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KINETICS, CATALYSIS, AND REACTION ENGINEERING

Process Analysis for Dimerization of Isobutene by Reactive Distillation

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Alkylates are a class of probable replacements for MTBE as gasoline additives that can be produced by dimerization of isobutene (to isooctene) with subsequent hydrogenation. The characteristics of the dimerization reaction make it a potential candidate for reactive distillation. The dimer, being heavier than C₄, can be maintained at a low concentration level in the reactive zone by simultaneous distillation, thereby suppressing the subsequent oligomer-producing reactions. In this work, the influence of important design and operating parameters on the performance of the reaction in a hybrid reactive distillation column is studied through process simulations. The results show that a high selectivity toward diisobutene can be achieved along with adequate temperature control in the presence as well as absence of polar components. Multiple steady states are observed in some cases that introduce additional complexities in the determination of the optimal windows for certain parameters. The process seems economically attractive, as it is capable of utilizing the existing reactive distillation assets and the feedstock for MTBE production by suitable revamping.

Introduction

As a widely used gasoline additive, methyl *tert*-butyl ether (MTBE) is being phased out after a suit against such a ban in California.¹ Therefore, the petrochemical industries are currently seeking replacements for MTBE. The leading candidates at this point appear to be alkylates that have an average octane number in the range of 93–96. A potential source of alkylates is isooctane formed by the dimerization of isobutene (to the dimer diisobutenes, DIB) with subsequent hydrogenation.² This process is especially attractive because it makes use of the existing MTBE feedstocks and plants following a simple and low-cost revamp. A successful world-scale plant is based on Fortum's NExOCTANE technology. The isobutene dimerization reaction takes place in the liquid phase in a fixed-bed reactor with acidic ion-exchange resin as the catalyst. The produced dimers and byproducts [e.g., isobutene oligomers such as the trimer triisobutenes (TIB), tetramer, etc.] are separated from the unreacted isobutene and inert C₄ compounds.

The dimerization of isobutene using ion-exchange resins has been investigated in the absence of polar components^{3,4} and as a side reaction of the MTBE synthesis^{5–7} where methanol is the polar component. The reaction, in the simplest sense, can be represented as a series-parallel network as shown in Figure 1. The reaction is highly exothermic ($\Delta H_R = -19.8$ kcal/mol)⁸ and leads to the formation of undesired oligomers, which not only are unsuitable as gasoline additives but also promote

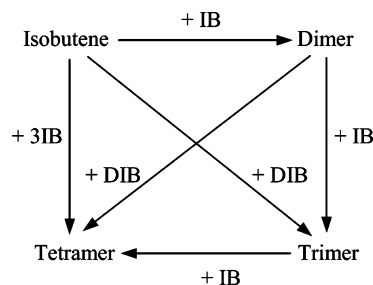


Figure 1. Reaction scheme for isobutene dimerization and oligomerization.

catalyst deactivation.⁶ The presence of polar solvents inhibits the accessibility of isobutene to the active centers on the catalyst, thereby reducing the reaction rates with a simultaneous decrease in oligomer formation.^{6,9–11} Honkela and Krause¹¹ compared the effect of methanol, MTBE, and *tert*-butyl alcohol (TBA) and concluded that TBA is a better selectivity-enhancing agent. TBA undergoes dehydration to produce isobutene (the reactant for dimerization) and water, which is also polar and can improve the selectivity toward the dimer. Moreover, TBA has a high octane number and is currently also being used as a gasoline additive.¹²

The nature of the isobutene dimerization reaction (i.e., fast and exothermic), the difference in the volatilities of the species involved (difference of normal boiling points between C₄ and dimer is more than 100 °C), and the matching temperatures for reaction and distillation have led to this reaction being considered as a potential candidate for implementation in a reactive distillation column. The dimer, because of its higher boiling point, is separated by simultaneous distillation. Therefore, its concentration can be maintained at a low level in the reactive zone, thereby suppressing subsequent oligomer-producing reactions. If the reactive distillation (RD) technology is found

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suitable for the dimerization reaction, the RD columns currently being used for MTBE production can also be revamped and applied for isobutene dimerization. Recently, Ouni et al.¹³ reported a case study of this reaction in RD with 78 ideal stages, which might require a large investment from an industrial point of view.

Despite numerous studies and applications of the various aspects of reactive distillation in the past two decades,^{14,15} the selectivity analysis of reactive distillation is not highlighted in the literature and needs the attention of researchers in the future. In our opinion, isobutene dimerization with all of the associated side reactions in reactive distillation can be a representative system for such studies. In this contribution, this process is analyzed on the basis of simulation studies. The influence of the most important design and operating parameters is investigated with reference to a base-case configuration. The influence of a polar component is illustrated in the form of its feed amount and location. Special attention is given to the selectivity toward the desired product DIB, conversion of IB, and the process multiplicity. On the basis of the simulation results, potential RD configurations, with and without polar components, are finally suggested from an industrial point of view.

Kinetic Model for Dimerization Reaction

The reaction kinetics of C₄ alkene dimerization and oligomerization has been studied over the years. One of the most recent kinetic models on isobutene dimerization comes from Honkela and Krause,¹⁶ who studied the kinetics in a continuous stirred tank reactor (CSTR) with a commercial ion-exchange resin catalyst and TBA as the polar selectivity-enhancing solvent, in the temperature range from 60 to 120 °C. The authors argued that tetramers need not to be considered in the model because of their negligible concentration. It was suggested that the trimer and tetramer are formed by bimolecular reaction through sequential addition of isobutene molecules. Therefore, if the formation of trimers is suppressed, the amount of tetramers formed should be even smaller and negligible. Moreover, in the cited work, the amount of TBA was very small (less than 3.5 mol % in the feed), and only a small part of the TBA dehydrated under the studied experimental conditions. Hence, in their kinetic model, TBA dehydration was not considered explicitly, and the effect of polar components (TBA and water) was combined into a single component represented by TBA. Therefore, only the following two reactions were taken into account in their kinetic model and are also adopted in this work



The corresponding Langmuir–Hinshelwood- (L–H-) type rate expressions are

$$r_1 = \frac{k_{\text{DIB}} a_{\text{IB}}^2}{(a_{\text{IB}} + B_{\text{TBA}} a_{\text{TBA}} + B_{\text{solvent}} a_{\text{solvent}})^2} \quad (1)$$

$$r_2 = \frac{k_{\text{TIB}} a_{\text{IB}} a_{\text{DIB}}}{(a_{\text{IB}} + B_{\text{TBA}} a_{\text{TBA}} + B_{\text{solvent}} a_{\text{solvent}})^3} \quad (2)$$

A C₄ feedstock typically contains isobutene and some other C₄ components (see Table 1 of Qi et al.¹⁷). At reaction conditions, the linear butenes, *n*-butene and 2-butene, can also co-dimerize to produce C₈ isomers other than DIB.¹⁰ However, this reaction is much slower than isobutene dimerization,⁹ and

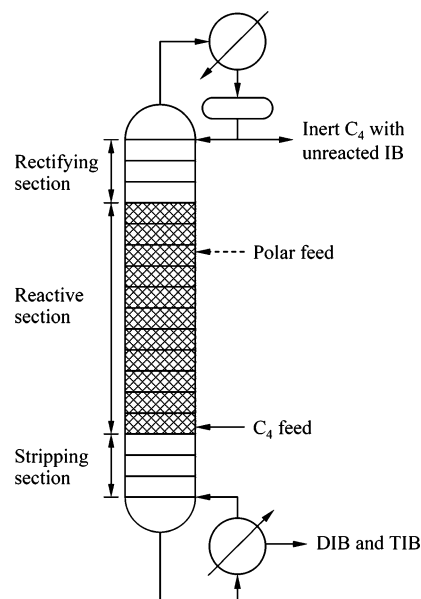


Figure 2. Schematic of the reactive distillation column for isobutene dimerization.

hence, apart from isobutene, all other components from the C₄ cut can be considered as inert substances from a reaction point of view. For the sake of simplicity, we combine all of the inert components of the C₄ cut into a single pseudocomponent, represented by *n*-butene, because of their very similar physical and thermodynamic properties. The only inert component in the feed used by Honkela and Krause¹⁶ in their experiments was isopentane, which also acted as a solvent. Because kinetics with an inert C₄ is not available, we assume that the effect of the inert C₄ as a solvent is the same as that of isopentane from the reaction kinetics point of view. Because reliable kinetics for the nonpolar case is not available and the discussed kinetics used a very small amount of polar components, we assume that it can be extrapolated suitably to the case in the absence of any polar component.

Mathematical Model for the Reactive Distillation Column

The hybrid reactive distillation column considered for the model consists of three zones as shown in Figure 2. The reactions occur only in the reactive zone where the catalyst is present in the form of a structured packing material. The main feed is located near the bottom of the reactive zone. Polar components can also be fed separately near the top of the reactive zone. Separation of the inert (from the C₄ feed) and purification of the product take place in the rectifying section and the stripping section, respectively.

A dynamic equilibrium stage model is applied to simulate the reactive distillation column for studying the process feasibility. The main assumptions are as follows: (1) Stage 1 represents the total condenser, and stage *N* represents the partial reboiler. (2) The nonideality of the liquid phase is described by means of activity coefficients predicted by the modified UNIFAC method.¹⁸ (3) The nonideality of the vapor phase is taken into account in the form of fugacity coefficients calculated using the Peng–Robinson–Stryjek–Vera (PRSV) equation of state for moderately nonideal systems in the presence of polar components such as water and alcohols.¹⁹ The binary interaction parameters are obtained from the HYSYS process simulation package.²⁰ (4) The solid catalyst is quasihomogeneous with the liquid phase, i.e., the liquid composition at each of the catalytically active sites is treated as the bulk liquid composition.

Table 1. Potential Reactive Distillation Configurations with and without Polar Components

	case 1: nonpolar base case	case 2: nonpolar case for high IB conversion	case 3: polar case	case 4: good polar configuration	case 5: polar case for high IB conversion
		Configuration			
reactive stages	4–26	4–26	4–26	4–26	4–26
total stages	30	30	30	30	30
pressure (MPa)	1.5	1.5	1.5	1.5	1.5
reflux ratio	6.0	10.0	6.0	10.0	10.0
reboil ratio	10.0	15.0	10.0	15.0	15.0
reboiler duty (MW)	1.802	2.794	1.830	2.891	2.827
Damköhler number, Da	0.45	3.05	1.5	1.7	16.5
total catalyst loading (kg)	120.80	818.75	402.66	456.35	4429.31
C_4 feed flow rate (kmol/h)	100.0	100.0	100.0	100.0	100.0
C_4 feed concentration (IB/ n -B, mol %)	0.4:0.6	0.4:0.6	0.4:0.6	0.4:0.6	0.4:0.6
ratio of polar to main feed	—	—	1:100	1.8:100	2:100
position of polar feed	—	—	6	12	7
		Performance			
IB conversion (%)	91.15	99.00	90.02	94.26	99.02
DIB selectivity (%)	90.03	80.00	94.61	94.23	92.33
		Top Product Concentration			
n -butene	0.9477	0.9945	0.9407	0.9660	0.9942
isobutene	0.0523	0.0055	0.0591	0.0340	0.0057
DIB	$<1.0 \times 10^{-6}$	$<1.0 \times 10^{-6}$	$<1.0 \times 10^{-6}$	$<1.0 \times 10^{-6}$	$<1.0 \times 10^{-6}$
TIB	—	—	$<1.0 \times 10^{-6}$	$<1.0 \times 10^{-6}$	$<1.0 \times 10^{-6}$
TBA	—	—	1.69×10^{-4}	2.76×10^{-6}	7.91×10^{-5}
		Bottom Product Concentration			
n -butene	0.0367	0.0289	0.0297	0.0269	0.0110
isobutene	0.0143	0.0035	0.0131	0.0097	0.0024
DIB	0.8837	0.8290	0.8733	0.8435	0.8472
TIB	0.0652	0.1385	0.0332	0.0344	0.0469
TBA	—	—	0.0507	0.0854	0.0925

(5) The pressure drop, the heat losses across the column walls, and the effect of fluid dynamics are neglected.

For kinetically controlled reactive distillation systems, the Damköhler number (Da) is usually used to characterize the reaction conditions. Here, Da is defined as

$$Da = \frac{W_T k_{f,ref}^{het}}{F_T} \quad (3)$$

where F_T is the total feed flow rate to the column; W_T is the total amount of catalyst in the column; and $k_{f,ref}^{het}$ is the forward rate constant evaluated at a reference temperature, which is conventionally the lowest-boiling pure component in the system (i.e., boiling point of isobutene at the column pressure). The catalyst loading is equally divided on the reactive stages.

The model is formulated as a system of differential algebraic equations of the conventional MESH (material balance, equilibrium relations, summation equations, and enthalpy balance) equations. The DIVA simulation environment²¹ was used to solve the above model in either steady-state or dynamic mode as per the requirements. DIVA contains robust solvers specially tailored for large sparse systems with arbitrary structural properties.

In the following sections, we analyze the process using the presented model. First, we consider a base case in the absence of polar components. Then, we investigate the effects of important design and operating parameters: number of reactive stages, catalyst loading, position of C_4 feed pressure, reflux and reboil ratios, and amount and position of the polar feed. The conversion of the reactant IB is defined as

$$X_{IB} (\%) = \left(1 - \frac{Dx_{IB,D} + Bx_{IB,B}}{F_{IB,F}} \right) \times 100 \quad (4)$$

Because the amounts of DIB and TIB in the distillate are always very low (<1 ppm) in the simulations, the selectivity of the

desired product DIB is defined as:

$$S_{DIB} (\%) = \frac{2x_{DIB,bottom}}{2x_{DIB,bottom} + 3x_{TIB,bottom}} \times 100 \quad (5)$$

In the following discussion, the conversion always refers to IB and the selectivity to DIB if not stated otherwise.

Process Analysis

Base Case. The base-case configuration in the absence of polar components is listed in Table 1 (case 1). These conditions are close to the optimal values as discussed in the following sections. The composition and temperature profiles for this base case are illustrated in Figure 3. The corresponding column performance is reported in Table 1. Both the conversion of isobutene and the selectivity to DIB are higher than 90% because of the coupled effect of reaction and distillation. Once DIB is formed, it is effectively removed from the reactive zone to the bottom. Therefore, the concentration of DIB in the reactive zone is maintained at a relatively low level, which suppresses the formation of TIB and higher oligomers. From Figure 3b, it is clear that RD is capable of maintaining an almost-constant temperature profile within the reactive zone, which is not possible in a fixed-bed reactor without external cooling. The relatively low temperature in the reactive zone is also helpful in reducing the oligomerization of isobutene. Additionally, in the case of RD, the heat of reaction is effectively removed by liquid-phase vaporization, which consequently reduces the heat duty of the reboiler.

The performance of the base-case configuration is close to the results reported by Ouni et al.¹³ However, further comparison is not possible because their kinetics and feed conditions (flow rates and compositions), which, according to our simulations, can significantly affect the performance, were not specified.

Effect of Number of Reactive Stages. Because of the large difference in the volatilities of the components involved, the

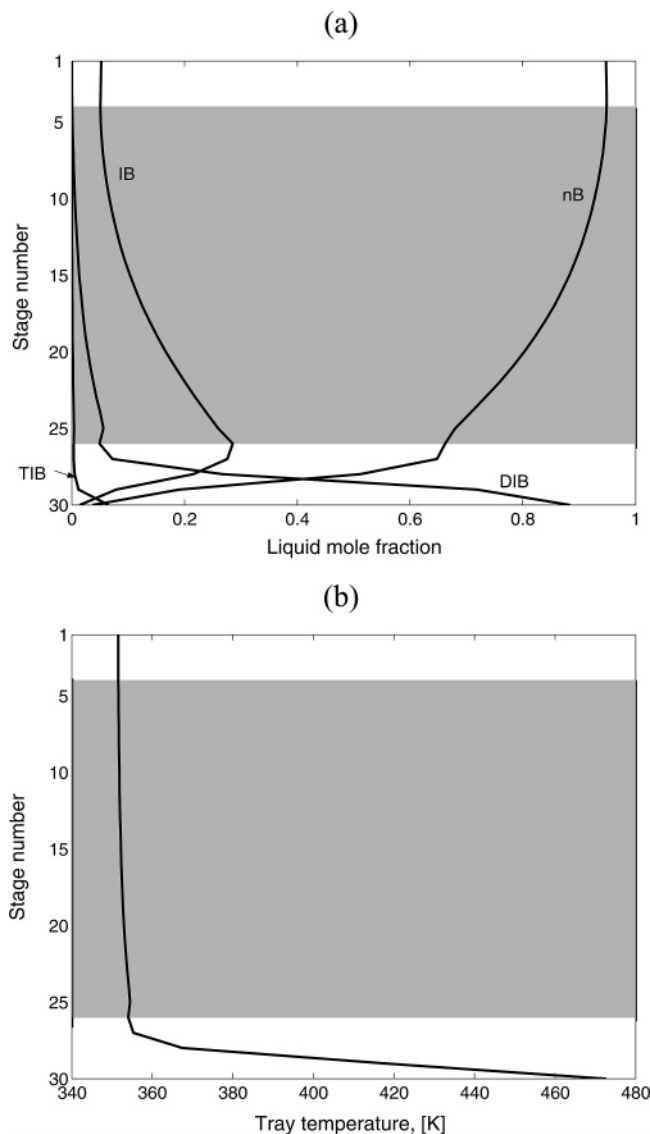


Figure 3. Profiles in the reactive distillation column for the base case: (a) concentration, (b) temperature. Shaded region indicates the reactive zone.

separation duty for such a system is light. Therefore, for this analysis, the rectifying and stripping stages were fixed at stages 3 and 4, respectively, according to the separation requirements, and only the reactive zone, i.e., the number of reactive stages, is varied while keeping the total catalyst loading constant. The feed is always located at the last reactive stage.

Figure 4 shows the effects of the number of reactive stages on the IB conversion and DIB selectivity. It can be seen that, as the number of reactive stages increases, both the conversion of IB and the selectivity toward DIB increase. The conversion increases from 85% for a single reactive stage to approximately 90% for 23 reactive stages. The increase in selectivity is more promising, rising from 70% to almost 90%. Because the emphasis is always on improving the DIB selectivity, more than 15 reactive stages are required for this purpose. Further, the improvement in both the selectivity and the conversion is not significant after 20 reactive stages. Hence, 23 reactive stages were selected for the base-case configuration, leading to a total of 30 stages for the hybrid RD column.

Effect of Catalyst Loading (Da). The catalyst loading is one of the most critical design parameters for the reactive distillation process. For the sake of convenience, the catalyst loading is represented in the form of the Damköhler number (Da). For

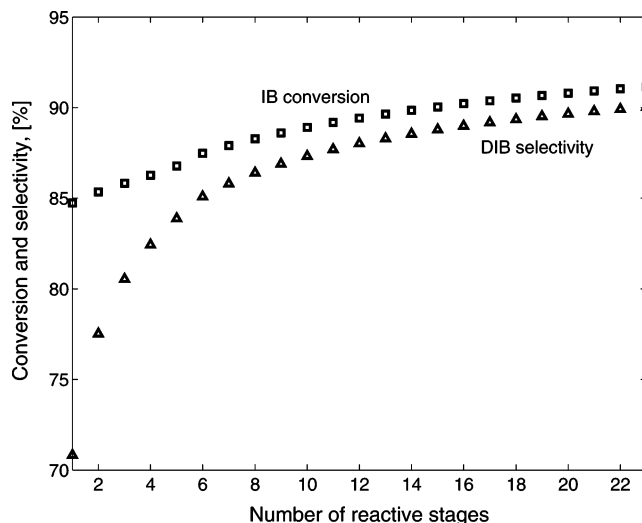


Figure 4. Effect of the number of reactive stages on column performance.

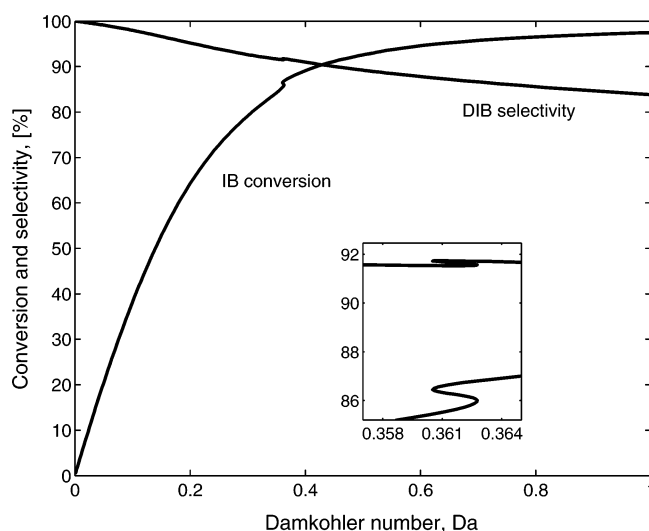


Figure 5. Effect of catalyst loading on column performance.

this analysis, the continuation parameter Da is varied from 0 (i.e., conventional nonreactive distillation) to 1 (~100% conversion of IB). Steady-state multiplicity (MSS) is detected in a small range of Da values as shown in the inset of Figure 5. It is observed that the IB conversion increases significantly with an increase in the catalyst loading. Above a Da value of 0.5, a large increase in catalyst loading is required for a small improvement in IB conversion. The selectivity to DIB decreases from 100% near zero IB conversion to about 84% at $Da = 1$. This trend was also observed in kinetics experiments on this reaction,^{6,9–11,16} but the loss of selectivity in those cases is much worse than the simulation results for reactive distillation. On the basis of the bifurcation diagram, the choice of Da is a compromise between high conversion and high selectivity. As a result, a Da value of 0.45 was used in the base-case configuration, which resulted in both conversion and selectivity exceeding 90%.

Effect of C_4 Feed Location. A judicious choice of the feed location can lead to improved column performance. The C_4 feed location was moved from stage number 16 near the center of the reactive zone down to stage number 28, i.e., two stages below the reactive zone of the base case. As shown in Figure 6, when the feed was moved down along the reactive zone, both the DIB selectivity and the IB conversion increased. The selectivity exhibited an optimum at the last reactive stage (i.e.,

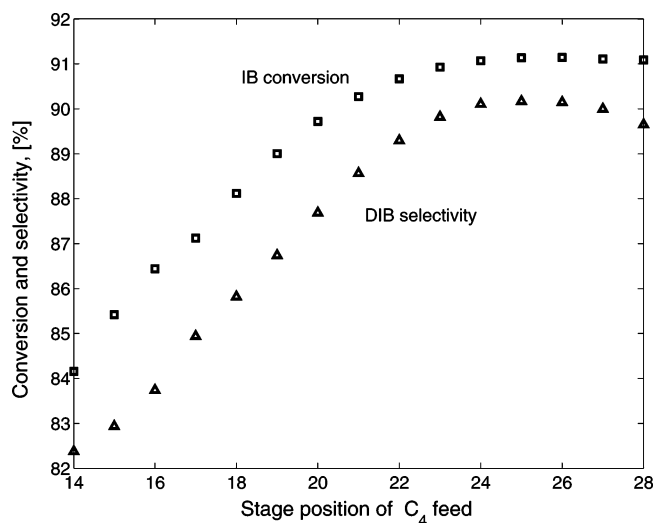


Figure 6. Effect of the C_4 feed location on column performance.

stage number 26), and there was no further improvement in conversion once the feed was moved below the reactive zone. Hence, the C_4 feed was fixed at the last reactive stage in the base-case configuration. In general, irrespective of the number of reactive stages present, the column always gives the best performance when the C_4 feed is located at the end of the reactive zone or just below or above the last reactive stage. This is expected, as isobutene is highly volatile compared to any other species in the system, so its introduction at the intermediate location in the reaction zone leads to underutilization of the catalyst bed below the feed.

Effect of Column Pressure. Because of the high volatilities of the C_4 cut, pressures higher than 5 atm are recommended for this system. Because high temperature is favorable for the dimerization reaction, operating the column at higher reaction temperatures might be preferable. In conventional processes such as a reactor followed by distillation or even distillation coupled with a side reactor, the temperatures of the reactor and distillation unit can be set independently at their optimum values. However, in reactive distillation, the stage temperatures for both reaction and distillation are identical and are dependent on the column pressure. For this system, an increase in pressure increases the bubble-point temperature, which leads to higher reaction rates. Considering the thermal limitations for the catalyst ($<120\text{ }^\circ\text{C}$), chemical reaction rate, and separation effect, the study of the effect of pressure was carried out in the range of 5–18 atm.

The obtained bifurcation diagram of the column performance is shown in Figure 7. As pressure increases, the IB conversion increases significantly because of higher reaction rates. However, there is hardly any sharp decrease in the DIB selectivity, which, according to the nature of the reaction, should have decreased by a significant amount for such a large increase in IB conversion. High selectivities can always be achieved at low conversions even in conventional processes, but at higher conversions, there is always a considerable drop in selectivity. In the case of RD, however, high selectivities are possible even with high conversions at higher pressures, and this makes the RD process very attractive. Another interesting feature is the existence of multiple steady states within a certain range of pressures near 13 atm. The region of steady-state multiplicity can shift or expand/contract depending on the values of the other operating parameters such as the catalyst loading and reflux and reboil ratios. For the base-case configuration, a pressure of 15 atm was selected to avoid control problems in the MSS

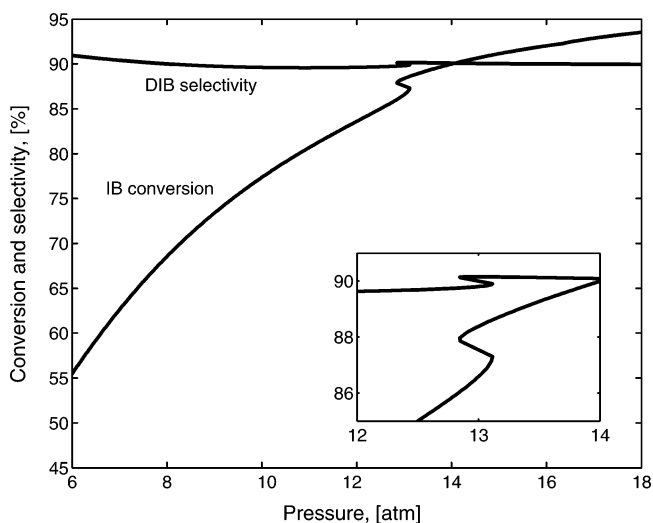


Figure 7. Effect of system pressure on column performance.

region. Higher pressures might give slightly better performances, but the resulting energy consumption and operating costs are also higher.

Effect of Reflux Ratio and Reboil Ratio. To find a suitable combination of the values for the reflux ratio r and the reboil ratio s , the following strategy was employed. The reflux ratio was chosen as the continuation parameter, and its effect was studied for various fixed values of the reboil ratio. The column performance at the pressure of the base case is shown in Figure 8. Multiple steady states are seen over a wide range of reflux ratios, and this range changes with the reboil ratio. It is difficult to generate the system behaviors at very low reflux ratios even with the smallest possible tolerances and step sizes of the continuation algorithm. However, when the pressure is reduced to 9 atm, steady states at lower reflux ratios are clearly observed, as shown in Figure 9. The steady states at low reflux ratio generally indicate low DIB selectivities, as was also reported by Ouni et al.¹³ Low selectivity is obviously undesired. Hence, the reactive distillation column needs to be operated at higher reflux ratios (preferably above 6), with the value depending on the reboil ratio selected. For the base-case configuration, the recommended values for r and s are 6.0 and 10.0, respectively.

Effect of Dosage of Polar Component. As mentioned earlier, the presence of polar components reduces the IB conversion but enhances the DIB selectivity. The polar component should effectively “wet” the catalyst in the reactive zone to obtain the best performance. Because the polar component TBA has a volatility closer to that of dimer and is heavier than C_4 , it is better to introduce a separate polar feed located either within or at the top of the reactive zone. For this analysis, the polar component was located at the topmost stage of the reactive zone, i.e., stage number 4.

The effect of the amount of polar feed was studied in terms of the feed flow rate ratio of the polar feed to the C_4 cut on a molar basis. Figure 10 shows the column performance in the presence of a polar component. As the amount of polar feed increased, the reaction rate decreased, which resulted in lower conversions of IB with the same catalyst loading. Yet, there was also an improvement in the DIB selectivity, as expected. However, this improvement was not as great as observed or claimed in kinetics experiments done with polar components in batch reactors and/or CSTRs.^{6,9–11,16} This is probably because of the RD column structure, which is already optimized for the effective separation of the dimer from the reactive zone in the nonpolar case.

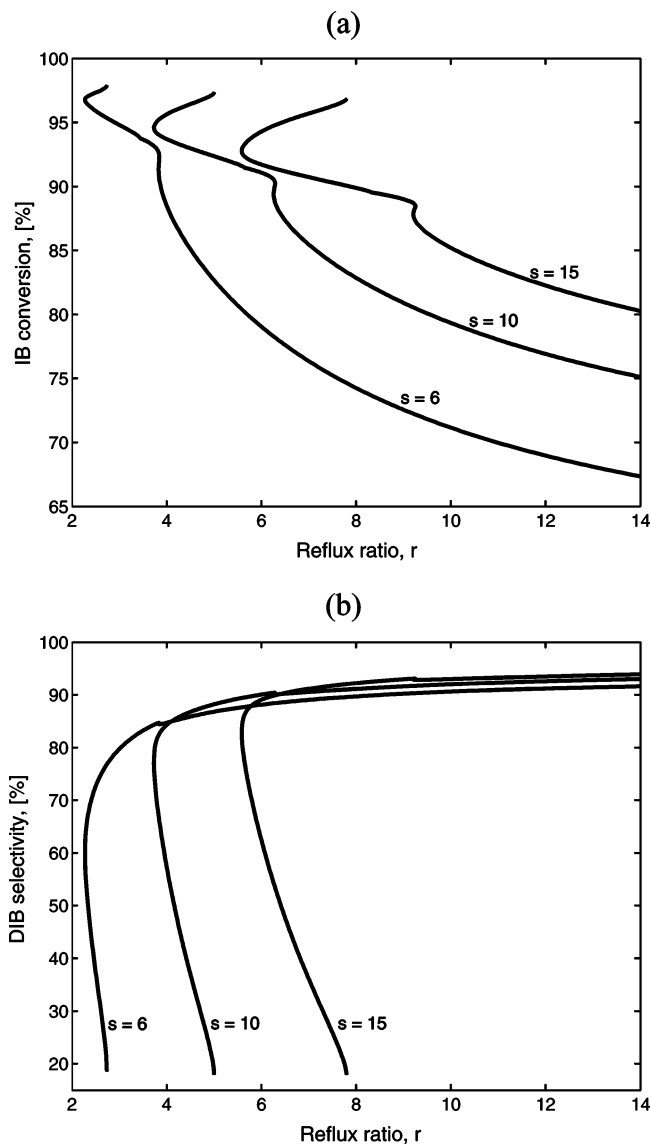


Figure 8. Effect of reflux and reboil ratios on column performance at 15 atm.

Higher amounts of polar feed (feed molar ratios above 0.02) are not presented here because, in those cases, the dehydration reaction of TBA to water needs to be taken into account separately. Second, the reduction in IB conversion was found to be very large as compared to the improvement in DIB selectivity. Therefore, to obtain a similar IB conversion as in the base-case configuration without a polar component (case 1), a significantly larger amount of catalyst would be required (refer to case 3 in Table 1).

Effect of Position of Polar Feed. As stated earlier, a decrease in IB conversion is usually accompanied by an enhancement in DIB selectivity even in the nonpolar case. Because the application of polar components reduced the IB conversion and simultaneously improved the DIB selectivity, it was difficult to judge at this stage whether the improvement in selectivity was due to the decrease in conversion or to the additional hindering of oligomerization by the polar components. Therefore, further investigations on this aspect are necessary.

To quantitatively measure the actual improvement in selectivity, comparisons must be done at the same conversion of IB. This was carried out by increasing the catalyst loading (i.e., Da) to achieve the same IB conversion as in the nonpolar case. For this study, the molar ratio of the polar feed to the main C_4

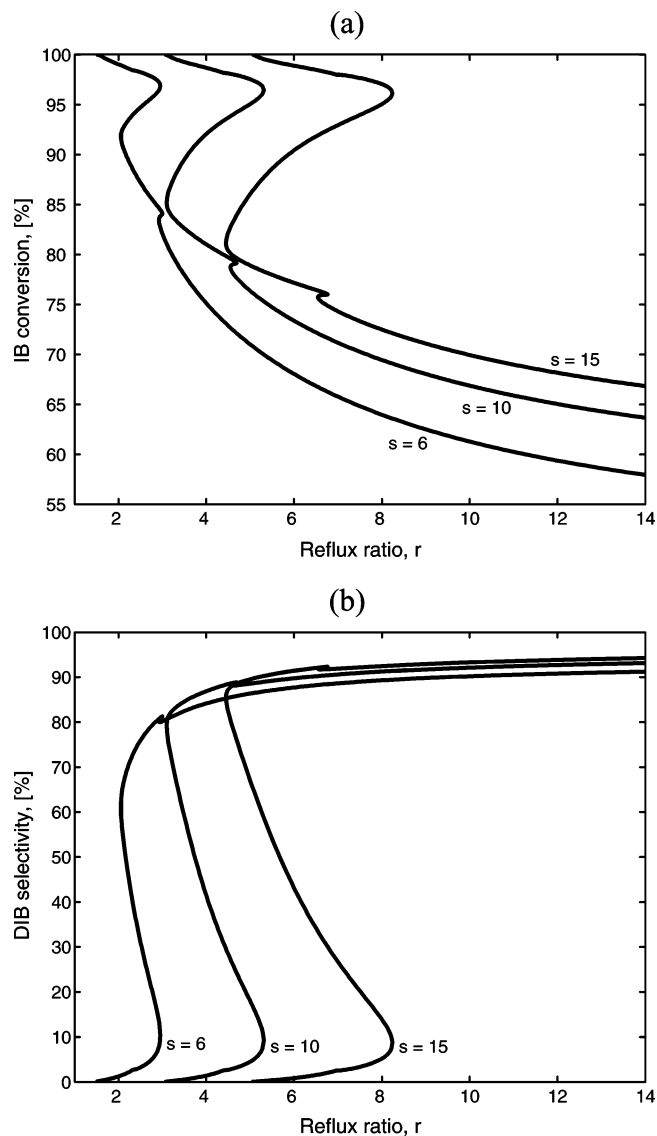


Figure 9. Effect of reflux and reboil ratios on column performance at 9 atm.

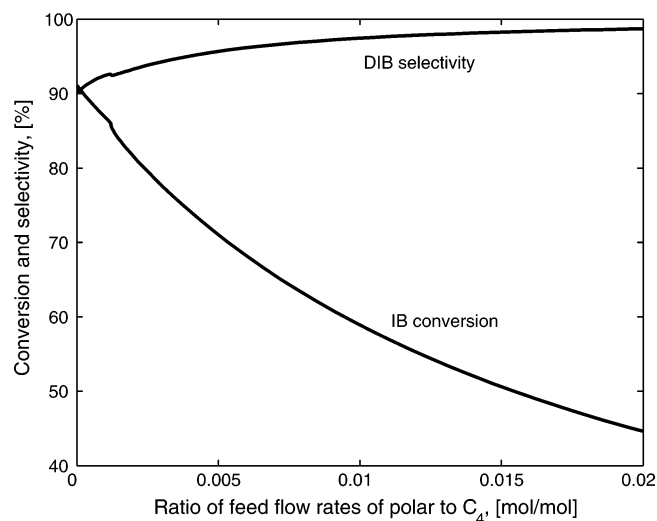


Figure 10. Effect of polar feed flow rate on column performance.

feed was fixed at 0.02. The position of the polar feed was moved down from the topmost reactive stage to the last reactive stage, and the corresponding selectivity for the same conversion as

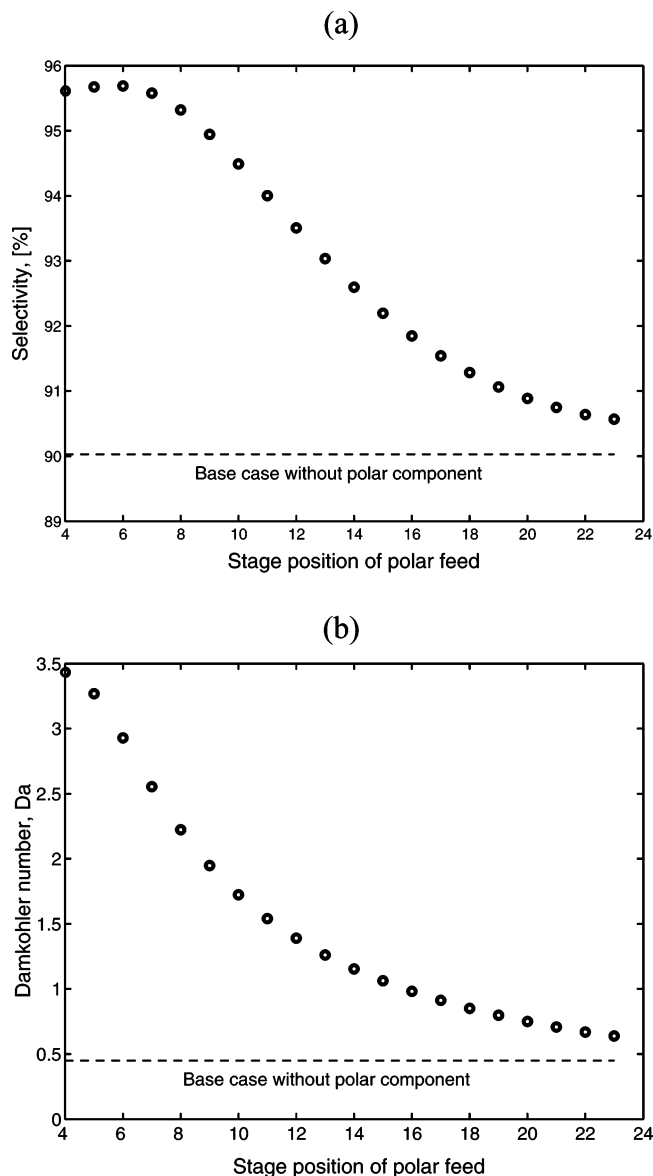


Figure 11. Effect of location of the polar feed for achieving the same conversion as the nonpolar base case on (a) DIB selectivity and (b) catalyst loading.

that of nonpolar base-case configuration was noted, as shown in Figure 11a. The corresponding catalyst loading (or Da value) required is shown in Figure 11b. It can be seen that the location of the polar feed near the top of the reactive zone (stage 6) led to the best DIB selectivity, which improved by more than 5% compared to the nonpolar base case. However, the corresponding catalyst loading was also very high. Figure 11b shows that the extra catalyst loading required for the same IB conversion decreased as the polar feed was moved down the column. When the polar feed was moved down along the reactive zone, there were fewer stages below the polar feed, which led to a lower selectivity enhancement and a lower additional catalyst loading. For the same IB conversion, it is again a tradeoff between DIB selectivity and higher operating costs because of a higher catalyst loading.

Discussion

Table 1 lists five potential RD configurations, in the presence and absence of polar solvent. These configurations were generated from the industrial point of view to provide guidelines

for choosing the operating parameters, the desired IB conversion and DIB selectivity, and to decide upon the inclusion of a polar component. The presence of polar component necessitates additional columns for their separation. Moreover, it has been reported that TBA is one of the natural decomposition products of MTBE, is completely soluble in water, and is harmful to human health.²² Hence, case studies without polar components are important and need to be investigated along with cases including polar components. In addition, the cases of very high conversions of IB are also considered because, in some downstream applications of C_4 mixtures, isobutene should be reduced as much as possible.

Case 1 is the nonpolar base-case configuration that has been discussed in detail in the previous sections. Case 2 is representative of a very high IB conversion of almost 99% with a relatively high selectivity to DIB. For this result, higher reflux and reboil ratios are required, and for the increment in conversion as compared to case 1, the increase in catalyst loading seems quite high. Case 3 is similar to case 1, with over 90% IB conversion but with better DIB selectivity because of the presence of the polar component. Case 4 is a typical configuration with both conversion and selectivity near 95% obtained by a combination of higher reflux and reboil ratios, a higher catalyst loading, and a judicious selection of the location of the polar feed. Finally, case 5 summarizes the list with very high conversion in the presence of polar components and thus requires the highest catalyst loading from among all of the configurations. Generally, for the same IB conversion, it is observed that DIB selectivity is better in polar cases than in nonpolar cases. However, the catalyst loading required is much higher.

Conclusions

The feasibility of the dimerization of isobutene in a reactive distillation column has been analyzed by using simulations. The influence of important parameters was investigated. It was found that a hybrid reactive distillation is capable of carrying out the reaction and simultaneously separating the products efficiently. High selectivity toward the desired product can be achieved with adequate temperature control, which is otherwise not possible with conventional reactors.

A comparison of the configurations with and without the polar component was presented from a technical point of view. It shows that the presence of a small amount of a polar component can promote better selectivity to diisobutene. However, a much higher catalyst loading and slightly higher reflux and reboil ratios are required, and the separation of polar component from the product necessitates additional units.

The reactive distillation process seems to be capable of utilizing the same feedstock and the existing reactive distillation hardware for MTBE synthesis to manufacture isooctane with suitable revamping. The dimer can be hydrogenated in the same RD column (by adding a separate hydrogenation section, stacking the dimerization and hydrogenation catalysts, or using bifunctional catalysts) or in a separate reactor to obtain isooctane. Even though RD technology seems advantageous, other configurations such as a reactor–separator network or a distillation column with a side reactor cannot be simply discounted without systematic cost studies. These are the subjects of our future work.

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Nomenclature

a_i = activity of component i

B = relative adsorption equilibrium constant, eqs 1 and 2

Da = Damköhler number

F_T = total molar feed to the column, kmol/h

k = reaction rate constant, mol/(h g_{cat})

r = reflux ratio

r_1, r_2 = rate of reactions, mol/(h g_{cat})

s = reboil ratio

W_T = total catalyst loading, kg

x_i = liquid molar fraction of component i

Abbreviations

DIB = diisobutenes (2,4,4-trimethylpentenes)

IB = isobutene (2-methylpropene)

MTBE = methyl *tert*-butyl ether

TBA = *tert*-butyl alcohol (2-methyl-2-propanol)

TIB = triisobutenes (2-methyl-1-propene trimer or isobutylene trimer)

Literature Cited

- (1) Executive Order D-52-02 by the Governor of the State of California, Mar 15, 2002.
- (2) Kolah, A. K.; Qi, Z.; Mahajani, S. M. Dimerised isobutene: An alternative to MTBE. *Chem. Innovation* **2001**, 31, 3, 15–21.
- (3) Haag, W. O. Oligomerization of Isobutylene on Cation Exchange Resins. *Chem. Eng. Prog. Symp. Ser.* **1967**, 63, 140.
- (4) O'Connor, C. T.; Kojima, M.; Schumann, W. K. The Oligomerization of C4 Alkenes over Cationic Exchange Resins. *Appl. Catal.* **1985**, 16, 193.
- (5) Rehfinger, A.; Hoffmann, U. Formation of Di-isobutene, Main Byproduct of Methyl Tertiary Butyl Ether Synthesis Catalyzed by Ion Exchange Resin. *Chem. Eng. Technol.* **1990**, 13, 150.
- (6) Izquierdo, J. F.; Vila, M.; Tejero, J.; Cunill, F.; Iborra, M. Kinetic Study of Isobutene Dimerization Catalyzed by a Macroporous Sulphonic Acid Resin. *Appl. Catal., A* **1993**, 106, 155.
- (7) Vila, M.; Cunill, F.; Izquierdo, J. F.; González, J.; Hernández, A. The Role of By-Products Formation in Methyl *tert*-Butyl Ether Synthesis Catalyzed by a Macroporous Acidic Resin. *Appl. Catal., A* **1994**, 117, L99.
- (8) Marchionna, M.; Di Girolamo, M.; Patrini, R. Light olefin dimerization to high quality gasoline components. *Catal. Today* **2001**, 65, 397–403.
- (9) Di Girolamo, M.; Lami, M.; Marchionna, M.; Pescarollo, E.; Tagliabue, L.; Ancillotti, F., Liquid-Phase Etherification/Dimerisation of Isobutene over Sulphonic Acid Resins. *Ind. Eng. Chem. Res.* **1997**, 36, 4452.
- (10) Di Girolamo, M.; Tagliabue, L. MTBE and Alkylate Coproduction: Fundamentals and Operating Experience. *Catal. Today* **1999**, 52, 307.
- (11) Honkela, M.; Krause, A. O. I. Influence of polar components in the dimerisation of isobutene. *Catal. Lett.* **2003**, 87, Nos. 3–4, 113.
- (12) Honkela, M. L.; Ouni, T.; Krause, A. O. I. Thermodynamics and Kinetics of the Dehydration of *tert*-Butyl Alcohol. *Ind. Eng. Chem. Res.* **2004**, 43, 4060–4065.
- (13) Ouni, T.; Jakobsson, K.; Pyhalahiti, A.; Aittamaa, J. Enhancing Productivity of Side Reactor Configuration through Optimizing the Reaction Conditions. *Chem. Eng. Res. Des.* **2004**, 82 (A2), 167–174.
- (14) Sundmacher, K.; Kienle, A. *Reactive Distillation—Status and Future Trends*; Wiley-VCH: Weinheim, Germany, 2003.
- (15) Hiwale, R. S.; Bhate, N. V.; Mahajan, Y. S.; Mahajani, S. M. Industrial Applications of Reactive Distillation: Recent Trends. *Int. J. Chem. React. Eng.* **2004**, 2, R1.
- (16) Honkela, M.; Krause, A. O. I. Kinetic Modeling of the Dimerization of Isobutene. *Ind. Eng. Chem. Res.* **2004**, 43, 3251–3260.
- (17) Qi, Z.; Sundmacher, K.; Stein, E.; Kienle, A.; Kolah, A. Reactive Separation of Isobutene from C4 Crack Fractions by Catalytic Distillation Processes. *Sep. Purif. Technol.* **2002**, 26, 147–163.
- (18) Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, 32, 178–193.
- (19) Stryjek, R.; Vera, J. H. PRSV—An Improved Peng–Robinson Equation of State with New Mixing Rules for Strongly Nonideal Mixtures. *Can. J. Chem. Eng.* **1986**, 64, 334–340.
- (20) HYSYS; AEA Technology, Hyprotech Ltd.: Calgary, Canada, 2001.
- (21) Mangold, M.; Kienle, A.; Gilles, E. D.; Mohl, K. D. Nonlinear computation in DIVA—Method and applications. *Chem. Eng. Sci.* **2000**, 55, 441–454.
- (22) Linder, S. C. MTBE May Not Be the Only Gasoline Oxygenate You Should Be Worrying About. *LUSTLine* **2000**, (Feb, Bulletin 34), 18–20.

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