

Kinetic Studies on the Dimerization of Isobutene with Ion-Exchange Resin in the Presence of Water as a Selectivity Enhancer

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The dimerization of isobutene (IB) followed by hydrogenation is looked upon as an important route to produce the octane booster isooctane (IO), because of doubts being raised about methyl *tert*-butyl ether (MTBE) being a clean fuel additive because of its substantial solubility in water. In the present work, the dimerization of IB has been carried out in a batch reactor over a temperature range of 65–95 °C in the presence of ion-exchange resin as a catalyst and isooctane as a solvent. The influence of various parameters such as temperature, catalyst loading, concentration of water, and initial concentration of IB was examined. Because several side reactions are involved in this reacting system, the selectivity of IB toward the dimers is an important issue. The presence of a polar compound in the reaction mixture plays a vital role as an inhibitor to the side reactions and improves the selectivity toward the dimers. In the present system, water was used as an inhibitor, which leads to the formation of *tert*-butyl alcohol (TBA) through the hydration of IB. A rigorous kinetic model is proposed to explain the experimental data. All of the reactions such as the reversible dehydration of TBA, dimerization, trimerization, and oligomerization of IB are considered explicitly in the kinetic models. The developed kinetic models would be versatile enough to design a commercial reactor such as a fixed-bed reactor or a reactive distillation column.

Introduction

The standards for environmental pollution regulation are getting tougher in almost all parts of the world. Refineries in every part of the world are forced to abide by the local laws and to provide more environmentally friendly gasoline.¹ To reduce evaporative emissions and to ensure complete combustion, oxygenates and highly branched paraffins are added to gasoline. The commonly used oxygenated compound methyl *tert*-butyl ether (MTBE) has been banned as a gasoline blend in California since January 2004, as MTBE is associated with groundwater contamination.² The possible phaseout of MTBE might cause a major decline in the downstream consumption of isobutene (IB) from fluid-catalytic-cracking and steam-cracking product streams. As a result, gasoline additives prepared from IB are likely to have an edge over the non-C₄ additives, e.g., *tert*-amyl methyl ether (TAME), ethanol, etc.^{3,4}

Alkylates are branched paraffins with carbon numbers in the range C₈–C₁₂ [e.g., isooctane (IO)]. They are nonaromatic, nonolefinic, low-sulfur, high-octane, paraffin-blend stocks. Alkylates have properties comparable to those of MTBE.¹ An appropriate blend of C₅–C₆ isomers with alkylates would match the volatility of gasoline and can be a reasonable replacement of MTBE. It is synthesized either by direct alkylation of isobutane with C₄ olefins or by indirect alkylation, i.e., dimerization of IB to form diisobutenes (DIBs) followed by saturation with hydrogen.

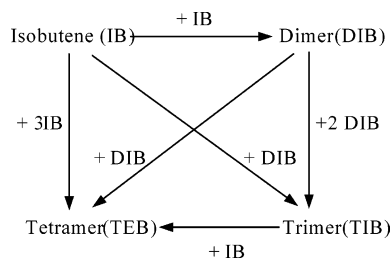


Figure 1. Reaction network of oligermization of IB³ (TEBs = tetra-isobutenes).

Table 1. Previous Studies on the Dimerization of IB^a

catalyst	conversion/ selectivity (%)	<i>T</i> (°C)	selectivity enhancer	solvent	ref
aluminosilicates (Si/Al = 60–90)	88/85	150	NA	NA	3
Amberlyst-15	NA, 72	NA	—	C ₄	5
Amberlyst-15	30–70	0–80	NA	hexane/ pentane	6
Amberlyst-15	60–68/90	125	H ₂ O/TBA	NA	7
Amberlyst-15	NA/99	NA	TBA	IO	8
Amberlyst-15	NA	75	MeOH/MTBE	NA	9
Lewatit K2631	NA	40–80	MeOH/MTBE	NA	10
SPA	66.2	160–210	NA	heavy paraffin	11
ion-exchange resin	97/24	80	—	isopentane	12
	89/48	80	MeOH	isopentane	
	53/86	80	TBA	isopentane	
ion-exchange resin	60/90	100	TBA	isopentane	13
	40–45/93	80	TBA	isopentane	

^a NA = data not available.

The reaction network that includes the desired dimerization in the presence of the acid catalyst is presented in Figure 1, which shows that, along with dimerization, several other

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Table 2. Physical Properties of the Ion-Exchange Resin Catalyst Used in This Work

property	value
cross-linking (%)	15
total capacity (mequiv/g)	4.9
porosity (%)	40
specific surface area (m ² /g)	35
pore diameter (Å)	400
temperature stability (°C)	120
screen size (U.S. mesh)	16-50
moisture content in wet form (%)	40

reactions can take place, and hence, the selectivity toward the dimers is a major concern. Much of the work on dimerization was carried out either before 1980 or in the late 1990s. The gap of almost two decades can be attributed to the dominance of MTBE as a gasoline additive during this period.³ A survey of significant published studies on IB oligomerization gives a fair idea of the influence of different parameters on the reaction performance and is presented in Table 1. Different polar components, such as methanol,^{9,10} MTBE,^{9,10} and *tert*-butyl alcohol (TBA),^{7,8,12,13} have been studied as selectivity enhancers, of which TBA was found to be promising.¹³ However, most commercial ion-exchange resins are available in the wet form (20–50% moisture), and even with further drying of such resins at temperatures above 100 °C for 12 h, it is difficult to reduce the moisture content below 3%.¹⁴ Thus, water is an integral part of such catalysts, and it would be more appropriate to use water itself as a selectivity enhancer. In addition, water reacts with IB to form TBA. Thus, it is important to consider water and TBA together as the selectivity enhancer system rather than considering TBA or water alone. In a prior work,¹³ the kinetic model did not account for the activity of water separately and considered the activities of TBA and water to be equal. However, the activity coefficient for water, under the operating conditions of interest, is 6–7 times greater than that of TBA, and hence, it is necessary to consider the effects of the two components separately, especially in the operating range in which TBA is likely to dehydrate and give IB and water.

The aim of this study is to develop a quantitative kinetic model, based on batch reactor experiments, that considers the IB oligomerization and hydration and TBA dehydration reactions separately. The effects of water and TBA inhibition are isolated and considered separately in the kinetic model. Also, the previous studies were performed with solvents such as hexane and pentane, whereas in this work, the reactions are studied in the presence of IO as a solvent, considering the possibility of its presence in the proposed reactive distillation process for simultaneous dimerization and hydrogenation.¹⁵

Experimental Section

Materials. Master Standards, Mumbai, India, supplied IB (99%). IO (99.5%) and TBA (98%) were obtained from Merck Ltd., Mumbai, India. DIB was supplied by Schenectady Herdillia Ltd., Mumbai, India. A C₄ stream of required composition was obtained from BPCL Refinery, Mumbai, India. Thermax Ltd., Maharashtra, India, supplied Tulsion T-63. The catalyst was dried at 80 °C at 50 mmHg for about 12 h. All kinetic experiments were performed using Tulsion T-63 as the catalyst. The physical properties of the catalyst are given in Table 2 and are similar to those of the well-known Amberlyst-15 catalyst of Rohm and Haas company.

Apparatus and Procedure. A stainless steel autoclave (Amar Equipment Pvt. Ltd., Mumbai, India) of 1 × 10⁻⁴ m³ capacity,

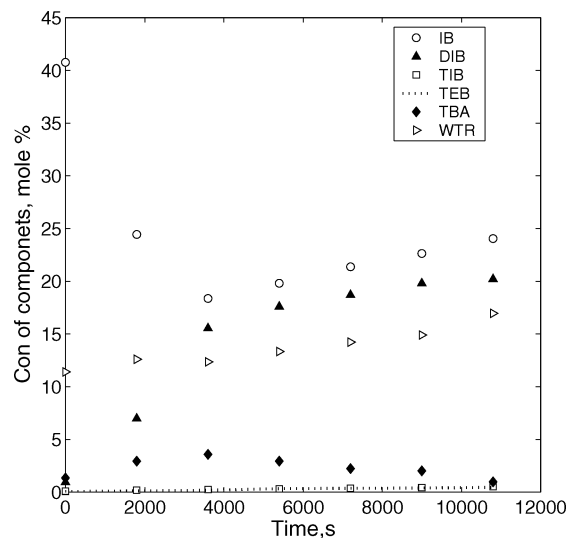


Figure 2. General course of the reaction. Catalyst = T-63, temperature = 80 °C, catalyst loading = 15.09 g/mol of IB, IB/IO ratio = 1.35 mol/mol, moisture content = 0.24 mol of water/mol of IB.

equipped with speed and temperature monitoring facilities and an automatic cooling system, was used for conducting all batch reactions. The desired quantities of catalyst, reactant, and solvent were charged to the reactor, and the reaction mixture was heated to the desired temperature with slow stirring. All experiments were performed at autogenous pressure that varies between 2 and 8 bar depending on the reaction temperature and falls as the reaction progresses because of IB consumption in the liquid-phase reaction. As the reaction temperature was reached, the speed of agitation was increased to the desired level, and the corresponding time was regarded as the zero reaction time. Samples were withdrawn at different time intervals using a sampler inserted in the liquid phase. Isobutene in the samples was allowed to vaporize, and isobutene-free samples were used for the analysis.

Analysis. The reactants and products were analyzed using a gas chromatograph (GC-MAK-911) equipped with a flame ionization detector (FID). A 25-m-long capillary column (BP-1, SGE, Victoria, Australia) was used to separate the different components in the reaction mixture using isooctane as an internal standard. The column temperature was maintained at 100 °C isothermally for the first 5 min and then raised at a rate of 30 °C/min to 290 °C for 20 min. The components that elute after triisobutenes (TIBs) are termed oligomers, i.e., tetraisobutenes (TEBs). The product mixture was fractionated by distillation under vacuum and used for the calibrations of trimers and oligomers. The various components in the reaction mixture and the separated products were characterized by authentic samples and/or by GC-MS. Water in the reaction mixture cannot be detected by FID, so the water concentration was calculated on the basis of the amount of TBA formed. Before using the catalyst for the reaction, the moisture content of the catalyst was determined by thermogravimetry with differential scanning calorimetry (TG-DSC; model STA-409PC, NETZSCH, Waldkraiburg, Germany).

Calculations for Conversion and Selectivity. The conversion of IB was calculated on the basis of the various products formed in the reactions

$$X = \frac{n_{IB,0} - (2n_{DIB} + 3n_{TIB} + 4n_{TEB} + n_{TBA})}{n_{IB,0}} \quad (1)$$

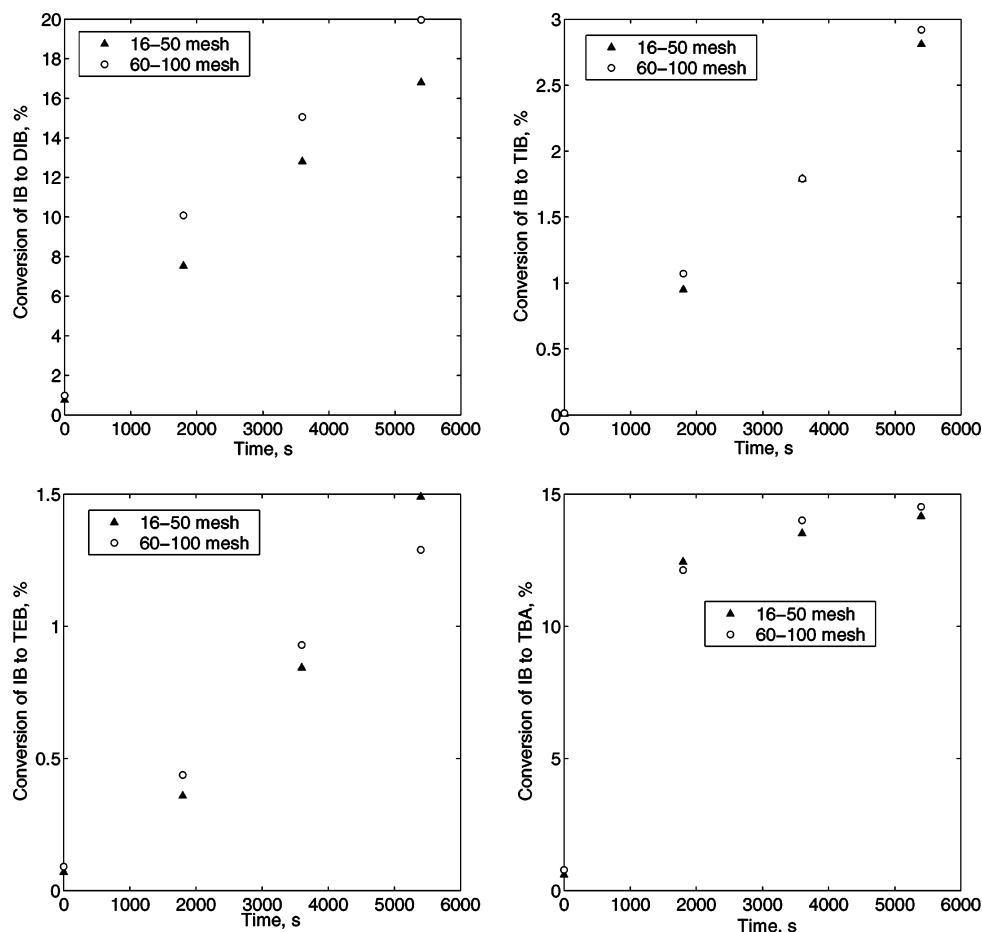


Figure 3. Effect of catalyst size. Catalyst = T-63, temperature = 80 °C, catalyst loading = 15.09 g/mol of IB, IB/IO ratio = 1.35 mol/mol; moisture content = 0.26 mol of water/mol of IB.

During calculations of the selectivity toward the dimer, TBA was not considered as a side product, given that it dehydrates back to IB when the concentration of IB drops below equilibrium concentration

$$S = \frac{2n_{\text{DIB}}}{2n_{\text{DIB}} + 3n_{\text{TIB}} + 4n_{\text{TEB}}} \quad (2)$$

Results and Discussion

General Course of the Reaction. As mentioned earlier, we define the zero reaction time as the time at which the desired temperature is attained. Hence, in all of the kinetic runs, we observe some conversion of IB that occurs before the desired temperature was reached. The extent of reaction during this heating period is relatively higher at higher catalyst loadings and temperature. The compositions at zero time are used as initial points for parameter estimations. Figure 2 shows typical concentration profiles of reactant and various products with respect to time. As the reaction proceeds, the concentration of DIBs increases selectively with a very slow increase in the concentrations of TIBs and oligomers. The formation of TBA is also observed during the course of the reaction as the catalyst contains moisture up to 0.08–0.40 mol/mol of IB. The concentration of TBA goes through a maximum as TBA is dehydrated back to IB and water because of the drop in IB concentration in reactor. As a result, an increase in the IB and water concentrations can be seen in Figure 2. The moisture plays a crucial role in the selectivity toward DIBs, given that water,

as a polar compound, covers the active catalytic sites, thereby reducing the rate of oligomerization reactions. Therefore, during the charging of the reactants under chilled conditions, adequate care was taken so that no external moisture from the humid atmosphere could leak into the reacting system. It was observed that the catalyst has a very strong affinity toward water, and hence, water remains in the catalyst phase up to 0.40 mol/mol of IB. It should be noted that the total number of moles in the reaction mixture decreases as a result of various reactions taking place. It was observed that catalyst activity is not affected for about 12 h of reuse, and hence, it is not necessary to consider catalyst deactivation during the course of reaction for the kinetic model development.

Mass-Transfer Effects. To ensure the absence of significant external mass-transfer resistance across the solid–liquid interface, the reactions were performed at different stirring speeds of 400, 600, and 800 rpm, and it was observed that the results were insensitive to the agitation above 600 rpm. Hence, all subsequent experiments were performed at 1000 rpm. As shown in Figure 3, the performance of the catalyst was not much influenced by the catalyst size over a range 15–100 mesh, and hence, internal diffusion effects can be neglected.

Effect of Temperature. The effect of temperature was studied over the range of 65–95 °C. Figure 4 shows the effect of temperature on the concentration profiles for the various products. At higher temperatures, DIB formation goes through a maximum. The decline in DIB concentration is due to their consumption in the subsequent reaction to form TIBs. As

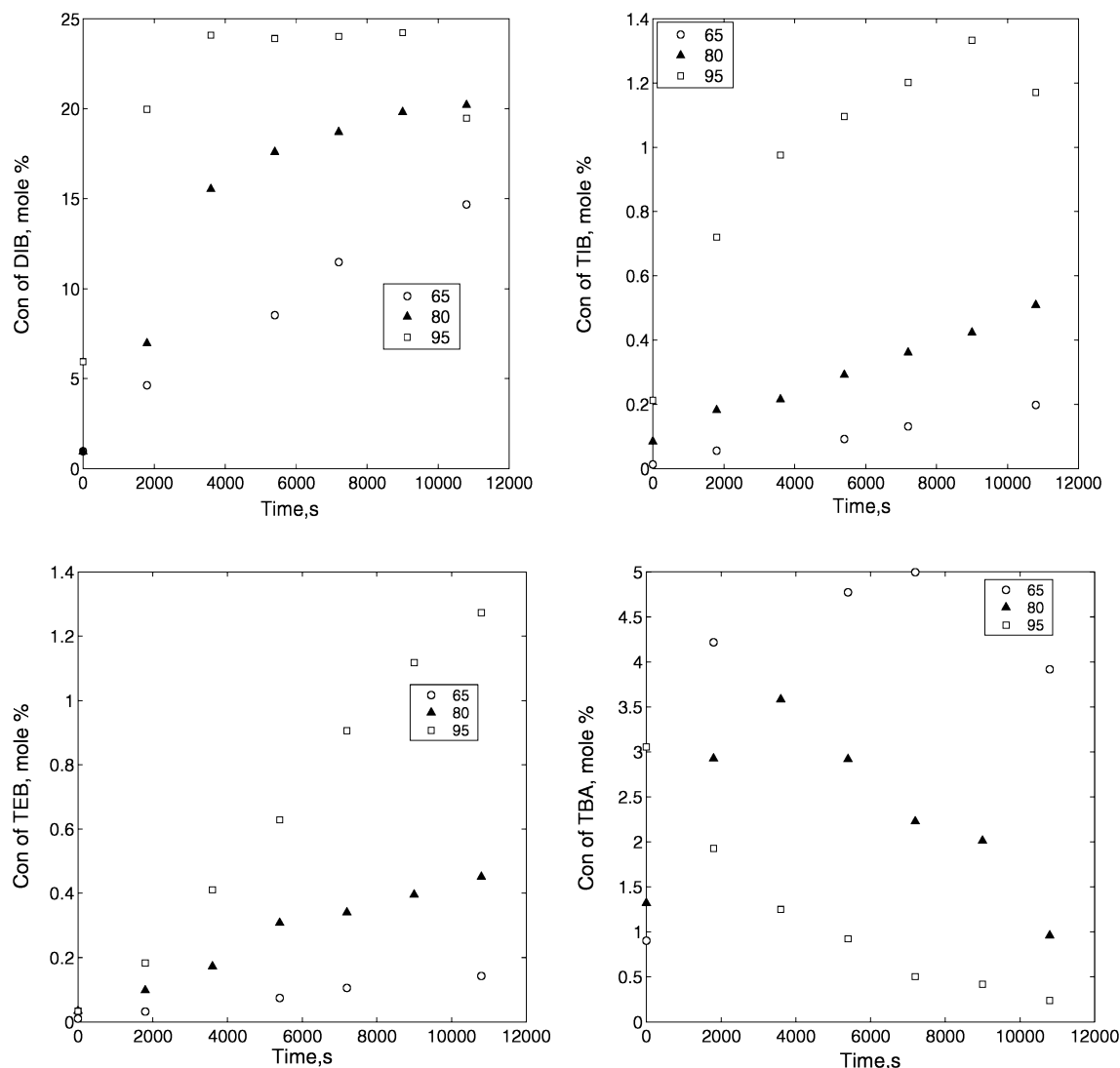


Figure 4. Effect of temperature on product profiles. Catalyst = T-63, catalyst loading = 15.09 g/mol of IB, IB/IO ratio = 1.35 mol/mol, moisture content = 0.24 mol of water/mol of IB. Symbols indicate temperatures in °C.

explained later, the TBA concentration always shows a trend opposite to that of DIB concentration, and it is found to be lower at higher temperatures. The concentrations of TIBs and TEBs increase with increasing temperature, and at higher temperatures, the TIB concentration goes through a maximum, as shown in Figure 4, as a result of the formation of TEBs in the subsequent reaction.

Effect of Catalyst Loading and Moisture Content. We found that both moisture concentration and the moisture-to-catalyst ratio influence the reaction kinetics. The moisture concentration alone, irrespective of the catalyst loading, influences the hydration reaction and, hence, the consumption of IB in this reaction. On the other hand, the moisture-to-catalyst ratio is related to the surface coverage and inhibition, which have an impact on the formation of side products, especially trimers.

To observe the true effect of catalyst loading and moisture concentration, two sets of experiments were performed. In both cases, the catalyst was dried at 50 mmHg and 80 °C for 12 h. In the first case, the desired amount of moisture was added to the reaction mixture, and the reactions were performed over a wide range of catalyst loadings (7–22 g/mol of IB) at identical initial water concentrations in the reactor. It is evident from

Figure 5a that, with an increase in the catalyst loading, the DIB concentration increases, and a significant rise in TIB concentration is also realized, especially when the catalyst loading was increased from 15 to 22 g/mol of IB. In these experiments, an increase in the catalyst loading has the same effect as a decrease in the moisture-to-catalyst ratio. This is because the moisture concentration in the reactor was the same in all of these experiments, but the moisture-to-catalyst ratio decreased with increasing catalyst loading. In the second set of experiments, different quantities of moisture were used (0.08–0.40 mol/mol of IB) at constant catalyst loading. It was found that, with an increase in moisture concentration, the TBA reaction competes with dimerization, and hence, the concentration of DIBs decreases, as shown in Figure 6. As already explained, the TIB concentration is higher at low moisture content (0.08 mol/mol of IB) than at higher moisture content (0.24–0.40 mol/mol of IB). This shows that the formation of TIBs is more sensitive to the moisture-to-catalyst ratio than is the formation of DIBs. This might be because, at the same moisture content, an increase in catalyst loading, i.e., a lower moisture-to-catalyst ratio, results in insufficient surface coverage by moisture, leading to a rise in TIB concentration. The effect of the moisture-to-catalyst ratio

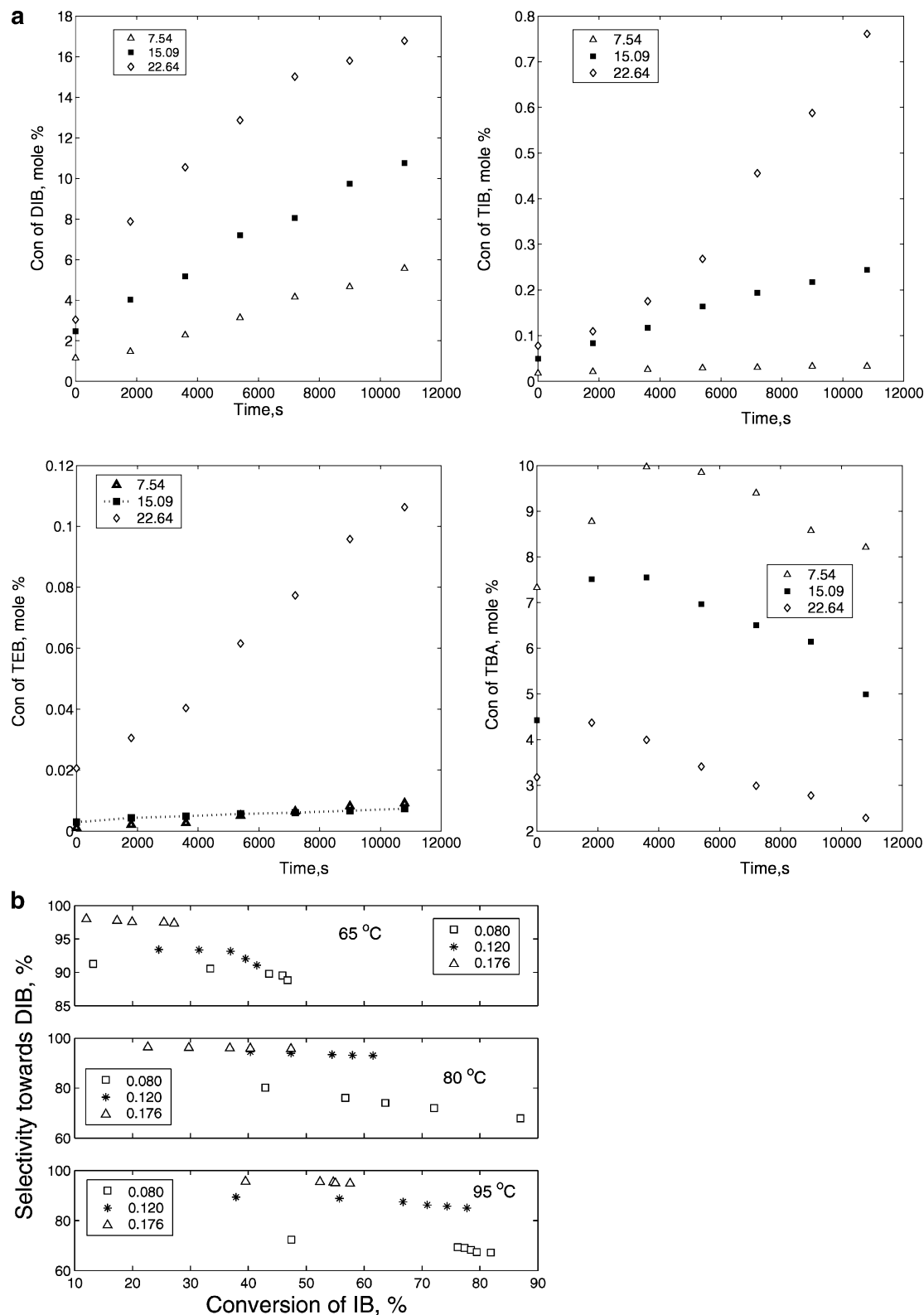


Figure 5. (a) Effect of catalyst loading on product profiles. Catalyst = T-63, IB/IO ratio = 1.35 mol/mol, moisture content = 0.24 mol/mol of IB, temperature = 80 °C. Symbols indicate grams of catalyst per mole of IB. (b) Effect of moisture and temperature on conversion of IB and selectivity to DIBs. Catalyst = T-63, catalyst loading = 15.09 g/mol of IB, IB/IO ratio = 1.35 mol/mol. Symbols indicate moles of water per mole of IB.

on the conversion of IB and selectivity to DIBs, at different temperatures, is shown in Figure 5b.

Under the operating conditions of interest, it was observed that the formation of TBA is much more rapid than that of the dimer and oligomers. Hence, in any run, depending on the quantity of moisture present, the hydration reaction occurs first,

resulting in the formation of TBA. Also, at any given point of time, because the TBA reaction is reversible, the concentration of TBA is controlled by the reaction equilibrium of the hydration reaction. When IB present in the reaction mixture is consumed to form DIBs, the equilibrium of the hydration reaction breaks, leading to rapid dehydration. Hence, in general, under otherwise

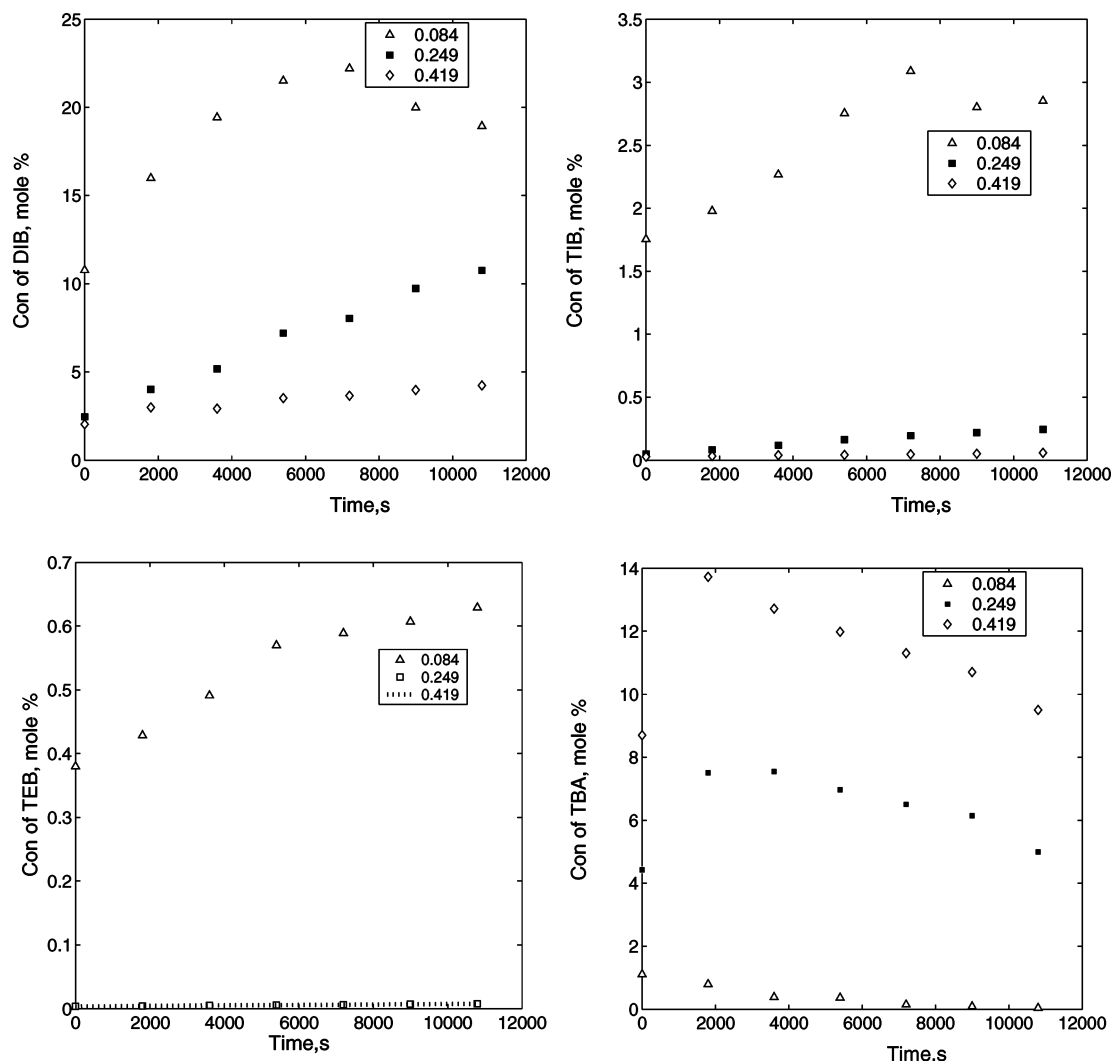


Figure 6. Effect of moisture content on product profiles. Catalyst = T-63, catalyst loading = 15.09 g/mol of IB, IB/IO ratio = 1.35 mol/mol, temperature = 80 °C. Symbols indicate moles of water per mole of IB.

Table 3. Composition of the C₄ Mixture

component	wt %
propane	2.42
propene	1.00
isobutane	24.42
<i>n</i> -butane	6.78
1-butene	7.31
isobutene	39.57
<i>t</i> -2-butene	8.93
<i>c</i> -2-butene	6.61
<i>i</i> -pentane	1.84
<i>n</i> -pentene	0.03
heavier	1.09

similar conditions, an increase in DIB concentration should result in a decrease in the concentration of TBA. This is very well reflected in the experimental results in Figures 5a and 6, as well as in the effect of temperature (Figure 4) discussed earlier.

Effect of Solvent. IB is normally available in the form of a C₄ stream from various sources such as fluid catalytic cracking (FCC), isobutane dehydrogenation, etc. Hence, it would be appropriate to study the dimerization in the presence of other C₄ compounds. A C₄ stream obtained from BPCL Refinery (14% IB, w/w) was mixed with pure IB so as to adjust the feed concentration and to compare the results with isooctane as the

solvent. The composition of the C₄ mixture thus prepared is reported in Table 3. It was observed that the rate of the reaction was slightly less than that obtained with isooctane; however, the selectivity remained unchanged.

Effect of IB Concentration. The effect of the initial concentration of IB on the rate of reaction was studied for IB concentrations of 0.67 and 1.35 mol of IB/mol of IO. As expected, the initial rate of DIB formation is a factor of 2.12 less at the concentration of 0.67 mol of IB/mol of IO than at 1.35 mol of IB/mol of IO. For 36% conversion, the DIB selectivity at 0.67 mol of IB/mol of IO was 98.13%, and that at 1.35 mol of IB/mol of IO was 96.67%.

Kinetic Modeling. The possible routes leading to the formation of different oligomers of IB are shown in Figure 1. However, we performed few experiments starting with pure DIBs, and found that no TIB and/or tetraisobutene (TEB) formation occurred under the operating conditions studied. Thus, we confirmed that both TIBs and TEBs are primarily formed by a combination of series and parallel reactions, i.e., IB reacts with DIBs to give TIBs and further reacts with TIBs to give TEBs. Hence, the direct formation of TIBs and TEBs from IB is eliminated from the kinetic modeling. TBA is also formed as a result of a reversible reaction of IB with water. The reactions that are considered in kinetic modeling

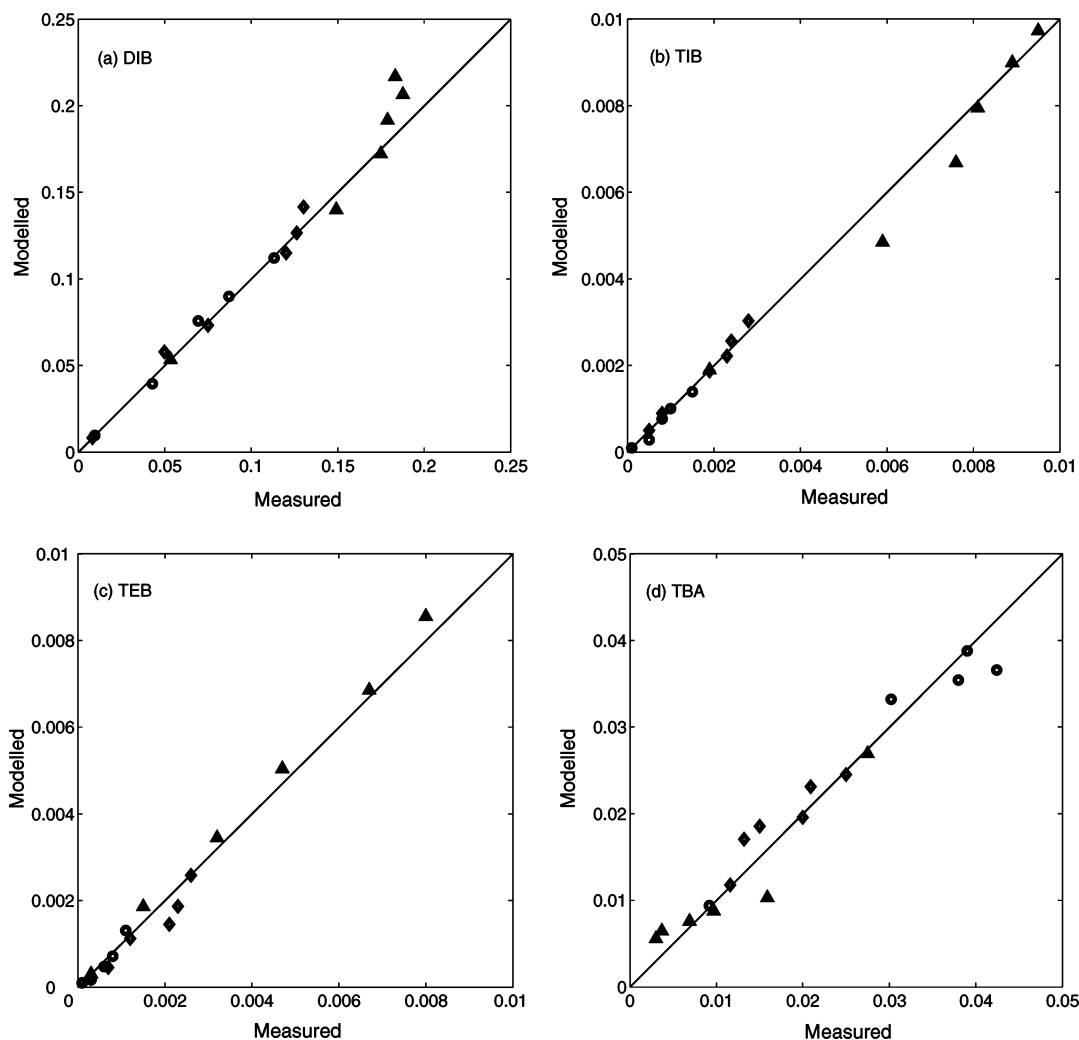
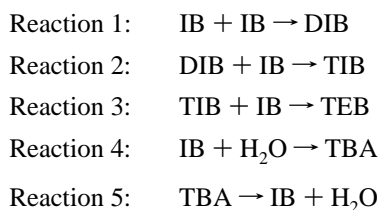
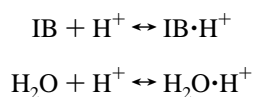


Figure 7. Effect of temperature on product profiles comparison between modeled and measured values. Model 1. Markers: \diamond $-65\text{ }^{\circ}\text{C}$ \circ $-80\text{ }^{\circ}\text{C}$ \triangle $-95\text{ }^{\circ}\text{C}$ other conditions same as Figure 2.

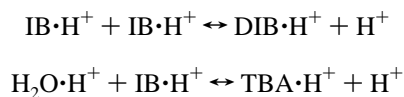
are as follows



The effect of the presence of water and TBA is very significant, as shown earlier. With an increase in water content, the rate of conversion of IB decreases, and the selectivity toward DIBs increases. This effect is due to the coverage of the catalyst active sites by the relatively polar water and TBA molecules, thus reducing the formation of TIBs and TEBs. The extent of adsorption of relatively nonpolar components, i.e., IB, DIBs, TIBs, TEBs, and IO, is assumed to be negligible compared to that of water and TBA. The kinetic models were developed (Table 4) considering the following surface reaction mechanism: IB and water adsorb on the catalyst surface to give adsorbed IB and water as



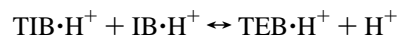
The adsorbed IB combines with adsorbed IB and water to give adsorbed DIBs and TBA



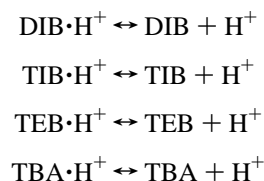
Adsorbed DIBs combine further with adsorbed IB and an active site to give the TIB complex¹³



Similarly, the adsorbed TIB gives the TEB complex



The desorption of all of the species to give the respective products is given by



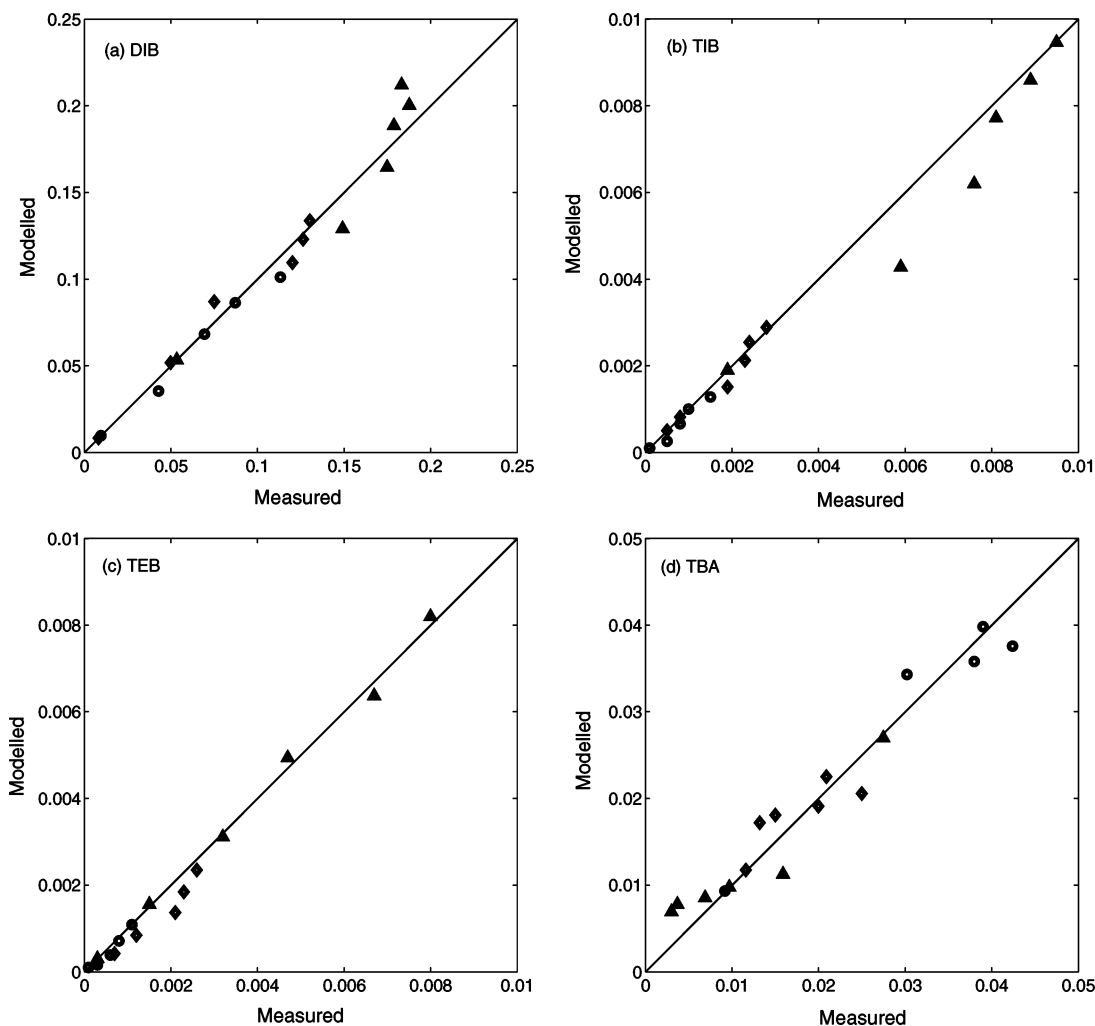


Figure 8. Effect of temperature on product profiles: Comparison between modeled and measured values for model 2. \diamond , $-65\text{ }^{\circ}\text{C}$; \circ , $-80\text{ }^{\circ}\text{C}$; \triangle , $-95\text{ }^{\circ}\text{C}$. All other conditions are the same as in Figure 2.

Table 4. Model Equations for the Reacting System

reaction	model 1	model 2	model 3
1	$\frac{k_1 a_{\text{IB}}^2}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}} + K_{\text{TBA}} a_{\text{TBA}})^2}$	$\frac{k_1 a_{\text{IB}}^2}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}}^\alpha + K_{\text{TBA}} a_{\text{TBA}}^\beta)^2}$	$k_1 a_{\text{IB}}^2$
2	$\frac{k_2 a_{\text{IB}} a_{\text{DIB}}}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}} + K_{\text{TBA}} a_{\text{TBA}})^3}$	$\frac{k_2 a_{\text{IB}} a_{\text{DIB}}}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}}^\alpha + K_{\text{TBA}} a_{\text{TBA}}^\beta)^3}$	$k_2 a_{\text{IB}} a_{\text{DIB}}$
3	$\frac{k_3 a_{\text{IB}} a_{\text{TIB}}}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}} + K_{\text{TBA}} a_{\text{TBA}})^2}$	$\frac{k_3 a_{\text{IB}} a_{\text{TIB}}}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}}^\alpha + K_{\text{TBA}} a_{\text{TBA}}^\beta)^2}$	$k_3 a_{\text{IB}} a_{\text{TIB}}$
4	$\frac{k_4 a_{\text{IB}} a_{\text{H}_2\text{O}}}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}} + K_{\text{TBA}} a_{\text{TBA}})^2}$	$\frac{k_4 a_{\text{IB}} a_{\text{H}_2\text{O}}^\alpha}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}}^\alpha + K_{\text{TBA}} a_{\text{TBA}}^\beta)^2}$	$k_4 a_{\text{IB}} a_{\text{H}_2\text{O}}$
5	$\frac{k_5 a_{\text{TBA}}}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}} + K_{\text{TBA}} a_{\text{TBA}})^2}$	$\frac{k_5 a_{\text{TBA}}^\beta}{(1 + K_{\text{WTR}} a_{\text{H}_2\text{O}}^\alpha + K_{\text{TBA}} a_{\text{TBA}}^\beta)^2}$	$k_5 a_{\text{TBA}}$

Model 1 is a typical Langmuir–Hinshelwood (LH)^{13,16} type model and has 12 parameters to be estimated. Model 2 is a modified form of LH,¹⁷ with α and β as additional parameters that take into account the nonlinear distribution of water and TBA in the resin and bulk phases. Therefore, there are 14 parameters to be estimated in this model. Model 3 is the simplest form of rate expression, which assumes the coexistence of the resin and bulk phase with thermodynamic equilibrium established at all times making the activities of the compounds in the two phases equal. There is no need to consider the adsorption

of the component(s) explicitly in this model. The number of parameters to be estimated in this model is 10.

Parameter Estimation. The mole balance for the batch reactor for each of the components is as follows

$$\frac{dn_i}{dt} = M_{\text{cat}} \sum_{k=1}^{N_R} v_{i,k} r_k \quad (\text{for } i = \text{each component}) \quad (3)$$

The temperature dependency of the rate constant can be

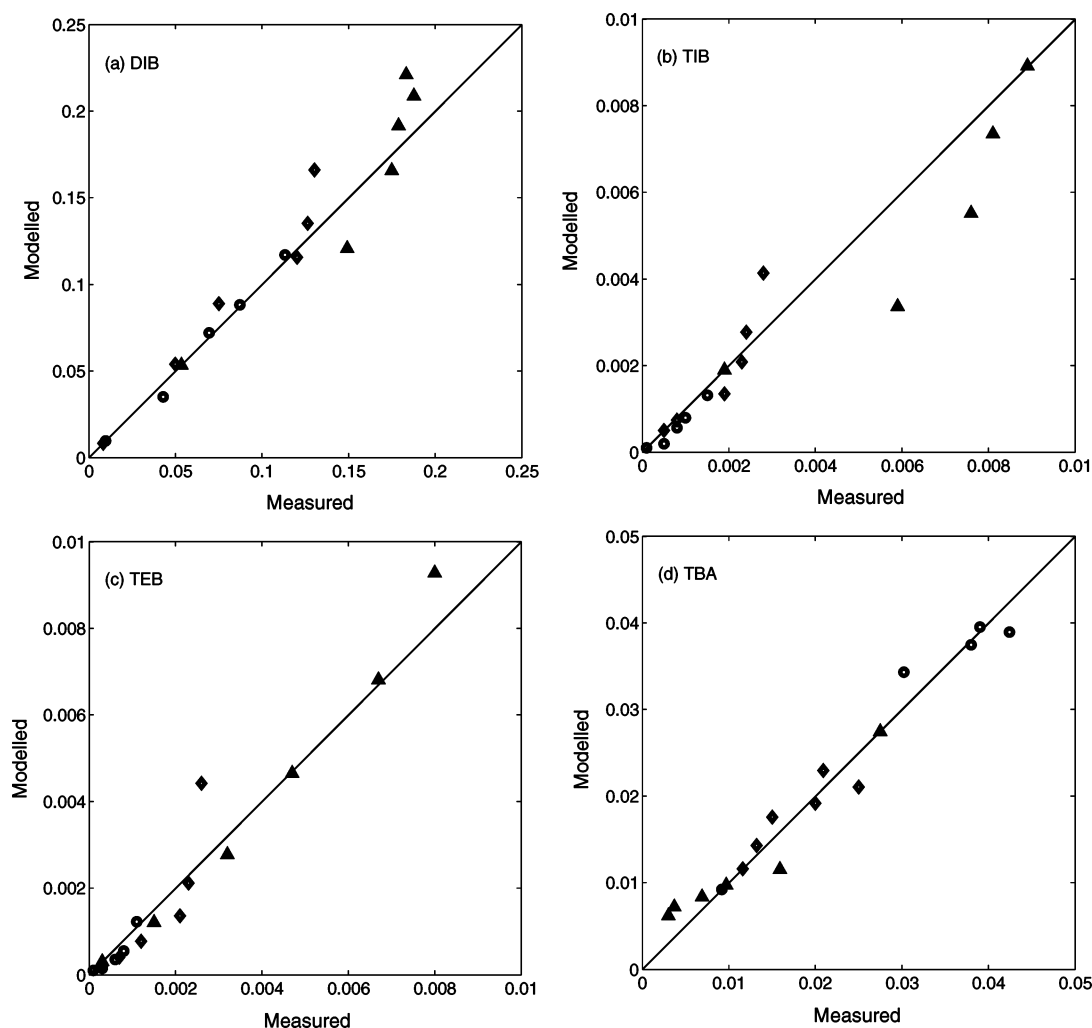


Figure 9. Effect of temperature on product profiles: Comparison between modeled and measured values for model 3. ◇, $-65\text{ }^{\circ}\text{C}$; ○, $-80\text{ }^{\circ}\text{C}$; △, $-95\text{ }^{\circ}\text{C}$. All other conditions are the same as in Figure 2.

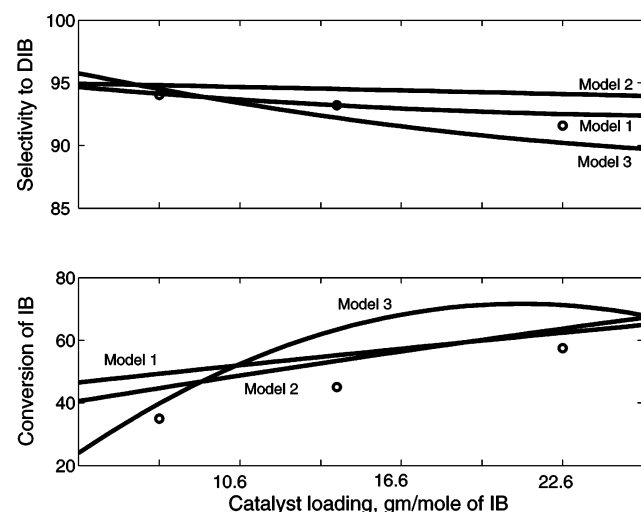


Figure 10. Comparison of the effect of catalyst loading on the conversion of IB and selectivity to DIBs. Symbols: experimental data. All other conditions are the same as in Figure 2.

expressed by the Arrhenius equation as

$$k_i = k_{i,0} \exp\left(\frac{-E_{i,0}}{RT}\right) \quad (4)$$

The overall objective function for optimization to minimize the

Table 5. Parameters and Objective Function Values for Different Models

parameter ^a	model 1	model 2	model 3
$k_{1,0}$	2.98×10^6	9.03×10^6	2.23×10^2
$k_{2,0}$	7.37×10^8	5.99×10^9	5.71×10^3
$k_{3,0}$	7.50×10^1	2.29×10^2	1.23×10^{-2}
$k_{4,0}$	4.83×10^3	1.12×10^4	1.51×10^{-2}
$k_{5,0}$	4.12×10^{11}	8.70×10^8	2.92×10^6
$E_{1,0}$	51.49	52.59	47.91
$E_{2,0}$	60.45	63.67	63.08
$E_{3,0}$	16.01	17.27	14.83
$E_{4,0}$	19.51	29.23	22.45
$E_{5,0}$	75.54	57.06	70.94
K_{WTR}	23.01	25.71	—
K_{TBA}	22.85	25.13	—
α	—	1.18	—
β	—	0.627	—
Φ	0.032	0.027	0.048

^a The units for k_0 are $\text{kmol}/(\text{kg s})$, and those for E_0 are kJ/mol .

difference between the measured and modeled values is given by

$$\min \Phi = \sum_{\text{all samples}} (x_{i,\text{calculated}} - x_{i,\text{measured}}) \quad (5)$$

For optimization, a SQP (sequential quadratic programming) approach from the NAG library was used in the simulation environment DIVA¹⁸ to regress the data given in Figures 4–6. The nonidealities of the liquid phase were described using the

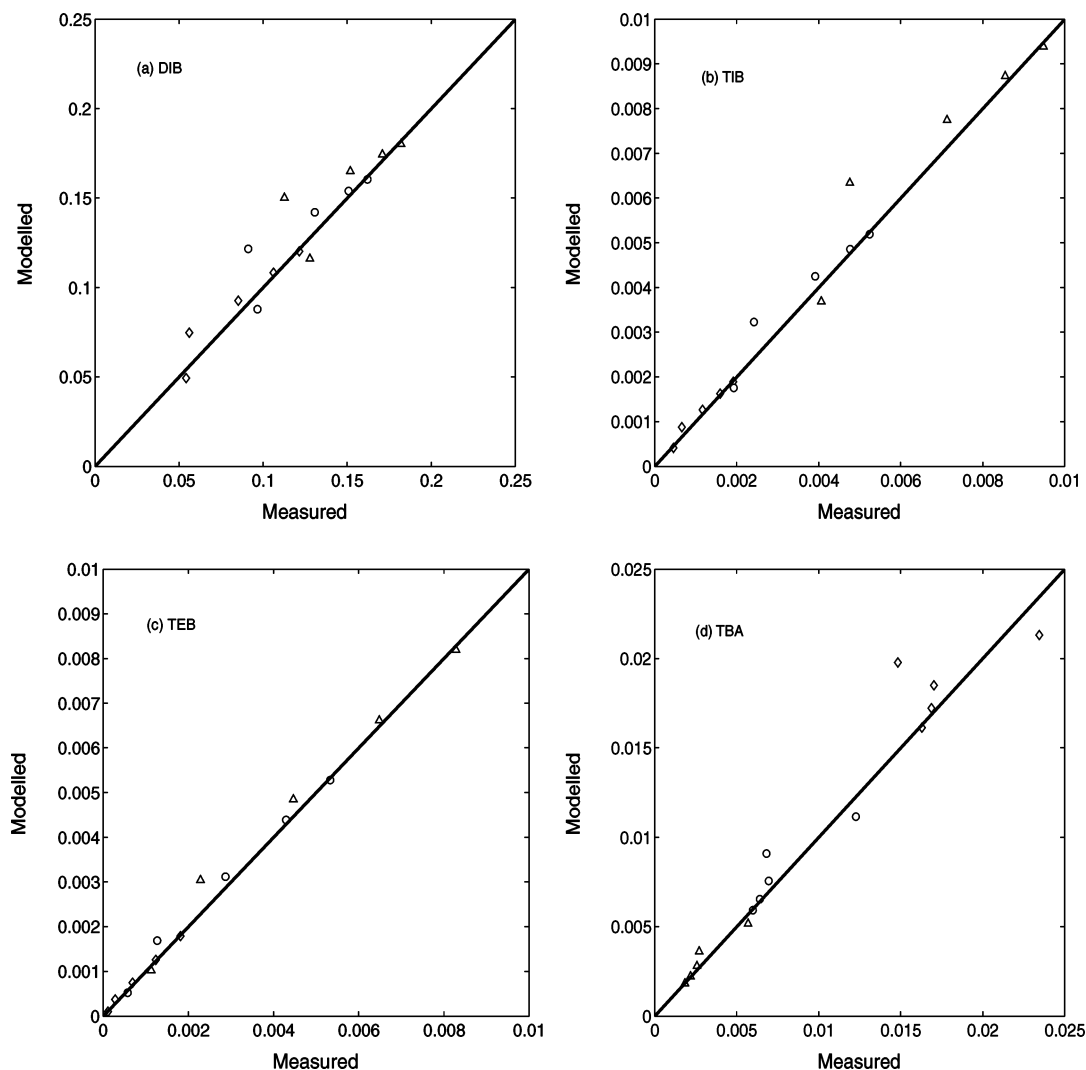


Figure 11. Effect of moisture on product profiles: Comparison between modeled and measured values for model 1. \diamond , $-65\text{ }^{\circ}\text{C}$; \circ , $-80\text{ }^{\circ}\text{C}$; \triangle , $-95\text{ }^{\circ}\text{C}$. Moisture content = 0.14 mol/mol of IB, and all other conditions are the same as in Figure 2

UNIQUAC method, and the thermodynamic parameters were obtained from the commercial package ASPEN Plus data bank. The estimated parameters for these models are given in Table 5, and the comparisons between measured and modeled concentrations for all three models are shown in Figures 7–10, which indicate that models 1 and 2 give the best fit to the observed results and model 3 underpredicts the formation of TEB. However, both models 1 and 2 slightly overpredict the effect of catalyst loading. The additional parameters α and β in model 2 do not give much improvement in data fitting, and hence, for all practical purposes, either model 1 or model 2 can be used for the design of a large-scale reactor. The comparison of model predictions for different moisture contents are shown in Figures 11 and 12 for model 1, which shows that, at the lower moisture content, the model slightly overpredicts the DIB concentration. The activation energy values of the dimerization and trimerization reactions are considerably higher (2 times for dimerization and 30 times for trimerization) than those reported earlier by Honkela and Karuse¹³ for a similar ion-exchange resin catalyst. The fact that these energies are quite high indicates the absence of intraparticle diffusion limitations.

Parametric Sensitivity. The sensitivity analysis for all of the parameters was performed using the sensitivity analysis method in DIVA. Table 6 reports the deviations from the base case when the parameters were disturbed by $\pm 10\%$ from the

Table 6. Effect of Parameter Disturbances on IB Conversion and DIB Selectivity^a

parameter	disturbance	conversion of IB (%)			selectivity to DIB (%)		
		model 1	model 2	model 3	model 1	model 2	model 3
$k_{1,0}$	-10%	53.85	55.31	60.44	92.55	92.66	92.95
	0%	56.02	57.37	62.95	92.83	92.97	93.09
	$+10\%$	57.97	59.21	65.17	93.08	93.24	93.21
$k_{2,0}$	-10%	55.95	57.44	62.86	93.41	92.41	93.74
	0%	56.02	57.37	62.95	92.83	92.97	93.09
	$+10\%$	56.10	55.31	63.06	92.26	92.66	92.44
$k_{3,0}$	-10%	56.01	57.35	62.94	92.88	93.02	93.14
	0%	56.02	57.37	62.95	92.83	92.97	93.09
	$+10\%$	56.04	57.38	62.98	92.78	92.92	93.04
$k_{4,0}$	-10%	55.50	56.62	62.88	92.96	93.16	93.09
	0%	56.02	57.37	62.95	92.83	92.97	93.09
	$+10\%$	56.54	58.10	63.03	92.70	92.78	93.08
$k_{5,0}$	-10%	56.59	58.19	63.04	92.69	92.75	93.08
	0%	56.02	57.37	62.95	92.83	92.97	93.09
	$+10\%$	55.55	56.69	62.89	92.95	93.14	93.09
K_{WTR}	-10%	60.33	61.65	—	91.41	91.56	—
	0%	56.02	57.37	—	92.83	92.97	—
	$+10\%$	51.73	53.47	—	93.98	94.01	—
K_{TBA}	-10%	56.13	92.89	—	92.79	92.89	—
	0%	56.02	57.37	—	92.83	92.97	—
	$+10\%$	55.93	57.21	—	92.85	93.01	—
α	-10%	—	61.80	—	—	91.46	—
	0%	—	57.37	—	—	92.97	—
	$+10\%$	—	53.63	—	—	94.03	—
β	-10%	—	55.75	—	—	93.37	—
	0%	—	57.37	—	—	92.97	—
	$+10\%$	—	58.97	—	—	92.54	—

^a Note: 0% indicates the conversion and selectivity at the optimized parameters under the conditions given in Figure 2 at the end of batch.

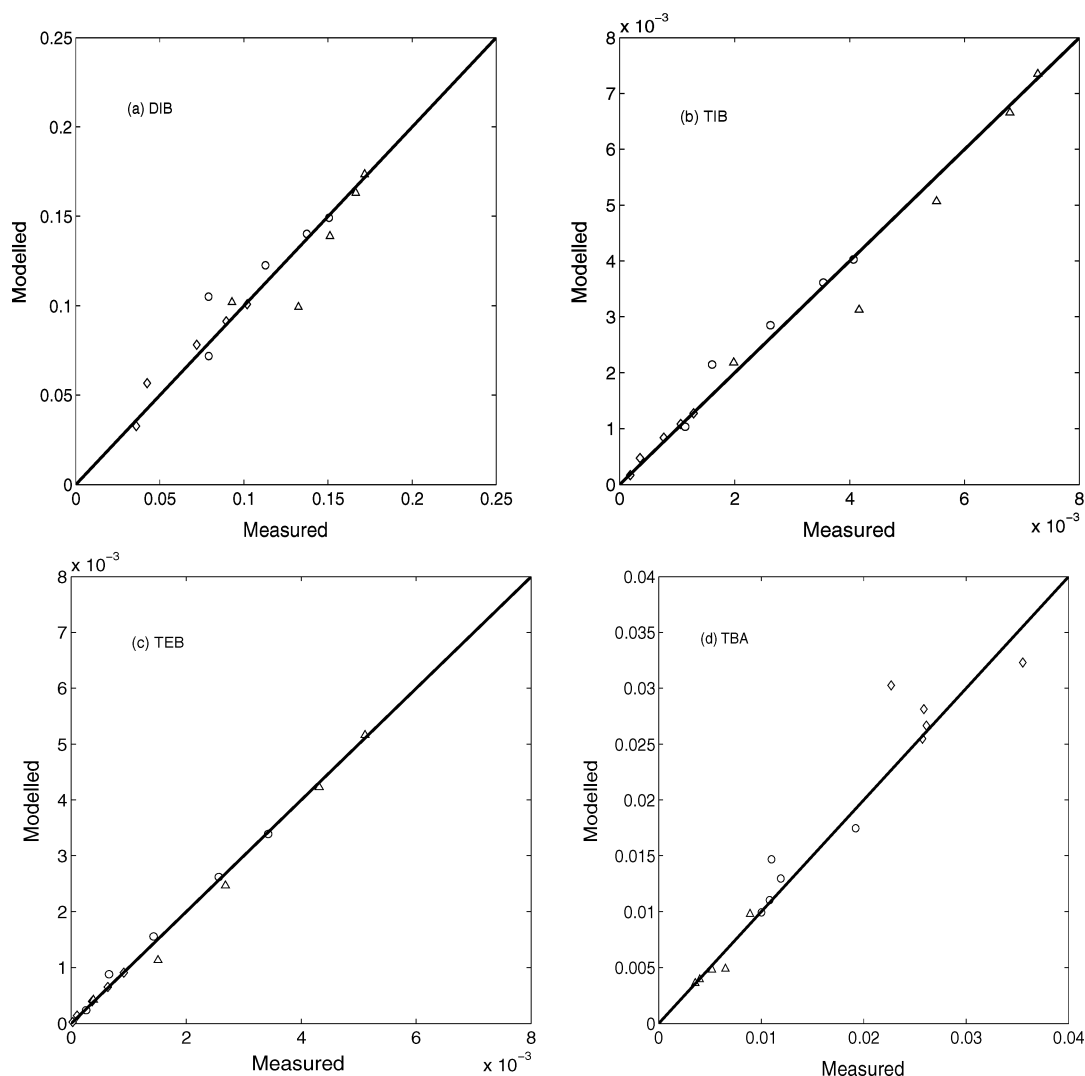


Figure 12. Effect of moisture on product profiles: Comparison between modeled and measured values for model 2. \diamond , $-65\text{ }^{\circ}\text{C}$; \circ , $-80\text{ }^{\circ}\text{C}$; \triangle , $-95\text{ }^{\circ}\text{C}$. Moisture content = 0.19 mol/mol of IB, and all other conditions are the same as in Figure 2

base-case values. It is observed that the conversion of IB and the selectivity toward DIBs are relatively more sensitive to parameters $k_{1,0}$ and K_{wtr} for model 1 and $k_{1,0}$ for model 3 and to almost all of the parameters for model 2.

Conclusions

Kinetic studies on the dimerization of IB were performed with an ion-exchange resin catalyst, water and TBA as selectivity enhancers, and isooctane as the solvent. The effects of various parameters such as temperature, catalyst loading, moisture content, etc., were studied, and it was observed that an initial moisture content up to 0.20–0.25 mol/mol of IB plays a vital role in determining the selectivity toward the dimers. Different kinetic models were proposed considering the formation of dimers, trimers, and tetramers and reversible IB hydration. LH and modified LH models predict the experimental data reasonably well.

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Nomenclature

- a_i = activity of component i
- $E_{i,0}$ = activation energy for reaction i , kJ/mol
- $k_{i,0}$ = rate constant for reaction i , kmol/(s.kg_{cat})
- K_i = adsorption coefficient
- M_{cat} = mass of catalyst, kg
- n_i = number of moles of component i , mol
- $n_{i,0}$ = initial number of moles of component i , mol
- N_R = number of reactions
- r_i = rate of reaction i , kmol/s
- S = selectivity toward dimer
- x_i = liquid mole fraction of component i
- X = conversion of isobutene
- $v_{i,j}$ = stichometric coefficient for component i in reaction j
- α = exponent for the activity of water
- β = exponent for the activity of TBA
- Φ = objective function for optimization

Abbreviations

- DIBs = diisobutenes
- IB = isobutene
- IO = isooctane
- LH = Langmuir–Hinshelwood
- MeOH = methanol

SPA = solid phosphoric acid
 TBA = *tert*-butyl alcohol
 TEBs = tetraisobutenes
 TIBs = triisobutenes
 WTR = water

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