K_B is a constant for reactions under similar conditions) in Eq. (13) (Fig. 10), a very good fitting ($R^2 = 0.97$) was observed and k_s was found to be 12.25 mmol/h/g_{cat}.

4. Conclusions

Modified chitosan catalyzed solvent-free synthesis of jasminaldehyde was investigated in detail for its kinetics and reaction

mechanism. The rates were calculated in terms of formation of jasminaldehyde and 2-pentyl nonenal. Kinetic investigations were performed as a function of the amount of the catalyst, heptanal, benzaldehyde and temperature. The rate of formation of jasminaldehyde was first order at the lower amount of catalyst and showed saturation at higher amounts. A critical amount of heptanal was needed for the formation of jasminaldehyde. The maximum rate was observed for heptanal to benzaldehyde ratio of 1:4. Based on these observations a plausible reaction mechanism for chitosan catalyzed synthesis of jasminaldehyde was proposed. The rate model based on Langmuir–Hinshelwood mechanism for bimolecular reactions was used to compare the experimental and model rates for the formation of jasminaldehyde and found to have the best fit with R^2 value of 0.95. The rate constants for the formation of jasminaldehyde ($k_j = 43.43$ mmol/h/g_{cat}) and 2-pentyl nonenal ($k_s = 12.25$ mmol/h/g_{cat}) were determined. The modelling studies were indicative of RDS for jasminaldehyde formation as the bimolecular surface reaction and that for 2-pentyl nonenal as the proton abstraction.

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