

A moving bed reactor concept for alkane isomerization

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Abstract

We consider the isomerization of 2-methylpentane (2MP) to the di-branched isomer 2,2 dimethylbutane (22DMB) and examine various strategies for improving the conversion of 2MP, exceeding the limitation imposed by reaction equilibrium. Firstly, we examine the conventional reactor-followed-by-separation strategy. We show that a properly optimized true moving bed (TMB) adsorber with MFI zeolite is able to achieve near perfect separation of 2MP and 22DMB.

Next, we examine the strategy of in situ separation in a true moving bed reactor (TMBR). The success of the TMBR unit in achieving supra-equilibrium conversion depends crucially on proper choice of feed and product withdrawal strategies, as also on the number of column sections and flow rates to be employed. We demonstrate that a properly optimized TMBR unit can yield conversions in excess of 99%. We also examine the performance of a simulated moving bed reactor (SMBR) and find its performance inferior to that of the corresponding TMBR with conversion levels only of the order of 90%. Higher conversions are possible by increasing the number of columns in each section.

Our studies underline the significant advantages of in situ separations to improve the performance of an isomerization reactor.
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1. Introduction

Isomerization of alkanes, for the purposes of octane improvement, is a process of increasing importance in the petroleum industry [1–3]. The octane number increases with the degree of branching and so di-branched isomers are preferred products. Therefore in practice, it is necessary to separate the di-branched isomers from reaction products and recycle the mono-branched and linear alkanes back to the reactor. This separation is not an easy task because the principle of molecular sieving will not work [4,5]. In our earlier publications we have shown that separation of alkane isomers according to the degree of branching can be achieved using MFI zeolite as adsorbent by exploiting the principle of entropy, or packing effects [5,6]. Some experimental confirmation of this concept is available from the breakthrough

experiments in a *fixed bed* adsorber with MFI [4,7]. However, in these experiments the separation between di-branched and mono-branched isomers is not perfect and only partial separation is achieved.

In recent years it has been demonstrated that the *moving bed* adsorber, if properly optimized with respect to flow rates, can effect perfect separations [8]. The first major objective of the present communication is to show that the moving bed adsorber concept [9] can be used to separate di-branched and mono-branched alkanes into two substantially pure fractions using equilibrium separation principles that do not rely on differences in the intra-crystalline diffusivities. We use the design procedure described by Mazotti et al. [8].

The second major objective is to explore the advantages of combining reaction and separation functions in order to achieve supra-equilibrium conversions in the isomerization reactor. We aim to show that the simulated moving bed reactor (SMBR) offers the possibility of achieving approaching 100% conversion to the di-branched isomer.

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Nomenclature

b_i	Langmuir isotherm parameter of component i (Pa^{-1})
k	reaction constant ($\text{Pa}^{-1} \text{s}^{-1}$)
m_j	flow rate ratio. Ratio of the gas flow with respect to the solid phase velocity (dimensionless)
p_i	partial pressure of component i (Pa)
Q^F	volumetric flow rate of the components in feed stream ($\text{m}^3 \text{s}^{-1}$)
Q_i^j	volumetric flow rate of component i in stream j ($\text{m}^3 \text{s}^{-1}$)
r	reaction rate (s^{-1})
S	purity as defined in Eq. (3) (dimensionless)
T	temperature (K)

2. Isomerization reactor followed by true moving bed adsorber

For the purposes of illustration of concepts we consider the example the isomerization of 2-methylpentane (2MP) to 2,2 dimethylbutane (22DMB)



The reaction is reversible and the product from the isomerization reactor will consist of a mixture of 2MP (component 1) and 22DMB (component 2). Fig. 1 shows the schematic of a process with an isomerization reactor followed by a separation unit. We examine the performance of a *true* moving bed (TMB) adsorber employing MFI zeolite as the device for separating the desired product 22DMB from 2MP. Unreacted 2MP is separated from the inert carrier gas, that also functions as desorbent (indicated as D), and recycled back to the reactor. Both the isomerization reactor and the TMB units are assumed to operate at 473 K and 101 kPa. The Langmuir

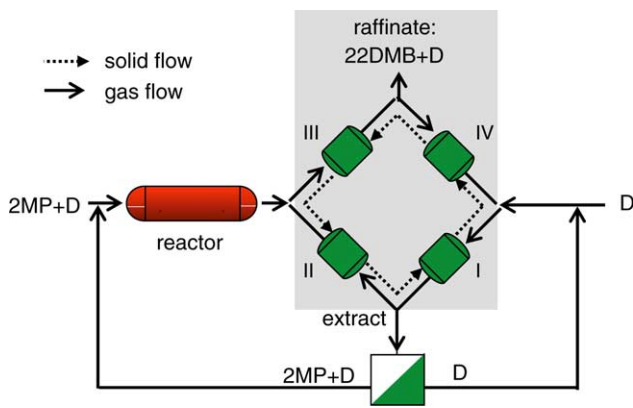


Fig. 1. Conventional reactor-separator unit using a TMB to separate the hexane mixture. The dotted lines denote the flow direction of the adsorbed solid phase.

Table 1

Langmuir parameters for 2MP and 22DMB at 473 K in MFI zeolite (data taken from Jolimaitre et al. [7])

	2MP	22DMB
Saturation loading, q_{sat} [mol kg^{-1}]	0.6935	0.6935
Langmuir parameter, b_i [Pa^{-1}]	1.27×10^{-4}	7.12×10^{-5}
Adsorptivity, γ , dimensionless	215.1	120.6

isotherm parameters at 473 K are given by Jolimaitre et al. [7] and are specified in Table 1 the multicomponent Langmuir isotherm is used for calculation of the component loadings. The Langmuir–Hinshelwood expression

$$r = \frac{k_f p_1 - k_b p_2}{1 + b_1 p_1 + b_2 p_2} \quad (2)$$

is used to represent the isomerization reaction rate [10]. In Eq. (2) p_i represent the partial pressures, and the b_i are the Langmuir adsorption constants. The forward and reverse reaction rate constants are both taken to be $k_f = k_b = 5 \times 10^{-6} \text{ Pa}^{-1} \text{ s}^{-1}$; these values are chosen for illustration purposes. At reaction equilibrium, therefore, the products leaving the reactor and entering the TMB unit will be equimolar in 2MP and 22DMB. This can be seen from the typical concentration profiles sketched in Fig. 2a. The conversion in the reactor is 50%, which corresponds to that at reaction equilibrium.

Following the paper of Mazzotti et al. [8], the TMB unit is divided into four sections as shown in Fig. 1. Each section has a specific task. In Section 1 the more strongly adsorbed component 2MP is desorbed and carried in the gas phase to the extract where it is withdrawn. The less strongly adsorbed product 22DMB is desorbed in Section 2 and carried by the gas phase towards the raffinate. 2MP preferentially adsorbs in Section 3 and is carried in the adsorbed zeolite phase in the direction of the extract (the movement of the zeolite adsorbent is indicated by the dotted lines). Section 4 has the task to adsorb the remaining 22DMB in order to carry it towards the raffinate, where it is withdrawn. This strategy results in complete separation. We can recover pure 2MP in the extract and pure 22DMB in the raffinate if and only if the operation conditions in the TMB unit, with respect to the fluid and solid phase velocities in the various sections, are chosen properly.

Mazzotti et al. [8] developed the *triangle* theory, which determines the operation parameters for complete separation. Using a rigorous analysis, they showed that the flow rate ratios, m_i , in each of the four sections of the TMB are important operation parameters. The flow rate ratios are defined as the ratio of the volumetric gas flow rate versus the volumetric flow rate of the adsorbed solid phase. In particular the flow rate ratios in Sections 2 and 3 are critical for optimal operation. Applying Mazzotti's design method yields an operation window depending on the flow rate ratios in Sections 2 and 3 and on the feed composition. The grey colored triangular region in Fig. 2b is the optimum operating window, where the calculations are based on the parameters given in Table 1; other input data are specified in the legend to Fig. 2. Per-

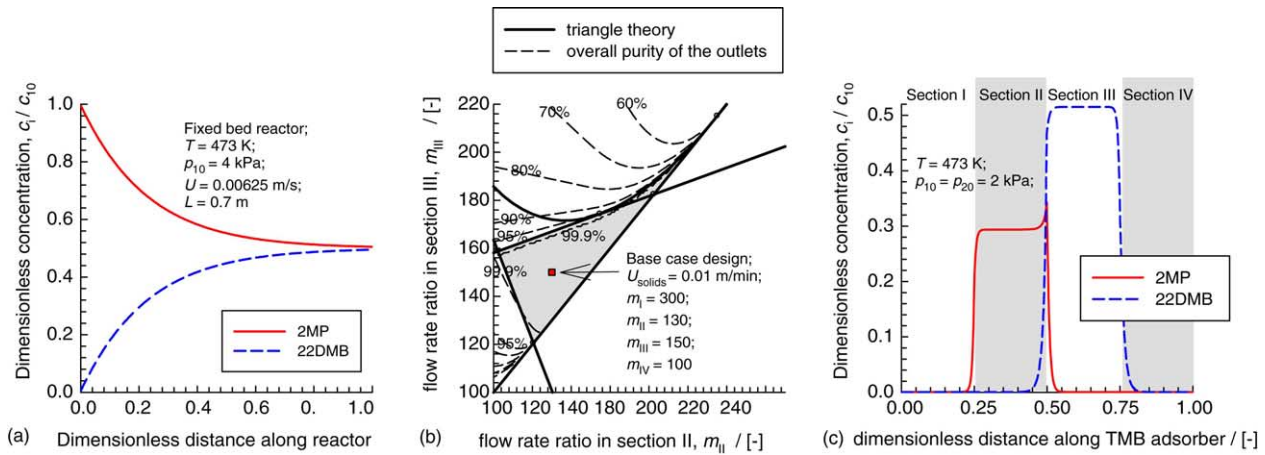


Fig. 2. (a) Concentration profiles in the fixed bed reactor of $L = 0.7$ m operating at a gas velocity of 0.00625 m/s. (b) Determination of the operation point for the TMB unit using the triangle theory. (c) Composition profile along the dimensionless length of the TMB unit. Note, the physical locations of the dimensionless TMB length at 0 and 1 coincide at the feed location of the desorbent. For the calculations shown in (b) the following parameter values were used. Length of each of the four TMB sections = 0.25 m, bed voidage = 0.4 , temperature = 473 K, pressure = 101 kPa, partial pressures of 2MP and 22DMB in feed to the TMB unit = 2 kPa, density of MFI zeolite adsorbent = 620.8 kg/m³. The simulation results for the composition profiles in (c) are for the operating point with $m_I = 300$; $m_{II} = 130$, $m_{III} = 150$, and $m_{IV} = 100$ as indicated by the square symbol in (b).

fect separation can be obtained in a triangle shaped region on the m_{II} – m_{III} subspace, i.e. the products in the extract and raffinate phases are pure 2MP and 22DMB, respectively. The triangle becomes narrower if the mixture feed concentration is increased. For robust operation it is not desirable to operate close to any of the boundaries of the triangle. In order to guarantee robust process behavior, we choose for each component partial pressures of 2 kPa in the TMB feed stream. It must be noted that the use of diluted process streams will result in large recycles of inert (desorbent) and larger equipment sizes. With the assumption that the isomerization reactor reaches equilibrium conversion, with $k_f = k_b$, the feed stream to the reactor contains 4 kPa of pure 2MP. As indicated by the grey area in Fig. 2b this choice yields an adequate sized operation window.

It is to be noted that the flow rate ratios m_i are a couple of orders of magnitude larger compared to the example calculations presented by Mazzotti et al. [8]; this is due to the much higher *adsorptivities* (as defined in their paper [8]), for 2MP and 22DMB in MFI zeolite and reported in Table 1. Once the flow rate ratios are chosen, the gas velocities in the four sections can be calculated from the solid phase velocity. For design purposes we choose 0.01 m/min as the solid phase velocity. The interstitial feed velocity of 2MP = 0.005 m/s results directly from mass balance considerations around the mixture feed.

In order to check the validity of the choice of the design parameters emerging from the triangle theory, we carried out detailed simulations of the TMB unit using a rigorous numerical model as detailed elsewhere [11], with the additional assumption of negligible intra-particle diffusion resistance. Furthermore, we did not account for pressure drop or axial dispersion along the TMB columns. The gas phase is assumed to be ideal. The carrier gas also functions as desorbent

and is not explicitly modeled as a component. The gaseous streams in each of the four sections consist mainly of inert, non-adsorbing carrier gas, and so can assume that the gas velocities are constant in each section.

The simulation results for the purities of the outlet streams of the TMB are shown by the dashed lines in Fig. 2b. We defined the overall purity

$$S = \frac{Q_{2MP}^{\text{extract}} + Q_{22DMB}^{\text{raffinate}}}{Q^F} \quad (3)$$

where Q_{2MP}^{extract} and $Q_{22DMB}^{\text{raffinate}}$ denote the volumetric flow rates of the desired components in the raffinate and extract. Obviously, the definition for the overall purity yields 100% for complete separation and values below this for configurations with impurities in the raffinate or extract. The dashed lines represent the result of our simulations for varying flow rates in the four sections. We note that as the operating conditions are chosen outside the triangular region the overall purity values are reduced to values significantly below 100%. The match between the triangular theory predictions and our TMB simulations is very good. Fig. 2c shows the simulation results for composition profiles for an operation point in the triangular region indicated with a square symbol, i.e. $m_I = 300$; $m_{II} = 130$, $m_{III} = 150$, and $m_{IV} = 100$. We obtain a purity of above 99.9%. Hence, if unreacted 2MP is recycled, as shown in the process flowsheet in Fig. 1 we are able to obtain total conversion.

3. Four-section TMBR configuration

We now investigate whether it would be advantageous to combine the reaction and separation function in the same unit.

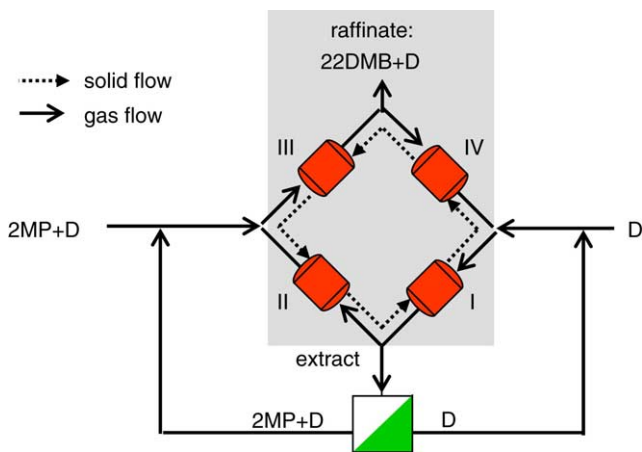


Fig. 3. Schematic drawing of a reactive true moving bed (TMBR) unit with external recycle.

Consider first a true moving bed reactor (TMBR) unit with four sections as shown in Fig. 3. The Langmuir–Hinshelwood reaction kinetics (2) with $k_f = k_b = 5 \times 10^{-6} \text{ Pa}^{-1} \text{ s}^{-1}$ described the intrinsic reaction rate. The data in Table 1 holds for the adsorption characteristics. As in the conventional process flow scheme, the partial pressure of the feed 2MP to the TMBR feed stream is taken to be 4 kPa. We demand high purities of the raffinate and extract streams in order to meet strict process specifications and maximize conversion. Simulations of the TMBR were carried out using the detailed numerical procedure described elsewhere [11]. Fig. 4a shows the composition profiles in the various sections of the TMBR unit. The operation point is identical to the one previously chosen for the non-reactive TMB unit and indicated by the square symbol in Fig. 2b, i.e. $m_{\text{II}} = 130$, $m_{\text{III}} = 150$. These simulations show that the conversion is below chemical equilibrium and reaches a value of only 33%. Nevertheless, we obtain reasonable purities of approximately 98%. This indicates that the reaction in section II and III only slightly interferes with the separation of the mixture. The low conversion of 33% achieved indicates that the separation of 2MP and 22DMB in

the TMBR is not favorable for the reaction. Generally speaking, for in situ separations within a reactor it is necessary to remove the product from the reaction zone and internally recycle the reactants. In the TMBR the reactant 2MP, however, is not internally recycled, but withdrawn at the extract in the TMBR. We can lower the amount of 2MP to be withdrawn as extract by increasing the gas flow rate in section II. The composition profile will shift 2MP toward Section 3 and so causes a larger internal recycle of 2MP. Fig. 4b illustrates this by means of the composition profile for a TMBR unit operating at $m_{\text{II}} = 160$ and $m_{\text{III}} = 180$. As can be seen, the concentration of 2MP becomes lower in Section 2 and 22DMB is mainly formed in Section 3 compared with the case in Fig. 4a. As a result we improve conversion exceeding equilibrium limitations, but also observe a drop in purity. By increasing the gas flow in Section 2, we implicitly increase the flow rate in Section 3. The short residence time in Section 3 suppresses complete adsorption of 2MP, and so the raffinate gets contaminated with 2MP.

We screened a wide region of the $m_{\text{II}}-m_{\text{III}}$ plane for different operating conditions and its influence on conversion (indicated by the dashed lines) and purity (indicated by solid lines); the results are summarized in Fig. 4c. Comparing the performance of the non-reactive TMB (Fig. 2b) and the TMBR unit (Fig. 4c) shows that high purities are obtained in the region where the triangle theory predicts complete separation. The lower purity levels (of maximum 98%) of the TMBR can be attributed to the presence of the reaction. Fig. 4c also shows that TMBR configurations aiming for conversion beyond chemical equilibrium require larger flow rates. Combining these observations leads us to the conclusion that reaction and separation are incompatible for a TMBR unit, using the configuration as sketched in Fig. 3.

4. Two-section TMBR configuration

In order to resolve the incompatibility of reaction and separation it is necessary to choose independently the gas phase

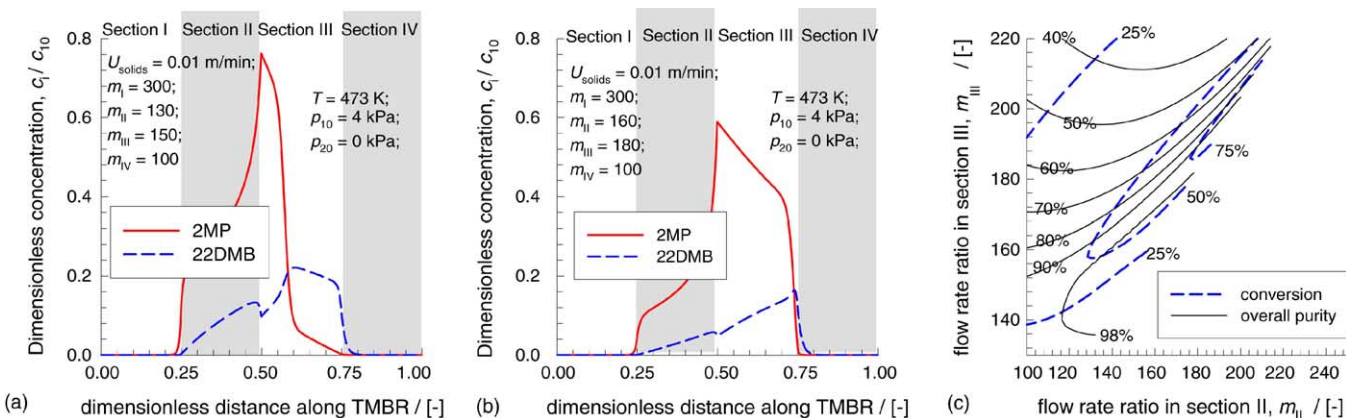


Fig. 4. Composition profiles within TMBR unit operating with (a) $m_{\text{II}} = 130$ $m_{\text{III}} = 150$ and (b) $m_{\text{II}} = 160$ $m_{\text{III}} = 180$. (c) Conversion and overall purity of a reactive TMB unit. Note the conversion calculation did not include the external recycle of 2MP.

velocities in Sections 2 and 3. The residence time in Section 2 should be short enough to ensure that 2MP is internally recycled. On the other hand it is advantageous to adjust the gas flow rate in Section 3 in such a way that the residence time is sufficient for the reaction. Therefore, we relax the restriction of only adding a feed stream at the node between Sections 2 and 3 and also allow a withdrawal. Let us consider a configuration where we withdraw carrier gas from the gas stream inlet stream of Section 3. Hence, the gas flow rate in Section 3 will be controlled by the amount of carrier gas withdrawn and the gas velocities in Section 2 can be chosen independently. If we choose the gas velocity in such a way that 2MP is swept from the section, the section loses its functionality and is redundant. The location of extract moves to the feed location. Furthermore, we are aiming for total conversion and so the entire stream leaving the reaction zone (Section 3) is the desired product stream. Section 4 becomes redundant too.

These design considerations lead to a configuration shown in Fig. 5. The Sections 2 and 4 have been eliminated. The extract and feed locations coincide. Furthermore, we have to ensure that a fraction of carrier gas is recycled to the inlet of Section 1. Separation of the carrier gas (desorbent) from 2MP is relatively simple as the former is not condensable. Fig. 6a shows a typical composition profile of the modified configuration of the TMBR. The flow rate ratios are $m_I = 200$ and $m_{III} = 25$. 2MP is fed at a pressure of 4 kPa and the inlet velocity is set to 0.005 m/s. These feed specifications correspond to that used for the case study in Fig. 2b. As can be seen from the composition profiles, Section 1 recycles 2MP internally, whereas reaction and separation takes mainly place in Section 3. We obtain an overall conversion of about 99.5%. Note the short residence time of Section 1 not only ensures that 2MP is transported back to the reaction zone, but also suppresses the reverse reaction.

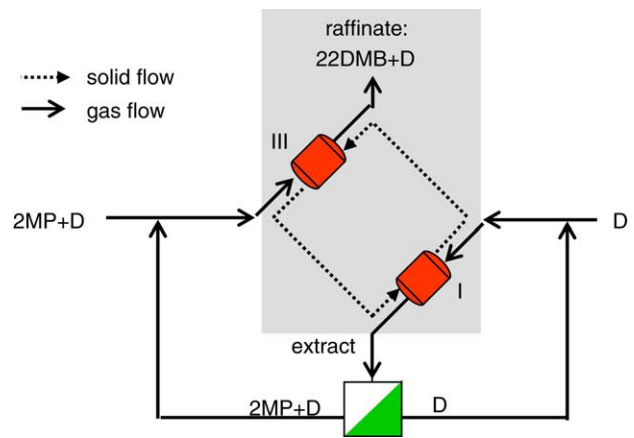


Fig. 5. Schematic drawing of an optimized two-section TMBR unit.

Fig. 6b shows the conversion levels for other flow rate ratio combinations. High conversion levels are only obtained for moderate gas flow rate in the reaction zone (Section 3) and high flow rates in the desorption zone (Section 1). The two-section TMBR has essential advantages compared with a traditional reactor-followed-by-separation scheme (Fig. 1) or the four-section TMBR (Fig. 3) as discussed previously. The effective recycle of the carrier gas (desorbent) is lower. The flow rate ratios in section II and III for the non-reactive case, however, are maintained at $m_{II} > 100$ and $m_{III} > 120$; see Figs. 2 and 4. In the two-section TMBR configuration the gas flow rate is an independent design parameter and it advantageous to choose a significantly lower value, $m_{III} = 25$. As in other in situ separations such as reactive distillation, the choice of the residence time depends on separation and reaction characteristics, in case of TMBR the residence time depends on the adsorption and reaction kinetics. Slow

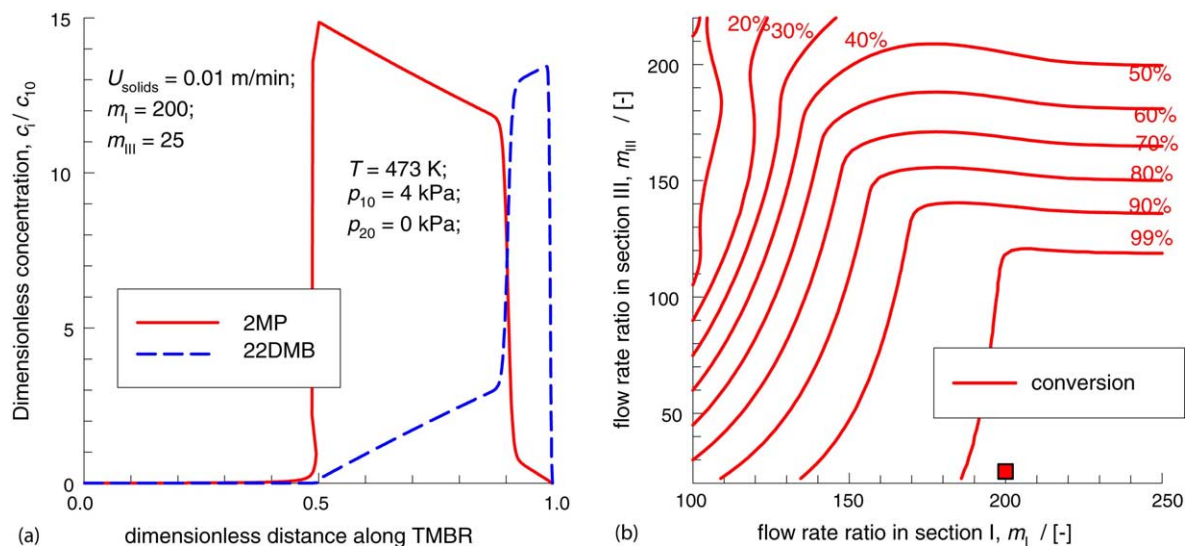


Fig. 6. (a) Composition profile of the two-section TMBR unit operating at $m_I = 200$ and $m_{III} = 25$. (b) Overall conversion with regard to the flow rate ratios m_I and m_{III} .

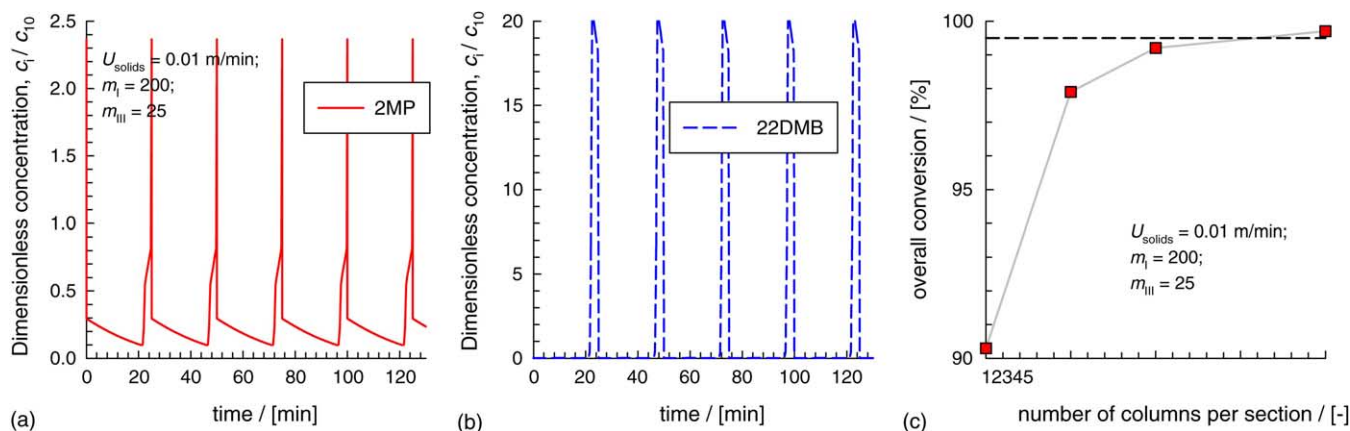


Fig. 7. Transient concentration profiles for (a) 2MP and (b) 22DMB at the product withdrawal of the SMBR corresponding to the two-section TMBR unit in Fig. 6a. Each section contains a single column. (c) Overall conversion of the two-section SMBR unit depending on the number of column in each section.

reaction and fast adsorption kinetics are favorable in order to obtain the desired conversion, purities and a large throughput. On the other hand, slow reaction and fast adsorption kinetics are undesirable with regard to the hardware design since it requires large units. Compared to the reactor – separator concept of Fig. 1, the reactor and the four sections of the TMB unit are replaced with just two sections of the TMBR. For the chosen set of operating conditions the size of the equipment in the TMBR is about 30% that of the conventional process.

5. Two-section SMBR configuration

In practice, true moving beds are not favored since it is technically difficult to continuously move the adsorbed solid phase. Therefore, the moving bed is emulated in a so-called *simulated* moving bed (SMB) unit. This is done by switching feeds and withdrawals from one section to the next section following the direction of the gas flow. Mazzotti et al. [8] have suggested rules for adjusting the gas velocities in a SMB unit based on the optimal design of a TMB unit. We applied these rules to determine the switching times and other parameters. The gas velocities practically equal the ones for the TMB since the flow rate ratios m_i are so large. Fig. 7a and b shows the compositions of 2MP and 22DMB at the product withdrawal point at quasi-steady state conditions. The simulations of the SMBR unit was carried out with the numerical procedure described elsewhere [11]. The configuration corresponds to the case study of the two-section TMBR described previously; see also Figs. 5 and 6. Each section consists of an adsorber-reactor column. We clearly see that there are traces of 2MP in the 22DMB product stream. The overall time-averaged conversion reaches 90.3%, which is significantly higher than that at reaction equilibrium but lower than that achieved in the corresponding TMBR. This indicates that the performance of the true moving bed is not well emulated.

If we divide a section in more columns we can improve the emulation of the TMB. Fig. 7c shows the dependence of the overall conversion with respect to the number of columns in each of the two sections. From the graph we see that at least three columns are needed to obtain a conversion of above 99%.

6. Conclusions

Using the example of the reversible reaction $2MP \rightleftharpoons 22DMB$ we have examined various strategies for improving the conversion beyond equilibrium levels. In the conventional reactor-followed-by-separation strategy, we show that a properly optimized true moving bed (TMB) adsorber with MFI zeolite is able to achieve near perfect separation of 2MP and 22DMB.

Significantly smaller equipment sizes, along with conversion levels of 99% are possible in a properly optimized true moving bed reactor (TMBR). The success of the TMBR unit in achieving supra-equilibrium conversion depends crucially on proper choice of feed and withdrawal strategies, as also on the number of column sections and flow rates to be employed. Emulation of the performance of a TMBR in simulated moving bed reactor is not perfect and additional column sections need to be used.

Our studies underline the significant advantages of in situ separations to improve the performance of an isomerization reactor.

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