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Aldol Condensation of Acetone with Reactive Distillation Using Water as a Selectivity Enhancer

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Aldol condensation of acetone in the presence of acid catalyst gives diacetone alcohol (DAA) as an intermediate product, which further dehydrates to give mesityl oxide (MO). By using reactive distillation (RD), one can improve selectivity toward DAA, by continuously removing it from the reactive zone and thereby suppressing the dehydration reaction. The presence of water in the reaction mixture has a predominant effect on the intrinsic reaction rates of the individual reactions. This rate-inhibiting effect of water can be advantageously used to improve the selectivity toward the desired intermediate products. The present study, through experiments and simulation, shows that introduction of water in RD can further increase the selectivity toward DAA. Batch kinetics of the reaction in the presence of water is studied, and a suitable kinetic expression is proposed. Further, the batch and continuous reactive distillation experiments are performed to assess the feasibility. The experimental results are explained with the help of an equilibrium-stage model, and the operating parameters for the desired performance are suggested based on the validated model.

Introduction

In the case of the reactions in organic media catalyzed by cation-exchange resins, water, being a polar compound, is known to have high affinity toward the catalyst sites. It competes with other reactants for active sites, leading to a drop in the number of available catalyst sites for the reaction. Thus, when water is present in the reaction mixture or is one of the reaction products, it has a predominant effect on the reaction rate.¹ This rate-inhibiting effect of water can be advantageously used to improve the selectivity toward the desired intermediate products by suppressing the undesired side reaction(s). Dimerization of isobutylene to diisobutylene (DIB) is one such example wherein the selectivity toward the desired product (DIB) may be improved by inhibiting the side reaction of triisobutylene formation. A detailed kinetic study of the isobutylene dimerization reaction with water as a selectivity enhancer has been reported in the literature.² In the present work, this strategy is applied for another industrially important reaction of aldol condensation of acetone.

Selective aldol condensation of acetone produces DAA, which further dehydrates to produce mesityl oxide (MO) and water. DAA is an industrially important compound with a number of industrial applications such as being a solvent in purification processes and a component of solvent blends for nitrocellulose, acrylic, and cellulose acetate lacquers and thinners, cleaning compounds, degreasers, stripping aids for textiles, and gum and resin removers in automobile carburetor cleaners. MO is also a useful compound with various applications, the most important of which is being the precursor for the production of a popular solvent, methyl isobutyl ketone (MIBK). Hydrogenation of MO under suitable conditions gives MIBK in high yields.³ Aldol condensation of MO and acetone further yields heavier products, such as isophorone. The reaction scheme is shown in Figure 1. The reaction is normally performed in the presence of base catalyst to improve selectivity toward more valuable DAA, because in the presence of acid catalyst the dehydration of DAA is very fast.

In our earlier work,⁴ we have shown that use of reactive distillation can offer substantially high selectivity toward DAA even in the presence of acidic cation-exchange resin as catalyst. We further explored the possibility of using reactive distillation to conveniently manipulate DAA/MO ratio and also suppress the formation of heavier products. In reactive distillation, one can judiciously manipulate the concentration profiles of the reactants and the products to achieve higher selectivity. DAA can be efficiently separated from the reactive zone upon its formation to reduce the extent of dehydration. In the present work, we explore the possibility of using water as a selectivity enhancer for DAA in reactive distillation for any further possible improvement. From the process-design point of view, the addition of extra water will not further complicate the downstream processing as even otherwise water is the product of the reaction and part of the product stream.

The effect of water on aldol condensation of acetone, and corresponding increase in the DAA selectivity using anion-exchange resin (Amberlite IRA-900), has been reported in the literature.^{5,6} The rate-inhibiting effect of water on aldol condensation of acetone to MO using cation-exchange resin (Amberlyst 16) in a batch reactor is also reported.⁷ However, the formation of DAA is neglected, and hence, the selectivity aspects have not been studied.

The present study addresses the effect of water on aldol condensation of acetone and the improvement in DAA selectivity using cation-exchange resin (Amberlyst 15). The aim is to improve DAA selectivity by using water in a reactive distillation column that operates close to or above the boiling point of acetone. To validate and predict the performance of a catalytic distillation column, liquid-phase kinetic data for DAA and MO formation that incorporate the effect of water concentration at temperatures near the boiling point of acetone are required. At present, such information is not available in the literature. The kinetic data were obtained in a laboratory batch reactor, and a kinetic model was developed. Batch reactive distillation (BRD) and continuous reactive distillation (CRD) studies have been performed to demonstrate the potential of water as a selectivity enhancer in reactive distillation. The results of CRD are compared with those obtained in the absence of the external addition of water to the reactive distillation column and

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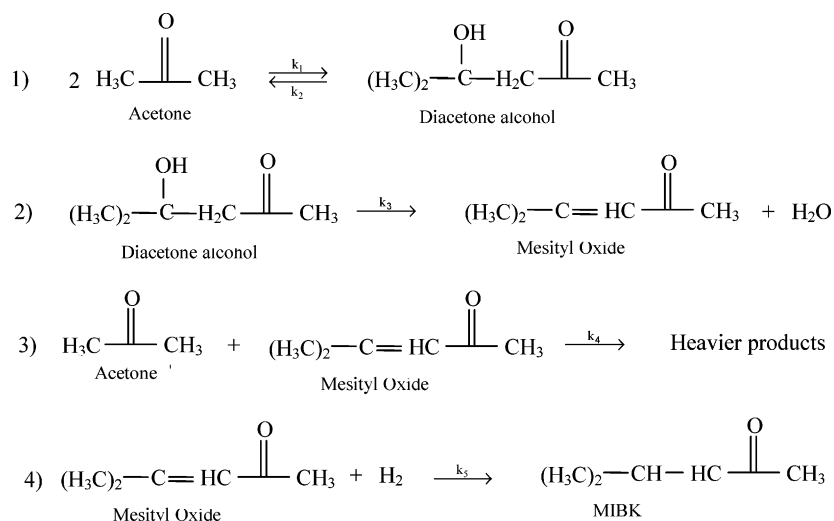


Figure 1. Reaction scheme for aldol condensation of acetone and related reactions.

Table 1. Properties of Amberlyst 15

property	units	Value
minimum exchange capacity (dry basis)	equiv/kg	4.7
internal surface area	m ² /g	50
particle size	mm	0.5 (≥90%)
density	g/L	780
shape		bead
maximum operating temperature	°C	120

supported by simulation studies that use the kinetics developed in the present work.

Experimental Work on Reaction Kinetics

Materials and Catalyst. Distilled water was used along with acetone as the initial feed. Acetone (AR grade, moisture < 0.02%) was supplied by Merck Ltd., India. The catalyst used in the experiments was commercial strong-acid cation-exchange resin Amberlyst 15 and was obtained from Rohm and Hass, Philadelphia, PA. The physical properties of the catalyst are listed in Table 1. Before its use, the fresh catalyst was carefully washed with pure water, isopropyl alcohol, dilute hydrochloric acid, and then again with pure water sequentially. It was then dried at 70 °C under vacuum for about 12 h to remove moisture present in it.

Apparatus and Procedure. The effect of water on aldol condensation of acetone reaction was studied in a 300 mL stainless steel batch autoclave (Parr, U.S.A.) with temperature and speed monitoring facility. The desired quantities of catalyst, water, and acetone (i.e., 185 g) were charged to the reactor and heated up to the desired temperature. The agitation was started, typically after 5 min, when the desired reaction temperature was attained. This time was considered as the zero reaction time. The samples (0.4 g) were removed after specific time intervals and were cooled through a coil immersed in chilled water to prevent acetone evaporation during the sampling. Various experiments were carried out in the absence of external and internal mass transfer resistances to study the effect of different parameters like temperature, water concentration (i.e., % w/w water in the reaction mixture), and catalyst loading (i.e., weight of catalyst in the reaction mixture) on the reaction kinetics in the presence of water.

Analysis. A gas chromatograph (GC-911; Mak Analytica India Ltd.) equipped with a flame ionization detector (FID) was used to analyze the reaction mixture for acetone, mesityl oxide, and diacetone alcohol. The analysis was carried out in a 30 m

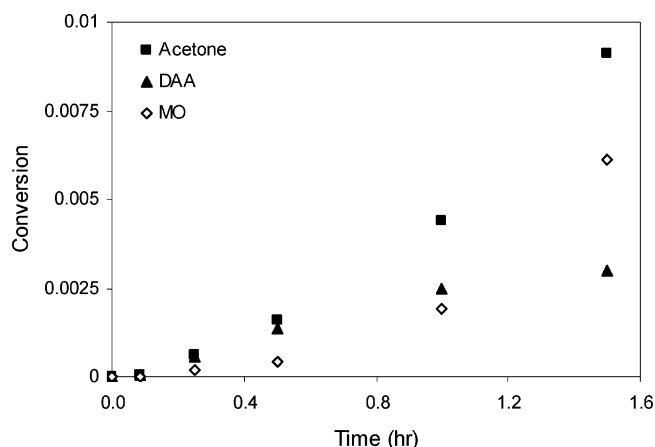


Figure 2. Conversion vs time at 55 °C and 3.5 % (w/w) of catalyst loading and 1% (w/w) of initial water.

long BP-5 column with an inner diameter of 0.55 mm. Nitrogen was used as a carrier gas at a flow rate of 0.5 mL/min with methyl ethyl ketone (MEK) as the external standard. The water concentration was calculated based on material balance. The molar amount of water formed was assumed to be the same as that of mesityl oxide because the amount of heavier products formed at low conversion level was negligible compared to the amount of acetone converted or mesityl oxide formed. This method of analysis is sufficiently accurate for this reaction system over a temperature range of 30–75 °C.

Calculations for Selectivity and Conversion. Conversion of acetone is calculated on the basis of initial moles of acetone

$$X = 1 - \frac{\text{moles of acetone present}}{\text{initial moles of acetone taken}} \quad (1)$$

Selectivity toward DAA is calculated as

$$S = \frac{2 \times \text{moles of DAA formed}}{\text{moles of acetone converted}} \quad (2)$$

General Course of the Reaction. Figure 2 shows the general course of reaction in the presence of water with respect to time in the batch reactor. Since the equilibrium conversion of acetone to DAA is very low, DAA concentration does not rise beyond a particular limit. The material balance based on the consumption of acetone and formation of MO and DAA shows that the

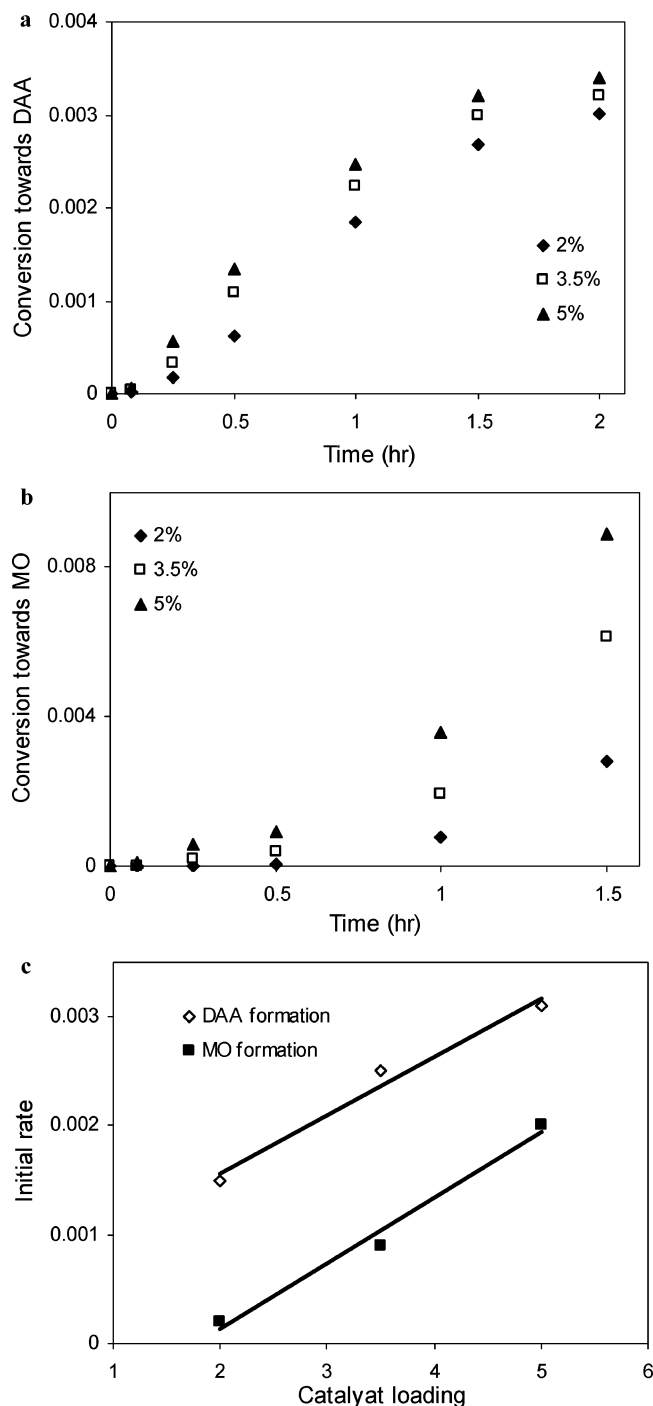


Figure 3. (a) Effect of catalyst loading on DAA formation at 55 °C, 1% w/w of initial water; (b) effect of catalyst loading on MO formation at 55 °C, 1% w/w of initial water; (c) effect of catalyst loading on initial rate of DAA and MO formation at 55 °C, 1% w/w of initial water.

conversion of acetone to the heavies is insignificant and is typically in the range 0.002–0.01% in all the runs.

Effect of Catalyst Loading. The effect of catalyst loading (i.e., % weight of catalyst in the reaction mixture) on DAA and MO formation in the presence of water was studied in the range of 1–5% w/w of total acetone feed. Parts a and b of Figure 3 show that the rates of formation of DAA and MO, respectively, increase with the catalyst loading. The initial rates for the individual components were found to increase linearly with catalyst loading, as shown in Figure 3c.

Effect of Temperature. The effect of temperature on acetone conversion to DAA and MO in the presence of water was

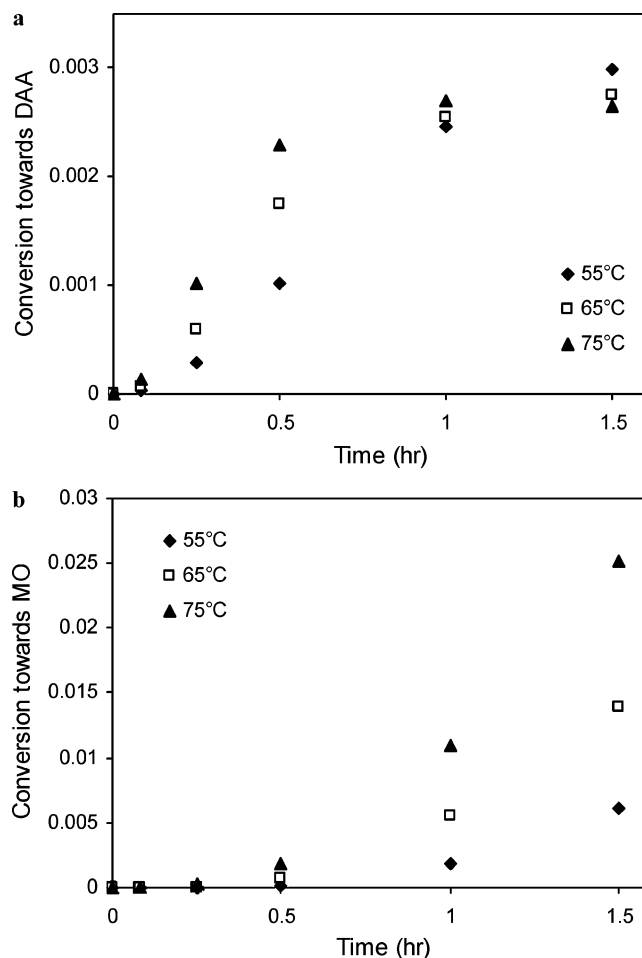


Figure 4. (a) Effect of temperature on DAA formation at 3.5% (w/w) of catalyst loading, 1% (w/w) of initial water; (b) effect of temperature on MO formation at 55 °C and 3.5% (w/w) of catalyst loading, 1% (w/w) of initial water.

studied over a range of 55–75 °C. Parts a and b of Figure 4 show the effect of temperature on DAA and MO formation, respectively. The selectivity toward DAA increases with the decrease in temperature, especially at higher conversion.

Effect of Water. Parts a and b of Figure 5 show the effect of water concentration (i.e., % weight of initial water in the reaction mixture) on the formation of DAA and MO, respectively. By increasing the initial water concentration, the overall conversion of acetone decreases. Moreover, since the inhibition effect of water is different for the two different individual reactions, selectivity is also altered. Figure 6 shows two different regions in the conversion vs selectivity plots at two different initial water concentrations. In the initial period, the selectivity toward DAA was found to increase with an increase in water content. In this period, DAA formation continuously increases. After this, a particular conversion crossover is realized. This is due to the fact that the first reaction being reversible nearly attains equilibrium and a further rise in DAA is not possible. The latter part of the reaction is dominated by conversion of DAA to MO, because of which the selectivity to DAA decreases. The increase in selectivity in the initial period is due to the favorable change in the relative rates of aldol condensation and dehydration as both the reactions are kinetically controlled. In our earlier studies on reactive distillation for the same reaction,⁴ it was observed that the reactive zone that is placed in the rectifying section is mostly occupied by acetone due to its volatile nature. Thus, the reaction environment and concentration region in RD are similar to the ones in the initial period of the

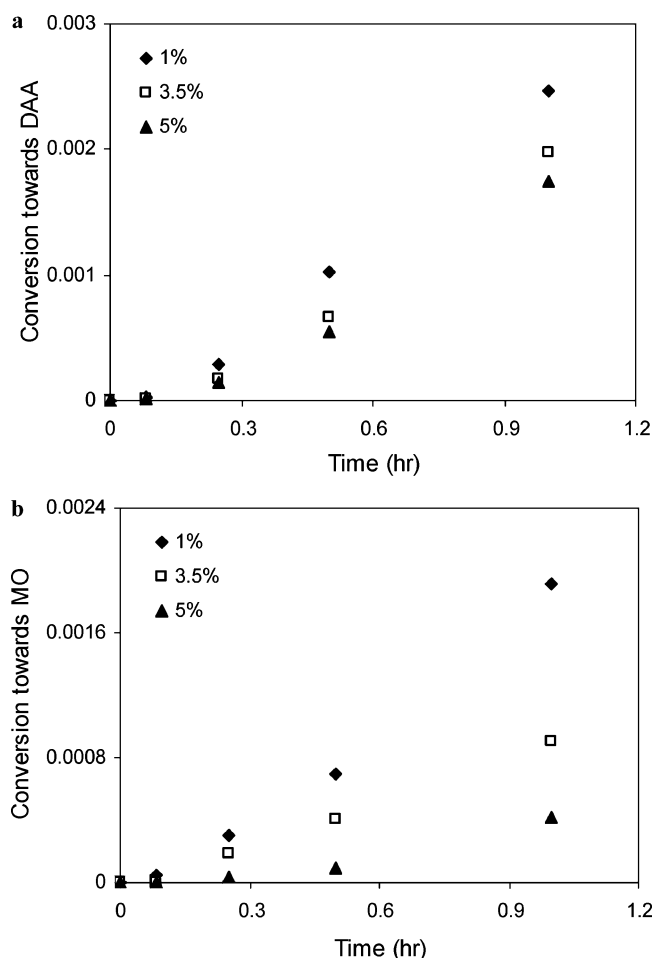


Figure 5. (a) Effect of water concentration on DAA formation at 55 °C, 3.5% (w/w) of catalyst loading; (b) effect of water concentration on MO formation at 55 °C, 3.5% (w/w) of catalyst loading.

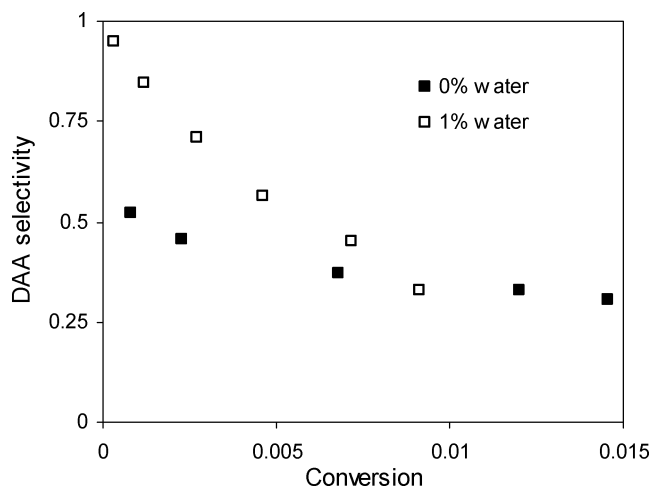


Figure 6. Effect of water on DAA selectivity at 55 °C and 3.5% (w/w) of catalyst loading.

batch reactor, and hence, it is expected that the selectivity to DAA may be enhanced by the addition of water in reactive distillation.

Kinetic Modeling

In our previous work,⁴ we verified the sequence of the steps involved in aldol condensation of acetone (i.e., acetone \leftrightarrow DAA \rightarrow MO + water) by performing independent experiments with various combinations of DAA, MO, water, and isopropyl alcohol

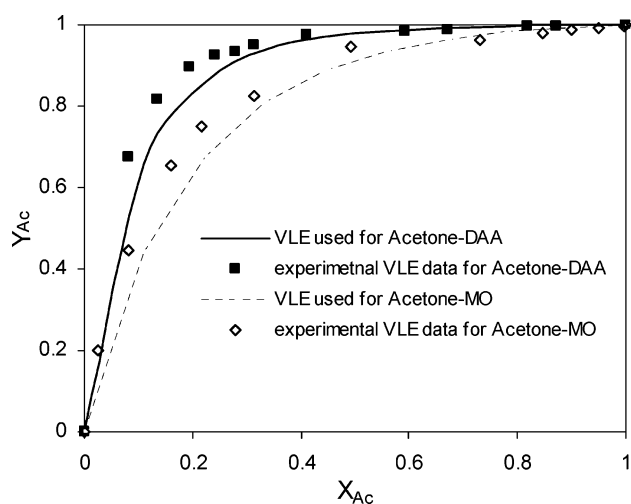
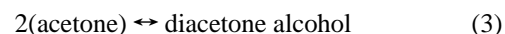


Figure 7. Comparison of x - y data used and generated in the present study for acetone-DAA and acetone-MO.

Table 2. Parameters for All Binaries

	acetone	DAA	MO	water
(a) UNIQUAC Model Binary Interaction Parameters (Temperature in K)				
acetone	0	79.56	-30.80	642.733
DAA	-36.17	0	212.5	1188.524
MO	61.65	-102.1	0	-56.94
water	-87.716	-351.086	1044	0
(b) Van der Waals Area (q) and Volume (r) Parameters				
	acetone	DAA	MO	water
R	2.5735	4.899	4.363	0.92
Q	2.336	4.308	3.86	1.4

(IPA) as feed(s) to a batch reactor. The reaction scheme considered for the kinetic modeling is as follows:



Kinetic modeling of reactions that are influenced by the presence of water needs special attention, as conventional sorption-based models fail to explain the rate-inhibition effects of water.⁸ Many authors^{5,8-11} try to capture the effect of water on reaction kinetics using semiempirical rate expressions to account for the inhibition effects of water, and the rate equation is extended by the inhibition factor η , which is a strong function of activity of water (a_w). We adopted the expression for inhibition factor (i.e., $\eta = e^{-K_w a_w}$) from Podrebarac et al.⁵ to explain this effect. The exponential term is used to explain the experimental observations that, at a higher concentration of water, the rate becomes insensitive to a further change in the water concentration. The effect of temperature on reaction rate is explained by using the Arrhenius equation. The parameters of the activity-based kinetic model (eqs 5 and 6) were estimated using 56 experimental data points.

$$r_{DAA} = \frac{dn_{DAA}}{dt} = M_{cat} (k_f e^{-K_{wf} a_w} a_{Ac}^2 - k_b e^{-K_{wb} a_w} a_{DAA}) - r_{MO} \quad (5)$$

$$r_{MO} = \frac{dn_{MO}}{dt} = M_{cat} k_{MO} e^{-K_{wMO} a_w} a_{DAA} \quad (6)$$

M_{cat} is the weight of catalyst. The UNIQUAC model was used to determine the activities of the components, and the UNIQUAC binary interaction parameters for all binaries were

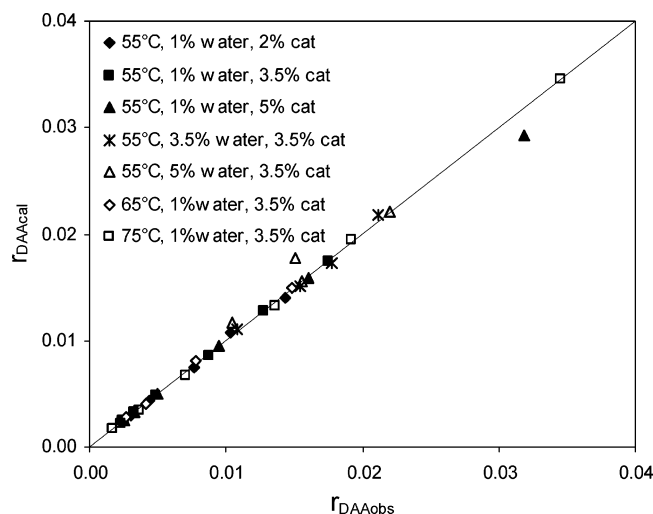


Figure 8. Calculated vs observed reaction rates for DAA formation.

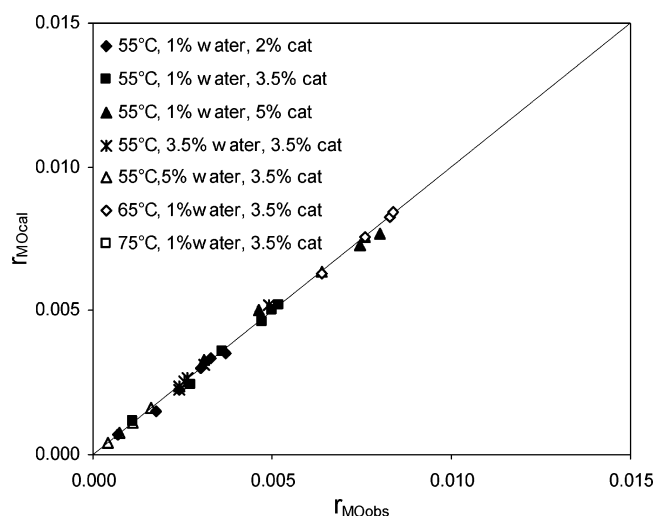


Figure 9. Calculated vs observed reaction rates for MO formation.

Table 3. Estimated Values of Parameters for Activity-Based Kinetic Models with 95% Confidence Limit

	estimated value	standard error
E_f (kJ/mol)	71.1	2.43
E_b (kJ/mol)	97.6	9.4
E_{MO} (kJ/mol)	61.3	5.9
k_{f0} (mol/kg/h)	1.17×10^{12}	80.7
k_{b0} (mol/kg/h)	3.31×10^{18}	759.1
k_{MO} (mol/kg/h)	1.1×10^{13}	147.8
K_{wf}	4.7	0.21
K_{wb}	2.2	0.35
K_{WMO}	12.1	0.97
SRS	5×10^{-5}	

determined by UNIFAC method using Aspen property plus¹² and are given in Table 2a. The validity of these parameters was independently checked with the help of the vapor–liquid equilibrium (VLE) data generated in the present work. We have generated the VLE data using a modified Othmer still¹³ for the binaries DAA–acetone and MO–acetone. Figure 7 shows the comparison of the experimental results with the predicted VLE behavior using the UNIQUAC model that uses the parameters given in parts a and b of Table 2. The agreement is satisfactory.

The Aspen Custom Modeler¹² (ACM) was used to estimate the kinetic parameters by regression. The program in ACM uses the least-squares method to minimize weighted absolute squared error between the observed and predicted values of the measure-

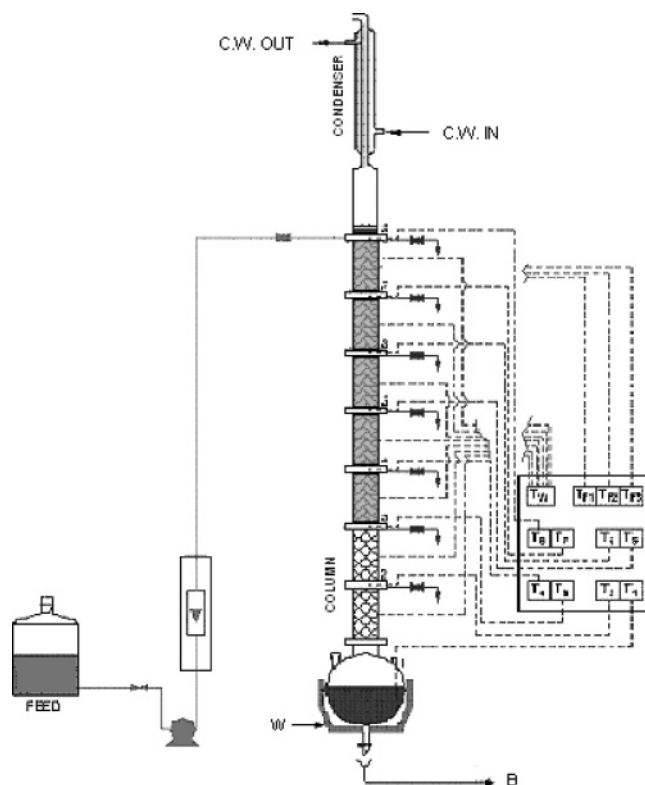


Figure 10. Reactive distillation setup. The shaded region of the column indicates reactive zone.

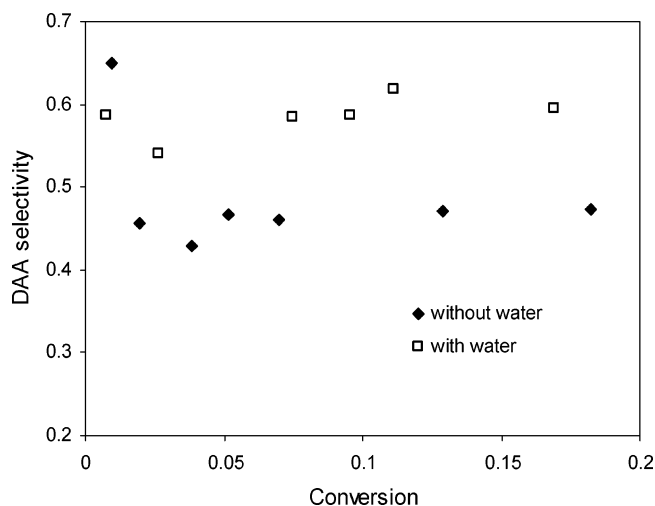


Figure 11. Effect of 1% (w/w) of initial water in acetone feed on DAA selectivity for 0.04 kg/m of catalyst concentration and 0.6 kW of reboiler duty.

ments. It determines the values of the parameters by solving the following minimization problem.

$$\min \left\{ \sum_{i=1}^{ND} \sum_{j=1}^N \sum_{k=1}^{M_{ij}} (Z_f(t_{ijk}) - Z_{ikj})^2 \right\} \quad (7)$$

where ND is the total number of dynamic experiments performed; z_j are the number of variables (i.e., concentrations of various species) measured over all the experiments, and M_{ij} is the number of measurements made in the experiment i . The regression results are summarized in Table 3, which includes the values of the kinetic parameters and the sum of residual square ($SRS = \sum_N (r_{exp} - r_{cal})^2$) with 95% confidence limit.

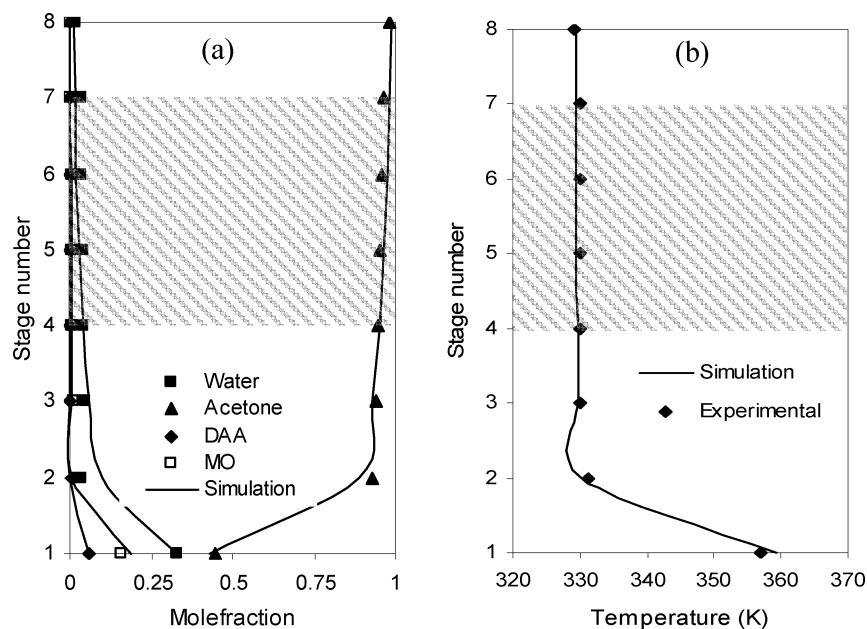


Figure 12. (a) Steady-state experimental and simulated composition profile along the length of column for 0.65 kW of reboiler duty, 0.107 kg/m of catalyst concentration, and 4.5% of water in feed; (b) steady-state experimental and simulated temperature profile along the length of column for 0.65 kW of reboiler duty, 0.107 kg/m of catalyst concentration, and 4.5% of water in feed. The shaded region indicates reactive zone.

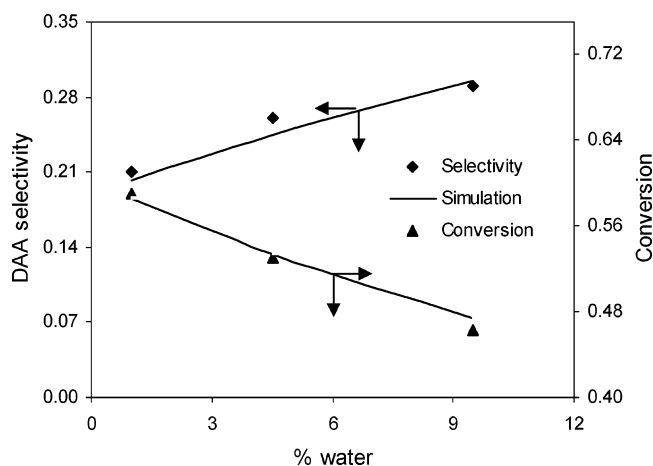


Figure 13. Effect of water concentration on DAA selectivity and on conversion of acetone at 0.65 kW and 0.107 kg/m of catalyst concentration.

The reaction rates, calculated from the slope of the concentration vs time curve, at different batch times for all the temperatures, initial water concentrations, and catalyst loadings are plotted as functions of the observed rates for DAA and MO formation in Figures 8 and 9, respectively. The agreement between experimental and predicted results is satisfactory.

Reactive Distillation

In our earlier work,⁴ we proposed reactive distillation (RD) for simultaneous production of DAA and MO using cation-exchange resin without water dosage. RD was found to offer better performance than the conventional reactor. It has distinct advantages of shifting the chemical equilibrium toward the formation of DAA and also suppressing the consecutive dehydration of DAA to MO. The best configuration of RD would be the one that has the reactive zone in the rectifying section because the reactant, acetone (boiling point (bp) of 56.3 °C), is the lightest compound compared to water (bp = 100 °C), MO (bp = 129.5 °C), and DAA (bp = 169.2 °C).¹⁴ Thus, acetone would be present in large proportion in the upper section of the column if operated under total reflux. A

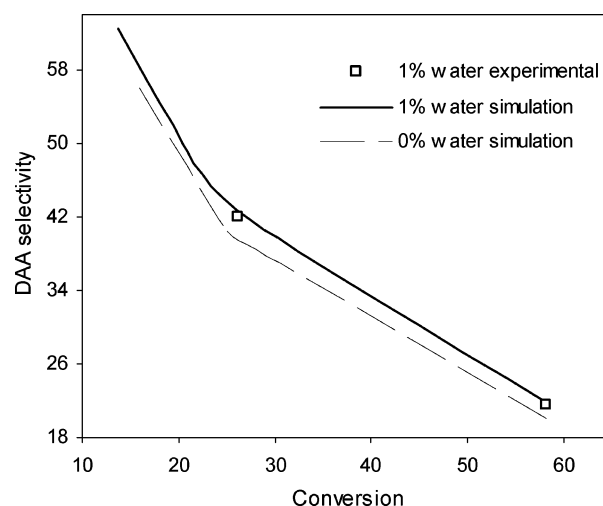


Figure 14. Effect of 1% w/w of initial water in acetone feed on DAA selectivity at 0.65 kW for various conversion levels.

nonreactive stripping section is necessary to effectively separate higher-boiling components such as water, DAA, and MO from the reactive zone and thereby suppress their further series reactions. One may obtain the DAA/MO ratio over a wide range by changing operating conditions such as reboiler duty and catalyst concentration ((kg of catalyst)/(m of reactive zone)). As explained before, water being a polar compound plays an important role in improving the DAA/MO ratio further by covering the active catalytic sites, thereby favorably influencing the relative rate of dehydration of DAA to MO. The combined effect of simultaneous separation of DAA and water inhibition can result in an increase in DAA selectivity and we have verified the same in the next section. It should be noted that MO and water form a minimum-boiling azeotrope at atmospheric pressure. However, in the present case, both MO and water will be removed as bottom products, and thus, the azeotrope is not relevant in context to the process feasibility. Except for the MO–water mixture, all the other binaries are nonazeotropic. In reactive distillation experiments, acetone is present on all the stages, which helps homogenize the reaction mixture and

avoids a possible liquid–liquid split that may result because of the miscibility gap between water and MO.

Apparatus. The reactive distillation (RD) setup, shown in Figure 10, consists of a reactive section (1.4 m) and a nonreactive section (0.6 m). The reactive section is packed with Sulzer Katapak packing filled with cation-exchange resin Amberlyst 15, and the nonreactive section is packed with HYFLUX packing from Evergreen India Ltd. The RD column is fully insulated with asbestos. Heat losses from the column and reboiler are in the range 20–50% depending upon the input reboiler duty. Temperature sensors and sampling ports are provided at several positions for monitoring the performance of an RD run. Since it is a single reactant system with no inerts present, the column was operated at total reflux.

Batch Reactive Distillation (BRD). Batch reactive distillation (BRD) was conducted in the setup shown in Figure 10. Experiments were conducted by charging acetone to the reboiler initially and removing samples at different time intervals from the reboiler to examine the performance under total reflux. Water was introduced at the top of the column at a rate of 0.5 mL/min. Figure 11 shows the results of BRD runs at 600 W (0.04 kg/m of catalyst concentration), indicating the impact of the presence of water. The plot shows that, in the absence of water, one can achieve selectivity of the order of 47% for 17% conversion, whereas, by adding 0.5 mL/min of water, there is a rise in selectivity to about 56% at the same conversion. It shows that the presence of water has a favorable effect on the selectivity of the intermediate compound (DAA).

Continuous Reactive Distillation (CRD). The setup shown in Figure 10 was also used to conduct the experiments under total reflux by feeding acetone with water continuously at the top of the reactive section. The product was continuously withdrawn from the reboiler as the bottom stream. Samples at several locations in the column were analyzed at different time intervals to monitor the performance. The attainment of steady state was ensured by constancy in temperature and concentration profiles with respect to time. At steady state, samples were removed from several locations in the column, including the reboiler, and were analyzed to determine the performance. The equilibrium-stage model-based simulations were performed using Aspen plus simulator (RADFRAC).¹² The heat losses from the column wall and reboiler were calibrated and were considered while giving input to the simulator. Similarly, the number of theoretical stages for the reactive and nonreactive sections was independently determined by performing simple distillation of the standard methanol–water mixture (NTSM for the reactive zone = 3; NTSM for the nonreactive zone = 6). The relevant model equations and underlying assumptions may be found elsewhere.¹⁵ It should be noted that the external mass transfer resistance at the solid–liquid interface is not considered here because the external mass transfer step is expected to be relatively fast compared to the intrinsic reaction, which is slowed down due to the presence of water. The detailed investigation using a three-phase model approach¹⁶ may be necessary to investigate the exact role of solid–liquid mass transfer. Nevertheless, the simplified model used here is able to explain the results over the conditions of interest. The kinetics used for the simulations is the one developed in the present work. VLE binary interaction parameters used in the UNIQUAC model have been reported in Table 2a.

The experimental and simulation results of continuous reactive distillation are shown in Figures 12–14. Parts a and b of Figure 12 show the steady-state concentration and temperature profiles for a representative CRD run. The results of experiments

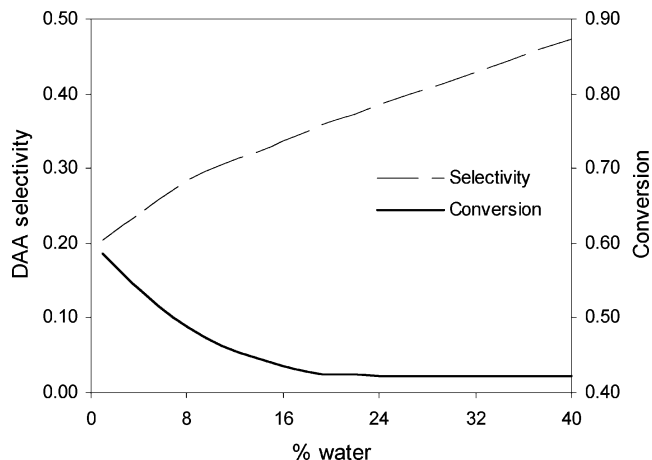


Figure 15. Effect of water concentration on DAA selectivity and overall acetone conversion at 0.65 kW and 0.107 kg/m of catalyst concentration.

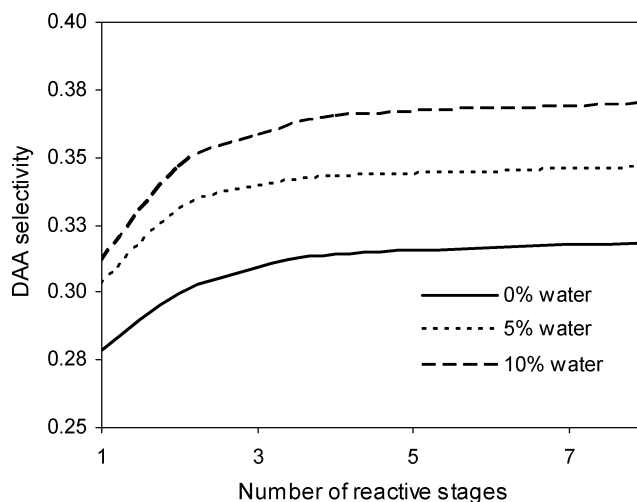


Figure 16. Effect of water concentration at 1 kW reboiler duty on selectivity of DAA with 60 g/h of acetone feed and with six nonreactive stages for conversion close to 100% (simulation results).

and simulations match reasonably well. Figure 13 shows the effect of water concentration on DAA selectivity for the same catalyst loading. CRD runs show that DAA and MO, with both of them being less volatile in comparison to acetone and water, leave the reactive stages as and when formed. With the increasing percentage of water in the feed, water concentration on the reactive stages increases, which results in unequal rate inhibition for the two reactions, thereby increasing selectivity toward DAA. However, we must note that, because of the increase in the water content, there is a decrease in overall conversion. This is expected because of the inhibition effect of water. The conversion can be increased by using a higher number of reactive stages with the same catalyst concentration on each stage or by increase the *per-stage* catalyst loading.¹⁴ Figure 14 shows the effect of water on DAA selectivity at a reboiler duty of 650 W for various conversion levels obtained by varying the total catalyst loading in the column.

As shown in Figure 15, when water concentration is low, it inhibits the reaction of MO and improves selectivity of DAA substantially. At a relatively larger concentration of water, the overall conversion becomes insensitive; however, the selectivity continues to rise with an increase in water concentration. The developed equilibrium-stage RD model predicts the results well for both low and high water concentrations in the acetone feed.

The column model thus validated can be further used to examine the effect of different parameters. Figure 16 shows the

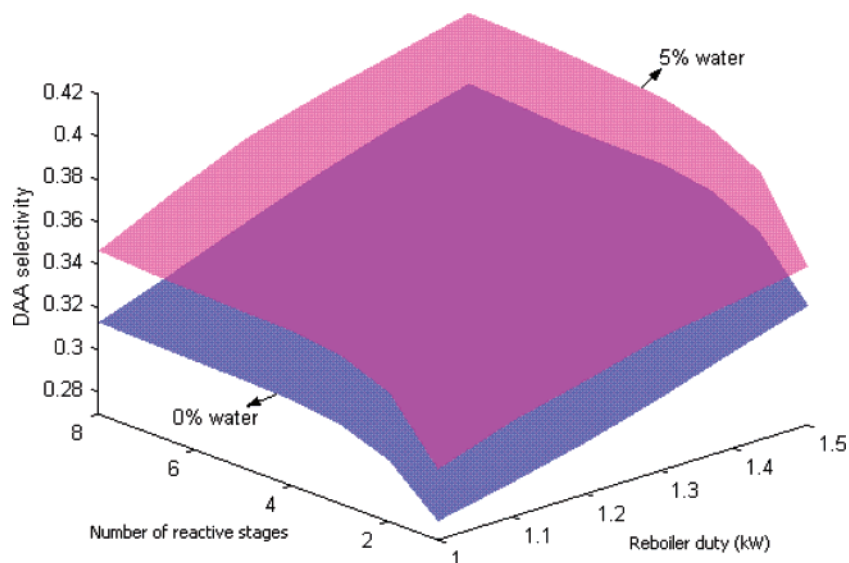


Figure 17. Effect of number of reactive stages and reboiler duty on DAA selectivity in the presence and in the absence of water⁴ in acetone feed with two nonreactive stages (simulation results).

CRD simulation results performed at a feed rate of 60 g/h and six nonreactive stages with reboiler duty of 1 kW, by varying water concentration. The catalyst loading was adjusted in such a way that an almost quantitative conversion level ($\sim 100\%$) is realized. By increasing the water concentration from 0 to 5% (w/w) in the acetone feed, selectivity of DAA increased from 30% to 34.6% for the same number of reactive stages and for the conversion close to 100%. Reboiler duty, water content in the feed, and the number of reactive stages are the key parameters that influence the selectivity for a given conversion. Figure 17 summarizes all these effects in a 3-D plot that compares the simulated results of our earlier studies⁴ for the absence of water in the feed with the results obtained in the present work (i.e., in the presence of water). In this case also, the total catalyst loading (170–200 g) is adjusted in such a way that quantitative conversion ($\sim 100\%$) is realized. From the plot, it is clear that there is an enhancement in the selectivity due to the presence of water, over a wide range of parameters. Increases in reboiler duty and the number of reactive stages go in favor of an increase in selectivity. By comparing the two surfaces corresponding to different water contents, one can conclude that increasing water content to 5% in the feed will have the same effect as that obtained by increasing the reboiler load from 1 to 1.5 kW at the same conversion levels. This shows a considerable reduction in the energy consumption because of the presence of water in the feed at the cost of a possible increase in the fixed cost due to the increase in catalyst loading. A detailed optimization study is necessary to arrive at the best process design.

Conclusion

Although RD can be used to obtain improved selectivity toward DAA, the formation of MO on the reactive stages cannot be completely avoided because dehydration of DAA is reasonably a fast reaction. Water acts as a rate inhibitor, and its continuous dosage in RD can increase the selectivity toward DAA substantially. The present studies have shown that one can vary water dosing rate along with catalyst loading to further improve the selectivity obtained in a normal RD column. However, introduction of water dosing slows the reaction down, and hence, higher total catalyst loading is necessary to obtain a similar conversion level. The parametric studies using the

experimentally validated model indicated that introduction of water reduces the energy consumption and that the reboiler duty required to achieve the same DAA yield otherwise is reduced significantly. The present study provides a cost-effective process alternative for the simultaneous production of diacetone alcohol and mesityl oxide.

Nomenclature

- a_i = activity of component i
- E_f = activation energy for DAA formation
- E_b = activation energy for DAA decomposition
- E_{MO} = activation energy for DAA dehydration
- k_{f0} = frequency factor for DAA formation
- k_{b0} = frequency factor for DAA decomposition
- k_{MO0} = frequency factor for DAA dehydration
- K_W = adsorption equilibrium constant of water
- K_{Wf} = adsorption equilibrium constant of water for DAA formation
- K_{Wb} = adsorption equilibrium constant of water for DAA decomposition
- K_{WMO} = adsorption equilibrium constant of water for DAA dehydration
- k_f = second-order rate constant for DAA formation
- k_b = first-order rate constant for DAA decomposition
- k_{MO} = first-order rate constant for DAA dehydration or MO formation
- M = mass (kg)
- M_{ij} = number of measurements made in the experiment i
- ND = total number of dynamic experiments performed
- NTSM = number of theoretical stages per meter
- n_i = number of moles (gmol) of component i
- r_i = reaction rate (gmol/min) of component i
- t = time
- z_j = number of variables measured over all the experiments

Suffixes

- Ac = acetone
- cat = catalyst
- DAA = diacetone alcohol
- i = general component

MO = mesityl oxide
 W = water
 T = temperature
 t = time (h)

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