

Kinetic study for oligomerization of acetaldehyde over cation exchange resin

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ABSTRACT

Several industrially important liquid phase reactions which involve acetaldehyde as the main reactant are practised in the presence of acidic catalyst. However, under these conditions, acetaldehyde also undergoes oligomerization via self-aldol condensation reactions to form multiple side products thereby reducing the selectivity of the desired product. In this work, we investigate the detailed kinetics of oligomerization over a commonly used commercial cation exchange resin, Amberlyst-15 as catalyst. It is found that, crotonaldehyde and subsequent heavy aldols are formed in the reaction. Molecular weight distribution of the oligomers formed during the reaction is verified with Flory's statistical method. Kinetic studies are performed in an autoclave over a temperature range of 343–363 K. The effect of different parameters such as temperature, concentration, catalyst loading, and catalyst reusability is examined. A kinetic model based on Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate expression is proposed to explain acetaldehyde oligomerization in the presence of acidic resin.

1. Introduction

Aldehydes are used in a number of synthesis reactions because of the polar nature of carbonyl group, which facilitates the addition of nucleophile, polymerization, reduction, and oxidation reactions. Several reactions such as aldehyde to amines, hydrazones, azomethines, hydrates, semicarbazones, alpha-amino acid, diol via prins reaction, 1,4-dicarbonyl compounds via stetter reactions, acylal etc. are performed in the presence of acidic catalysts [1]. Acetaldehyde is one of the reactive aldehydes used in several industrially important reactions as a starting material. A brief summary of few such representative reactions, the catalysts used, and the corresponding yields, is given in Table 1. It can be seen from the table that the reported yields are always lower than the quantitative (~100 %) yields mainly due to predominant parallel side reactions of acetaldehyde leading to formation of oligomers. It is thus necessary to study these parallel side reactions in detail and minimize their rates. Acetaldehyde being the simplest aldol donor in case of direct aldol reactions, yields a large number of side products through multiple reactions along with crotonaldehyde as a major product in the acidic medium under mild conditions (~303–323 K) [2–4]. Paraldehyde is another product realised in this reaction apart from crotonaldehyde and oligomers [2].

It is established that the oligomers are formed through self-aldol condensation of acetaldehyde [4]. Interestingly, aldol condensation also takes place in the presence of basic medium as well [5,6]. However, oligomer formation is much less in the presence of base catalysts and hence, when the objective is to produce crotonaldehyde, which has applications in the production of perfumery and pharmaceutical intermediates, the commercial process uses base catalyst [7,8]. It is this reason that the acid-catalysed synthesis of crotonaldehyde and the associated side reactions leading to condensation products is not studied well.

The self-aldol condensation of acetaldehyde over heterogeneous catalysts is studied in literature. For example, metal oxides (Mg, Zr) supported on silica yield crotonaldehyde along with polycondensation of acetaldehyde [9]. Many other solid catalysts such as oxides of magnesium, zirconium, titanium, hafnium, and tantalum supported on silica, alumina, and silica-alumina molecular sieves are used for crotonaldehyde synthesis. Selectivity for crotonaldehyde was reported to be as high as 94 % [7]. Functionalized heteropolyacid when used for crotonaldehyde synthesis, exhibits significant conversion (>97 %) and good chemical stability of the catalyst required for industrial production [8]. Catalyst prepared by impregnation of alkali metal or an alkaline earth metal as precatalyst with a rare earth metal as cocatalyst into a

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Table 1
Different products using acetaldehyde as a reactant in acid catalysed reactions.

S. No.	Product of interest	Catalyst	Reaction Temperature	Information on Side products	Ref.
Acylal formation					
1	1,1-ethylenediol dimethacrylate	FeCl ₃	273–287 K	39 % product yield	[20]
Prins reaction					
2	2,4,4,6 and 2,4,6 alkyl-diol	Sulfuric acid	283–313 K, 283–285 K	9–11% and 9% of acetaldehyde consumed as side product	[21]
3	Trans-2-alkyl-4-hydroxypiperidines	Heteropoly acid phosphomolybdic acid	298 K	79 % yield for main product while rest go for side reaction	[22]
Mannich reaction					
4	β-amino aldehydes	Proline	273 K	The product yield varies in the range of 40–58 %	[23]
5	(S)-4-nitro-3-phenylbutanal	Proline	298 K	75 % yield	[24]
Acetalization					
6	Dialkylacetal	Cation exchange resins	278–323 K	Not reported	[25,26,27,28]
7	Glycerol ethyl acetal	Cation exchange resins	313–358 K	Not reported	[29]
Self-Aldol condensation reaction					
8	Crotonaldehyde	Sulphuric acid [5], Amino acids [11]	295–298 K	Not reported	[5,11]
9	Crotonaldehyde	Metal oxides (Mg, Zr)	403 K	Crotonaldehyde selectivity is in range of 83–87%.	[9]
10	Crotonaldehyde	Metal (Mg, Zr, Ti, Hf, Ta) Oxides [7], Impregnated alkali/alkaline earth metal [10]	523–673 K [7], 593 K [10]	Crotonaldehyde selectivity is nearly 94 % [7], 88 % [10]	[7,10]
11	Crotonaldehyde	Heteropolyacid	298 K	Not reported	[8]
Cross Aldol condensation reaction					
12	3-methylpent-3-en-2-one (MPO)	Cation exchange resin, Clay supported solid catalyst	343–423 K	MPO yield 50–80%	[30,31]
13	3-methylpent-3-en-2-one	Sulfuric acid, Hydro chloric acid	278–343 K [31,32]; 323–343 K [33]	65 %–77.7 % [31,32]; 90% [33]	[31,32,33]

carrier made of alkali metals or alkaline earth metals is reported for self-aldol condensation reaction of acetaldehyde. Yield obtained by this catalyst was nearly 88 % [10]. Use of amino acids such as glycine, alanine, serine, arginine, and proline at room temperature (295–297 K) in water and aqueous salt solutions of NaCl, CaCl₂, Na₂SO₄, and MgSO₄ for the production of crotonaldehyde are also reported in the literature. Overall reaction is found to be first order with respect to acetaldehyde concentration at lower concentration of amino acid while at higher amino acid concentration, reaction follows second order kinetics [11]. However, there is no discussion on the oligomerization reaction in any of these studies reported in literature.

It is mentioned in the literature that acetaldehyde undergoes addition polymerization in the presence of acidic catalyst [3]. A viscous tarry mass is formed by oligomerization of aldehydes. The oligomers are formed by condensation of anywhere between 3–7 molecules of aldehyde. The molecular weight of polymers formed by acetaldehyde polymerization is in the range 320–340, which is also equivalent to the molecular weight of polymers formed by crotonaldehyde polymerization. This led to a conclusion that irrespective of the parent reactant, be it acetaldehyde or crotonaldehyde, oligomers formed are the same [12]. In another study, Yamamoto et al. have reported a bimodal molecular weight distribution of the oligomers with lighter ones in the range of 230 ± 30, and the heavier ones over 800 ± 100 [13]. To the best of our knowledge, barring few studies [3,4], there is not much information available on the structure of high-boilers. It is also reported in the case of aldolization reaction that the formation of oligomers is independent of the main reaction and may be considered as a parallel side reaction [14].

Few studies investigate kinetics of acetaldehyde self-aldol condensation however, oligomerization reaction is not taken into account in the reaction scheme and the kinetic parameters are estimated with the assumption that crotonaldehyde is the only product [11,15–17]. The importance of side products formed by oligomerization or any other routes has been ignored, and that the kinetics is inadequate while identifying the right reaction conditions and the reactor design. Hence, it is necessary to investigate all the reactions leading to condensation products and the associated kinetics for the given catalyst in detail. This would not only help in crotonaldehyde production, but also in

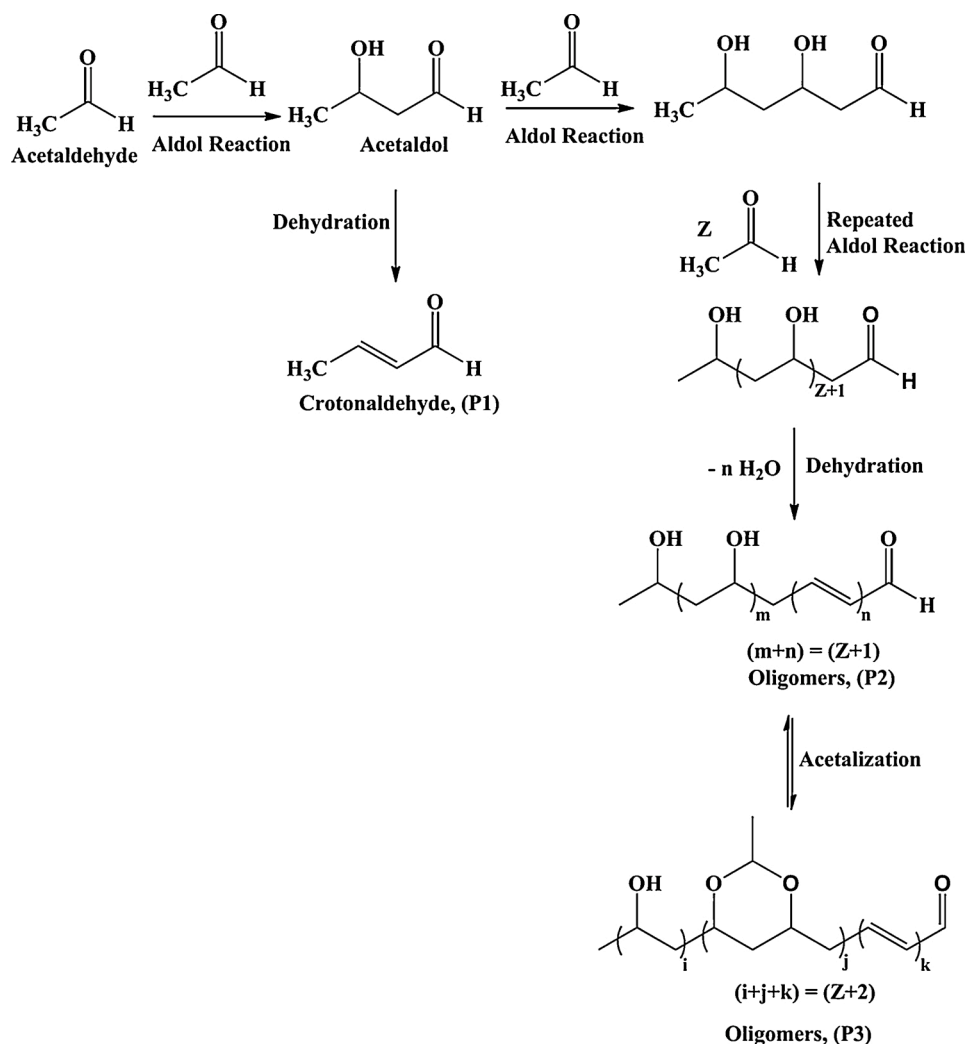
predicting the side products in several acid catalysed reactions in which acetaldehyde is used as one of the reactants. Based on the information available in literature [3], a reaction scheme showing different possible products formed due to alcohol condensation, repeated aldol condensation and subsequent dehydration of aldols is shown in [scheme 1](#). [Scheme 2](#) shows the mechanism for formation of aldol that involves reaction between oxonium ion as electrophile and enol form of acetaldehyde as nucleophile. It also shows the mechanism of dehydration and subsequent formation of some representative aldols by repeated aldol condensation reactions.

Cation exchange resins are promising solid acid catalysts and as seen in [Table 1](#), they are used for many industrial reactions such as cross aldol condensation, acetalization reaction involving acetaldehyde [18,19]. The objective of the present work is thus to develop the reaction scheme and the overall kinetics when acetaldehyde is contacted with acidic catalyst like cation exchange resin under mild conditions (<373 K). The molecular weight distribution of the condensation products is compared with the predictions of Flory's statistical method. The effect of different parameters such as solvent selection, temperature, catalyst loading is studied in the absence of internal and external mass transfer resistances. Finally, a suitable kinetic model is proposed to explain the experimental data. This model can be conveniently used in a broader reaction scheme wherein, oligomerization takes place as a parallel side reaction.

2. Experimental section

2.1. Chemicals and catalyst

The chemicals used for the experiments were acetaldehyde (98 % pure, Harmony Organics, Pune, India) and toluene (99.5 % pure, from Merck, Mumbai, India). The purity was verified by gas chromatography. The catalyst, dry Amberlyst-15 (Rohm and Hass, France), was obtained from S.D. Fine-chem Ltd., Mumbai, India. Catalyst was first dried in the oven for 6–7 hours at 373 K in vacuum (0.6 bar gauge). Amberlyst-15 is a macro reticular polystyrene-based cation exchange resin with an exchange capacity of 4.7 meq/g. Its average particle size is 600 μm and it has an active surface area of 50 m²/g.



Scheme 1. Possible reaction of acetaldehyde in the presence of acid catalyst.

2.2. Analysis

The samples were analyzed using gas chromatography (GC) (Nucon, GC 5756) equipped with a flame ionization detector (FID), and nitrogen (MED gas, Mumbai, India) as a carrier gas at a flow rate of 30 ml/min. A 25 m long capillary column TRB-5 (Teknokroma, Spain) was used to separate the components. Injector and detector were kept at 493 K. The temperature of the oven was programmed as 333 K-4 min-10 K/min (ramp)- 493 K.

The water content was analyzed separately using gas chromatography (GC) (Nucon, GC 5756) equipped with a thermal conductivity detector (TCD). A packed column, 2 m long PoraPak-Q of ID 2 mm, was used for this analysis. Injector and detector temperatures were set to 443 K, while the oven was maintained at 483 K. Hydrogen (MED gas, Mumbai, India) was used as a carrier gas at a flow rate of 30 ml/min. The average molecular weight of the oligomers was measured using vapour pressure osmometry (VPO).

2.3. Apparatus

All the experiments were performed in an autoclave reactor (250 ml liquid volume, Amar Equipments Ltd., Mumbai, India), with a working volume of 200 ml, equipped with temperature and pressure sensors, stirrer, sample port and safety valve. The calculated amounts of reactants were charged into the autoclave. The air trapped in the autoclave was released by pressurizing and depressurizing the reactor with

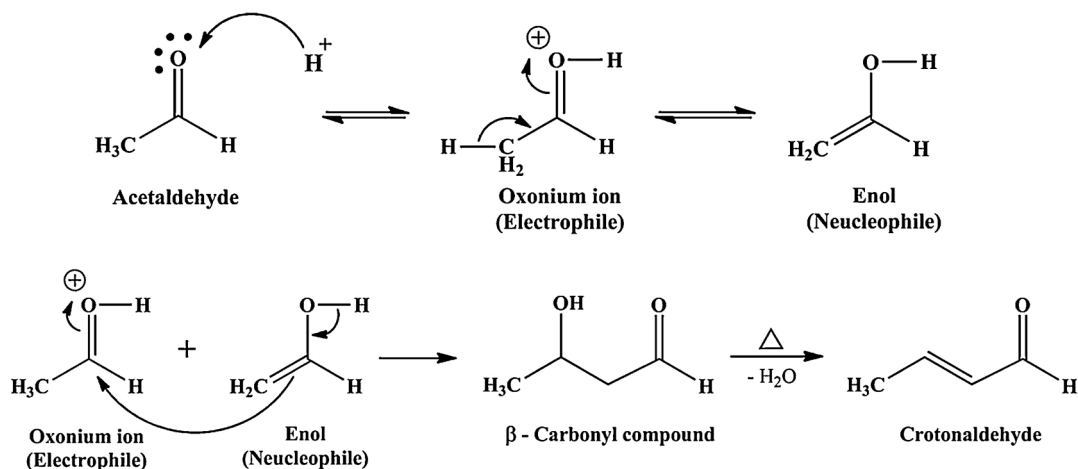
nitrogen for couple of times. The reactants were then heated at low RPM in the autoclave. Once the temperature attained the desired value, the catalyst was added, and the stirrer speed was raised to 600 rpm. The catalyst was added to the reactor using the specially designed catalyst charging tube. The tube was charged with the catalyst prior to the start of reaction. Once the desired temperature is attained, the valve of charging tube was opened to release the catalyst to the reactor. Amberlyst-15 showed good mechanical strength and at a stirrer speed of 600 rpm, it was found to remain intact during the entire operation. Samples were withdrawn periodically for analytical purpose. Determination of acetaldehyde concentration during the reaction was critical due to its high volatility at room temperature. However, zero physical loss of acetaldehyde was ensured by taking the reaction mixture in a prechilled vial filled with known amount of external solvent. The samples were further chilled for 20 min before subjecting them to GC analysis.

2.4. Product characterization

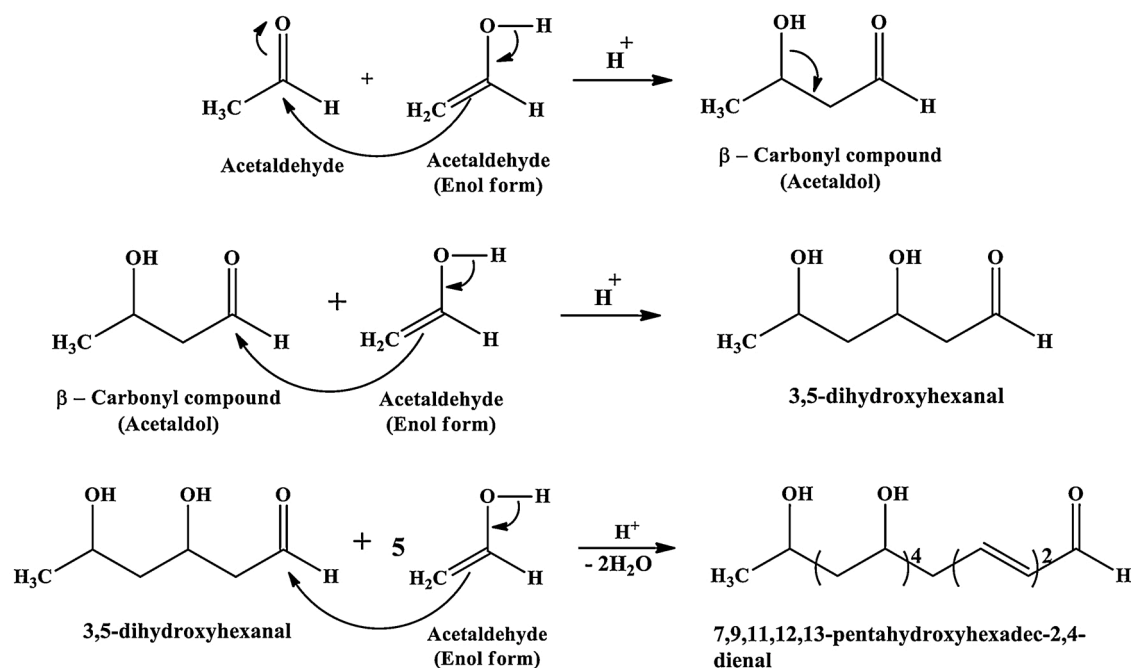
The experiments were performed for self-aldol reaction in the presence of Amberlyst-15 to know the extent of polymerization. Toluene was used as the internal solvent. Reactions were performed at 353 K at a mole ratio 1:3 (AcH: Toluene) and catalyst loading of 0.3 gms/gm of acetaldehyde. 7 g catalyst was used in 195 ml reaction mixture containing 0.52 mol of AcH and 1.57 mol of toluene. GC results confirmed the presence of products crotonaldehyde and traces of paraldehyde. The

Mechanism

1. Acetaldehyde to crotonaldehyde



2. Acetaldehyde to high boiler (representative)



Scheme 2. Reaction mechanism for repeated aldol condensation of acetaldehyde followed by dehydration in the presence of acidic catalyst.

non-volatile high-boilers were not detected on GC and can be determined by material balance. They are essentially the oligomers obtained by repeated aldol condensation reaction and cyclic/acyclic acetalization reaction. It is thus necessary to establish a detailed reaction pathway that considers the formation of all the side products.

The reaction mixtures obtained by performing reaction at different times were distilled to obtain heavy oligomers as residue for molecular weight measurement. Vapour pressure osmometry (VPO) analysis confirms that the average molecular weight of oligomers formed during the reaction increases with time and lies in the range 300–400 as shown in Fig. 1. These values are consistent with the values reported in literature for other catalysts [3,12,13]. The molecular mass distribution of the oligomers was analyzed by HR-LCMS in positive ion polarity and ESI source mode. From Fig. 2, it can be seen that the number of side products formed during acetaldehyde oligomerization were nearly twenty. However, components with considerable weight fractions in the

oligomer concentration profile are taken for further studies.

Fig. 3 shows the FTIR spectrum of the reaction sample after the evaporation of the volatiles. It clearly shows the characteristic peaks at 3200–3600 of –OH from the oligomer, formed by successive addition of aldol. The peak at 3000 corresponds to –CH stretching in aldehyde, and as expected, a strong peak corresponding to C=O is also evident at 1700. The peak near 1100 is expected to be of C–O in cyclic ether or acetal formed by the reaction of polyaldol with acetaldehyde. A representative cyclic ether is shown Scheme 1. The spectra, by and large coincides with the one reported in literature for a proline-derived organocatalysts coupled with Bronsted acids catalyst [3].

Acetaldehyde oligomers along with their molecular weights are given in Table 2. The molecular structures of the oligomers are predicted based on the chemistry of repeated aldol addition and dehydration. This led to the production of atactic polymeric species by the acetaldehyde monomer. Vogl (1974) support the atactic polymerization of

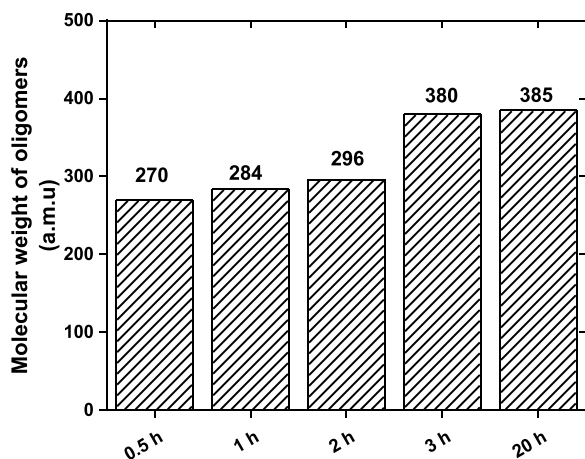


Fig. 1. Average molecular weights of the oligomers formed by acetaldehyde oligomerization with time. Catalyst: Amberlyst-15 (0.3 gms/gm of acetaldehyde, size: 600 μm), 363 K, 4 bar, 1:3 (AcH: Toluene) molar ratio, Speed of agitation: 600 RPM.

acetaldehyde to produce low molecular weight polymers in the presence of acidic catalyst [34].

2.5. Molecular weight distribution of the oligomers

Molecular weight distribution is an important parameter that determines the physical, chemical and rheological properties of the polymers [35]. Basis for theoretical derivation of molecular size distribution

is the equal reactivity of all functional groups during the polymerization [36]. One of the widely used methods for the molecular weight distribution is 'Flory's statistical method' [37]. This method represents the most probable distribution that can be obtained from the polymerization process [35]. It assumes that the reaction is independent of the size of the molecule to which the functional group is attached, and that the ring formation does not occur [38,39]. The ring formation for the case when molecules involved in the polymerization are less than five or more than

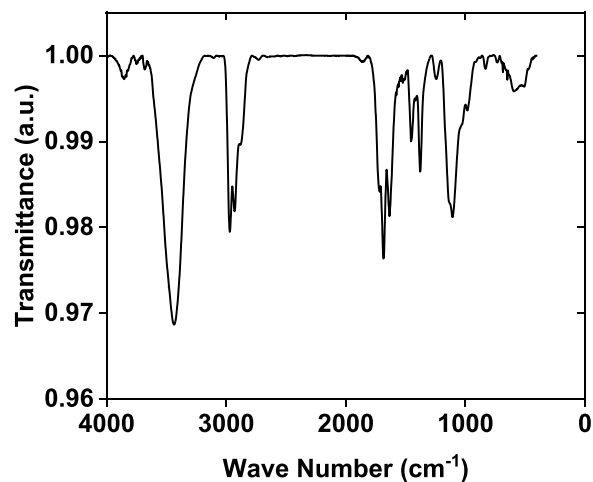


Fig. 3. FTIR analysis for the reaction products free of volatiles obtained with time. Reaction mixture AcH: Toluene (1:3), 353 K, 4% (w/w) catalyst loading (size: 600 μm).

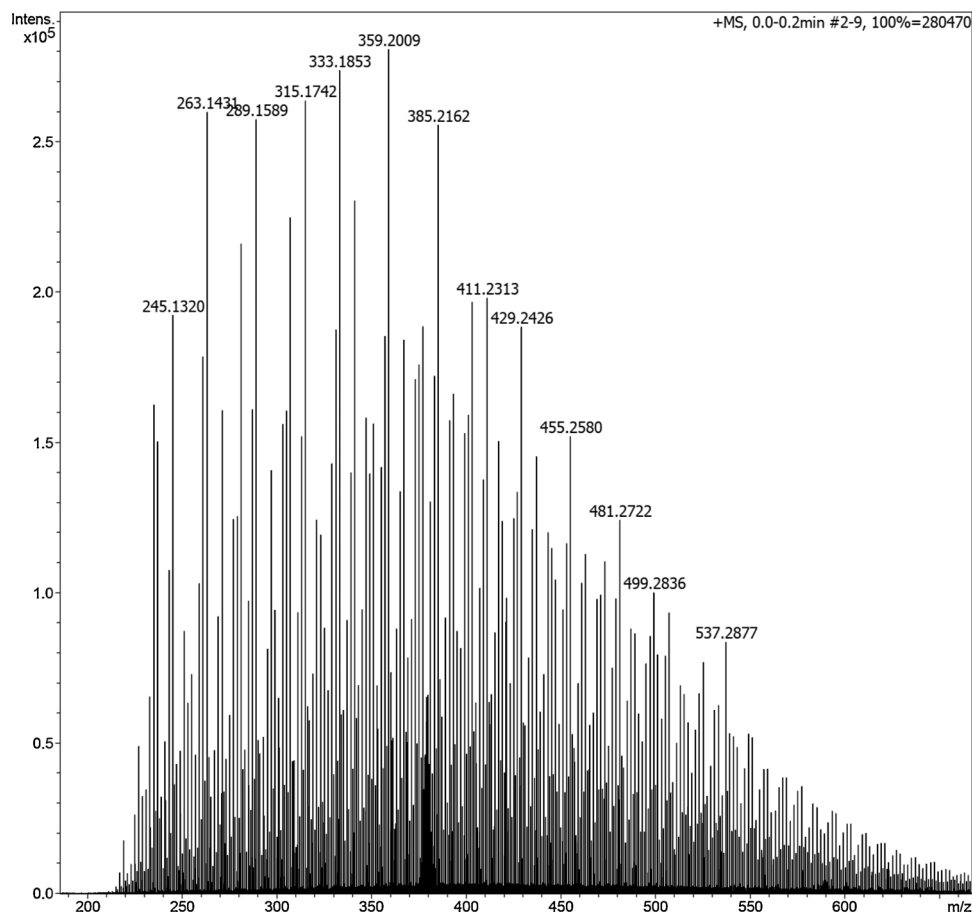


Fig. 2. HR-LCMS analysis of the heavies formed in acetaldehyde oligomerization reaction over Amberlyst-15.

Table 2
Acetaldehyde condensation products identified in HR-LCMS.

S. No.	Chemical name	Structure	Observed m/z
1	5,7,9,11-tetrahydroxydodec-2-enal		246
2	3,5,7,9,11-pentahydroxydodecanal		264
3	5,7,9,11,12-pentahydroxytetradec-2-enal		290
4	7,9,11,12,13-pentahydroxyhexadec-2,4-dienal		316
5	5,7,9,11,13,15-hexahydroxyhexadec-2-enal		334
6	7,9,11,13,15,17-hexahydroxyoctadeca-2,4-dienal		360
7	9,11,13,15,17,19-hexahydroxyicosa-2,4,6-trienal		386
8	11,13,15,17,19,21-hexahydroxydocosa-2,4,6,8-tetraenal		412
9	9,11,13,15,17,19,21-heptahydroxydocosa-2,4,6-trienal		430
10	11,13,15,17,19,21,23-heptahydroxytetracos-2,4,6,8-tetraenal		456
11	13,15,17,19,21,23,25-heptahydroxyhexacos-2,4,6,8,10-pentaenal		482
12	11,13,15,17,19,21,23,25-octahydroxyhexacos-2,4,6,8-tetraenal		500
13	7,9,11,13,15,17,19,21,23,25-decahydroxyhexacos-2,4-dienal		536

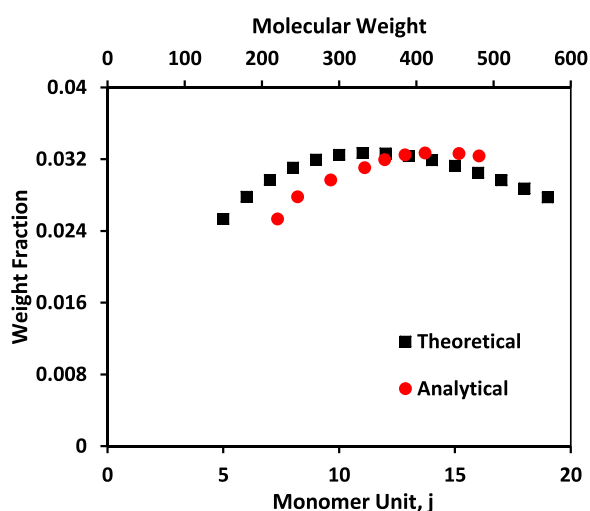


Fig. 4. Comparison of molecular weight distributions obtained by Flory's method ($p = 0.915$) and that by HR-LCMS.

seven is overruled under ordinary conditions [36].

Analytical representation obtained from HR-LCMS for the molecular weight distribution is shown in Fig. 3. Molecular weights of the

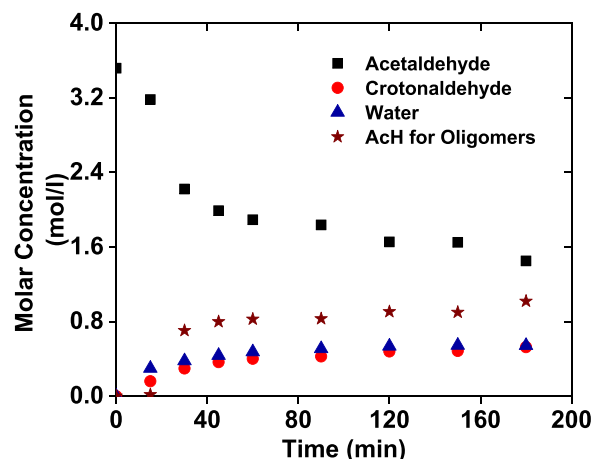


Fig. 5. Molar concentration of acetaldehyde, crotonaldehyde, water and acetaldehyde consumed in oligomers with time. Catalyst: Amberlyst-15 (0.3 gms/gm of acetaldehyde, size: 600 μm), 353 K, 4 bar, 1:2 (AcH: Toluene) molar ratio, Speed of agitation: 600 RPM.

abundant components listed in Table 2 are considered for Flory distribution. Flory weight fraction distribution can be calculated by the formula given by Eq. (1) [40].

$$w_j = j(1-p)^2 p^{j-1} \quad (1)$$

Where, j is the number of isomers combined to form a particular oligomer and p is the probability of the extent of the reaction. Theoretical weight distribution was solved using Eq. (1) and compared with analytically obtained molecular weights as shown in Fig. 4.

It can be concluded from the comparison that weight distribution is consistent with the theoretical value at the 0.915 probability of the extent of polymerization. This result can be further used for determination of different properties of the oligomers. The deviation may be due to the underlying assumptions of Flory's method. The method assumes that the reactivity of all the functional groups is similar and there is no ring formation. In our case, these assumptions may not exactly hold good.

3. Reaction kinetics

The kinetics of acetaldehyde oligomerization in the presence of acidic catalyst Amberlyst-15 was studied in a batch reactor. The effect of different parameters such as solvent selection, particle size, stirrer speed, temperature, composition, and catalyst loading were studied.

3.1. General course of the reaction

Fig. 5 illustrates the general course of a typical reaction performed in a batch reactor in the presence of Amberlyst-15 as catalyst, and toluene as an internal solvent under the condition mentioned therein. All the experiments were performed in the absence of external mass transfer resistance by maintaining 600 rpm stirrer speed using the catalyst procured from the manufacturer. The reactions were performed at different stirrer speeds around 600 rpm to ensure that their external mass transfer limitation was negligible.

All the concentrations were calculated based on GC except for oligomers, the proportion of which was determined by material balance. Although multiple oligomers were formed during the reaction, what is shown in the figure is the moles of acetaldehyde converted to oligomers formed at any given time. Fig. 5 shows the change in concentration of acetaldehyde, crotonaldehyde, water and acetaldehyde consumption in oligomers formation with time. Acetaldehyde concentration decreases with time, while crotonaldehyde and water show increasing trend. One

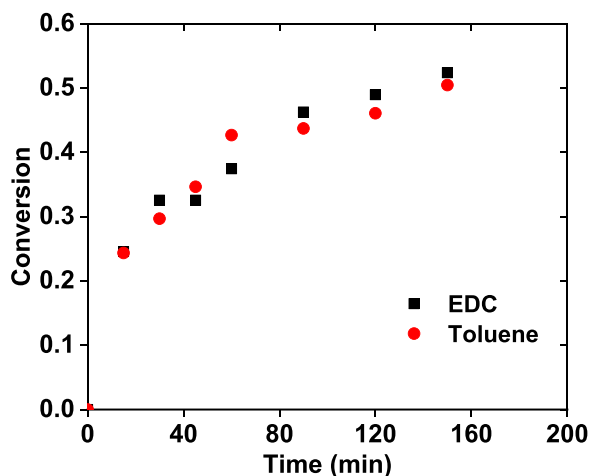


Fig. 6. Effect of solvent over acetaldehyde conversion, 4% (w/w) Amberlyst-15 (size: 600 μm), 353 K, 1:3 (AcH: EDC/ Toluene), 600 RPM, 4 bar.

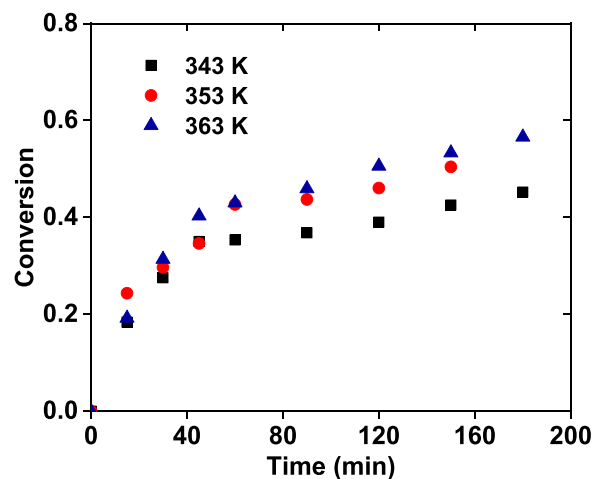


Fig. 8. Effect of temperature over AcH conversion, 1:3 (AcH: Toluene), 600 RPM, 4 bar, 4% (w/w) catalyst loading (size: 600 μm).

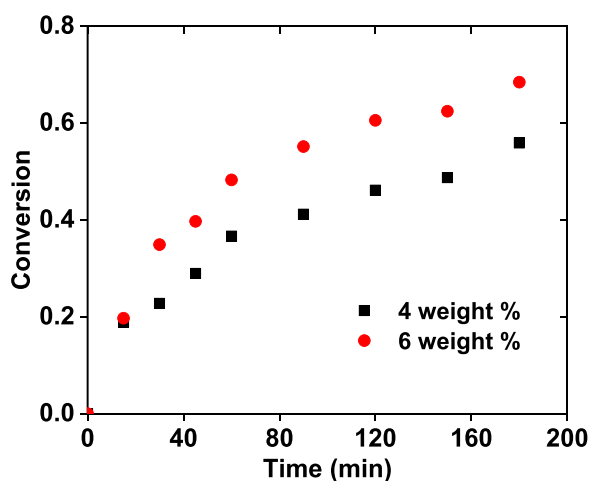


Fig. 7. Effect of catalyst loading (size: 600 μm). 363 K, 1:3 (AcH: Toluene), 600 RPM, 4 bar.

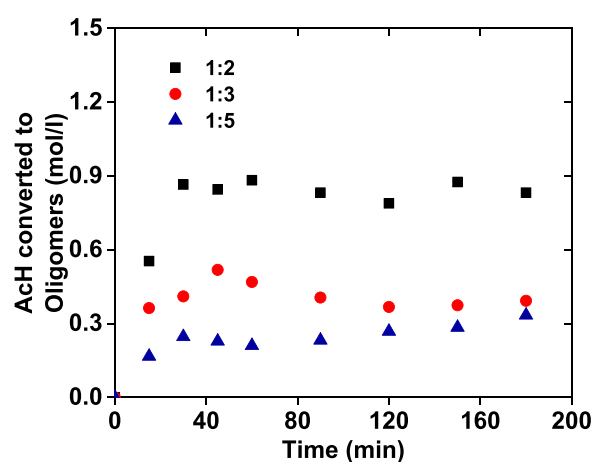


Fig. 9. Effect of feed concentration on the AcH conversion to oligomers, 343 K, 1: X (AcH: Toluene), 600 RPM, 4 bar, 4% (w/w) catalyst loading (size: 600 μm).

molecule of water is released with one molecule of crotonaldehyde while in case of oligomers, the exact amount of water formed is difficult to calculate stoichiometrically.

The standard criteria were used to ensure that the kinetic data indeed represents the intrinsic kinetics under the conditions of interest. The Weisz-Prater parameter was found to be less than 1, and takes the value from 0.114 to 0.267 over the entire conversion range, which implies that internal pore diffusion resistance is negligible. Also, the value of Mears' parameter varies from 0.0108 to 0.0260 as the reaction proceeds. All the values are less than 0.15, which confirms that the external mass transfer resistance is also negligible at 600 RPM. For the above calculations, molecular diffusivity was estimated by the standard equation [41] and a correlation for the external mass transfer coefficient is obtained from [42]. The detailed calculations are shown in the supporting information (SI).

3.2. Effect of type of solvent

In order to understand the effect of non-aqueous solvent, the reactions were performed using highly non-polar toluene and relatively polar ethylene dichloride (EDC) as solvents. Fig. 6 shows that there is a negligible effect of solvent over acetaldehyde conversion, which is in line with the results reported in literature [3]. The result is important as it indicated that even in the case of some other reactions in which

acetaldehyde is involved as one of the reactants (Table 1), the presence of other reactants and products is unlikely to affect the intrinsic kinetics of oligomerization due to self-condensation of acetaldehyde. Henceforth, toluene was taken as the solvent for all other experiments to study kinetics of oligomerization. However, it may be noted that the results with water as a solvent may be different because water has a strong affinity for the catalyst and it is known to alter the catalyst activity significantly [18].

3.3. Effect of catalyst loading

The catalyst loading was varied over the range 0.3–0.45 gms/gm of acetaldehyde and its effect on the conversion of acetaldehyde is shown in Fig. 7. As expected, the rate of reaction increases with an increase in catalyst loading due to the availability of a larger number of total active acidic sites.

3.4. Effect of temperature

The effect of temperature on acetaldehyde conversion is shown in Fig. 8. The rate of reaction increased with increase in temperature. However, the rise in reaction rate is not as much as one would expect for acid catalyst bimolecular reactions. The effect will get reflected in the value of activation energy as explained in the section of kinetic

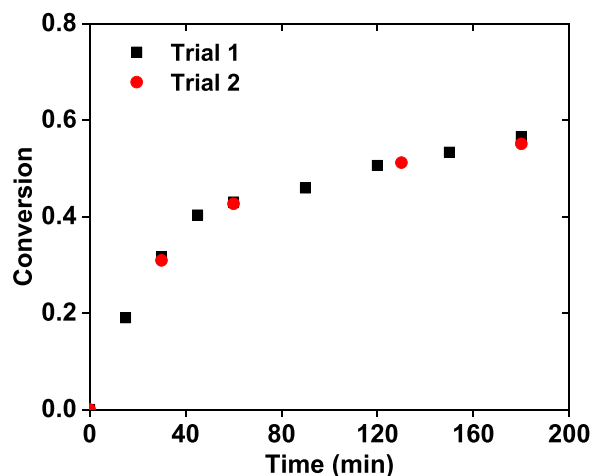


Fig. 10. Catalyst reusability study for oligomerization of acetaldehyde. Amberlyst-15 (4% w/w, size: 600 μm), Temperature: 363 K, 1:3 (AcH: Toluene), 600 RPM.

modelling. Reaction temperature is therefore an important parameter to be explored to minimise the formation of oligomers when formed as side products.

3.5. Effect of feed concentration

The effect of acetaldehyde concentration over reaction kinetics is studied for 1:2, 1:3 and 1:5 (AcH: Toluene) molar ratios and the results are shown in Fig. 9. The rate of reaction increases significantly with an increase in acetaldehyde concentration indicating higher order with respect to the substrate.

3.6. Effect of catalyst activity and reusability

Since high molecular weight components are formed in the reaction, it is necessary to investigate whether the batch reaction data presented here is influenced by possible *in-situ* deactivation of the catalyst due to deposition and pore blocking. Hence, repeated runs were performed with the same catalyst to assess the reusability of the catalyst. The catalyst after every run was filtered and dried for 8 h in vacuum (0.6 bar gauge) at 373 K. The dried catalyst was reused to repeat the reaction under otherwise similar conditions. As shown in Fig. 10, acetaldehyde conversion is unaffected, and that the deactivation during the period of a single batch run is insignificant.

4. Kinetic modeling

The kinetics of the reactions in the presence of heterogeneous catalysts can be generally explained by semi-empirical models such as pseudo-homogeneous (PH) model, or Eley-Rideal (ER) model, or Langmuir-Hinshelwood-Hougen-Watson (LHHW) model [40,43]. LHHW model is considered here to explain the kinetics based on the experimental results obtained at different temperatures, feed compositions, and catalyst loadings.

As mentioned above, more than twenty side products were formed during acetaldehyde oligomerization. Ideally it is necessary to consider the formation of all side products individually to propose the complete model. However, it is difficult to derive such a rigorous reaction scheme, owing to lack of knowledge on the formation of individual oligomer [44].

We have therefore proposed a simplified model by lumping all the oligomers in one pseudo component [44]. It was evident from the VPO analysis that, in a representative reaction (see Fig. 2) the average molecular weight of the oligomers over the reaction period is 327.5. Based

on the molar balance of the reactant and products, it was approximated that, eight moles of acetaldehyde oligomerize to form one mole of oligomer and two moles of water. Thus, the representative oligomer used for the estimation of all the kinetic parameters is 7,9,11,12,13-pentahydroxyhexadec-2,4-dienal with a molecular weight of 316, closer to the average molecular weight realized in most of the reactions. Based on this, the following non-elementary reaction scheme is assumed for kinetic modeling:



Where A, C, H, and W represent acetaldehyde, crotonaldehyde, 7,9,11,12,13-pentahydroxyhexadec-2,4-dienal, and water, respectively. It is known that the affinity for Amberlyst-15 is the highest for water, followed by acetaldehyde and crotonaldehyde. LHHW rate expressions (Eqs. 4 and 5) are used to account for the adsorption.

$$r_1 = \frac{k_1 C_A^2}{(1 + K_A C_A + K_C C_C + K_H C_H + K_W C_W)^2} \quad (4)$$

$$r_2 = \frac{k_2 C_A^n}{(1 + K_A C_A + K_C C_C + K_H C_H + K_W C_W)^n} \quad (5)$$

where, r_i is rate of reaction, C_i is concentration of the respective component, k_1 and k_2 are the rate constants for first and second reaction, and K_A , K_C , K_H , K_W are the adsorption constants for components acetaldehyde, crotonaldehyde, high-boiler, and water, respectively. The temperature dependence of rate constants and adsorption constants can be given by Eqs. (6) and (7).

$$k_r = k_r^0 \exp(-E_r/RT) \quad (6)$$

$$K_j = K_j^0 \exp(-\Delta H_j/RT) \quad (7)$$

Where, k_r is reaction rate constant, k_r^0 is the pre-exponential factor, E_r is the activation energy and K_j are adsorption constant, K_j^0 is the pre-exponential factor, and ΔH_j is the enthalpy of adsorption.

In order to reduce the number of optimization parameters, several variations of Eqs. (4) and (5) were tested. It was found from the estimated value of n in Eq. (5) happens to be 2.14 based on the data from for all the experimental runs. Hence, we assume the order to be 2. Furthermore, it was observed that the adsorption constants for components, except the relatively polar components water and acetaldehyde, on Amberlyst-15 were negligible. Based on this, a simplified lumped kinetic model represented by Eqs. (8) and (9) can be obtained.

$$r_1 = \frac{k_1 C_A^2}{(1 + K_A C_A + K_W C_W)^2} \quad (8)$$

$$r_2 = \frac{k_2 C_A^2}{(1 + K_A C_A + K_W C_W)^2} \quad (9)$$

Molar balance for the measured species is given by Eqs. (10)–(13).

$$\frac{dN_A}{dt} = m_{cat} (-2r_1 - 8r_2) \quad (10)$$

$$\frac{dN_C}{dt} = m_{cat} (+r_1) \quad (11)$$

$$\frac{dN_H}{dt} = m_{cat} (+r_2) \quad (12)$$

$$\frac{dN_W}{dt} = m_{cat} (r_1 + 2r_2) \quad (13)$$

Where, N_i is the number of moles of component i and m_{cat} is mass of the

Table 3

Estimated kinetic parameters with standard error for 95 % confidence limit.

Parameters	Value
k_{10} (l ² / (mol. s. g))	(2.05E + 07) ± (1.21E + 03)
k_{20} (l ² / (mol. s. g))	17137.27 ± 53.64
E_{10} (J/mol)	33400.34 ± 37.76
E_{20} (J/mol)	14689.41 ± 213.77
K_{A0} (l/mol)	282844.84 ± 371.98
K_{W0} (l/mol)	1.70 ± 3.49
ΔH_{A0} (J/mol)	14764.80 ± 26.4
ΔH_{W0} (J/mol)	-27679.1 ± 6022.68
SRS	0.0110

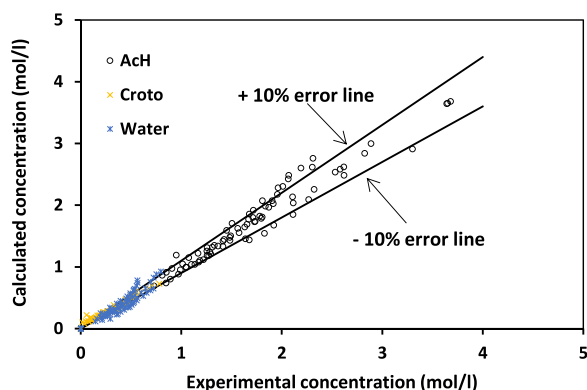


Fig. 11. Parity plot comparing experimental and calculated concentrations of all the components (acetaldehyde, crotonaldehyde and water) present in acetaldehyde oligomerization reaction mixture at different times in reactions performed under different conditions. AcH: Acetaldehyde, Croto: Crotonaldehyde.

catalyst taken for the experiment. The kinetic parameters are estimated using nonlinear regression method 'nlinfit' of MATLAB based on the 'Levenberg - Marquardt algorithm' and tabulated in Table 3. The objective is to minimize the sum of residual squares (SRS) between the experimental and calculated molar concentrations for all the components. A parity plot showing experimental and calculated concentration is shown in Fig. 11.

5. Conclusion

In the present work, the kinetic study of acetaldehyde oligomerization over acidic ion exchange resin, Amberlyst-15 is studied in detail. Along with crotonaldehyde, more than twenty oligomer products of self-condensation and dehydration are realised. The molecular weight distribution of the oligomers was nearly consistent with the theoretical value obtained by Flory's statistical method. The influences of different parameters such as type of solvent, internal and external mass transfer resistances, temperature, and concentrations were studied in detail. A simplified lumped kinetic model based on LHHW mechanism is proposed. The kinetic model and the rate parameters can be used for any reaction wherein, acetaldehyde self-condenses to form oligomers as a side-products in the presence of acidic catalyst at low to moderate temperatures (<373 K).

Authorship contribution

Sumit Kamal: Conception and design of study, Experimental data acquisition, Analysis and interpretation of data, Drafting the manuscript, Editing the manuscript

Sanjay M. Mahajani: Funding acquisition, Conception and design of study, Project administration, Review and editing the manuscript.

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Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcata.2020.117841>.

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