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Optimization of reactive SMB and Varicol systems

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Abstract

A comprehensive optimization study on a simulated moving bed reactor (SMBR) system is reported in this article for the direct synthesis of methyl tertiary butyl ether (MTBE) from tertiary butyl alcohol (TBA) and methanol. The applicability of the Varicol process, which is based on non-synchronous shift of the inlet and outlet ports, is explored for the first time for a reactive system. Multi-objective (two and three objective functions) optimization has been performed for both existing as well as design stage for SMBR and Varicol systems and their efficiencies are compared. The optimization problem involves relatively large number of decision variables; both continuous variables, such as flow rates in various sections and length of the columns and discrete variables, such as number of columns and column configuration. Pareto optimal solutions are obtained. It is observed that a five-column Varicol performs better than an equivalent five-column SMBR and its performance is nearly equal to that of a six-column SMBR in terms of purity and yield of MTBE and minimal eluent consumption. This is an important inference as it enables the reduction of fixed and operating costs while at the same time helps to achieve high purity and yield of the desired product and conversion of the limiting reactant. A state-of-the-art optimization technique, viz., non-dominated sorting genetic algorithm (NSGA), which allows handling of these complex optimization problems, is employed for this study. This is the first time that, not only the separating potential of Varicol has been extended to reaction systems, but also was optimized for multiple objectives.

Keywords: Simulated moving bed; Varicol; Multi-objective optimization; Genetic algorithm; Pareto set; MTBE

1. Introduction

Recently, a great deal of attention is being paid to simulated moving bed (SMB) technology as an alternative to classical elution chromatography. Introduced for the first time by Universal Oil Products (UOP) in the 1960s, SMB was used for separations that are either impossible or difficult using traditional separation techniques, such as distillation, which is highly energy-intensive. By virtue of its superior separating power, SMB has become one of the most popular techniques, finding its application in petrochemical and sugar industries and of late, there has been a remarkably increased interest in SMB in the pharmaceutical industry for enantio-separations (Storti, Mazzotti, Morbidelli & Carra, 1993; Mazzotti, Storti & Morbidelli, 1994; Mazzotti, Storti & Morbidelli, 1996a; Mazzotti, Baciocchi, Storti & Morbidelli, 1996b; Mazzotti, Kruglov, Neri, Gelosa & Morbidelli, 1996c; Mazzotti, Storti & Morbidelli, 1997a; Mazzotti, Storti & Morbidelli, 1997b; Mazzotti, Neri, Gelosa & Morbidelli, 1997c).

SMB is a practical implementation of the true moving bed (TMB) process, where the problems associated with the solid motion of the latter are avoided (Ruthven & Ching, 1989). The countercurrent movement between the mobile phase and the stationary phase in TMB is simulated by moving the input/output ports periodically and simultaneously along a series of fixed columns in the direction of the mobile phase flow, while holding the bed stationary. Hence, periodic discrete steps in the SMB replace the continuous motion of the fluid and solid in the TMB. Recently, a modification of SMB technology for chiral separation was reported (Ludemann-Hombourger, Nicoud & Bailly, 2000; Ludemann-Hombourger, Pigorini, Nicoud, Ross & Terfloth, 2002; Zhang, Hidajat & Ray, 2001a), which they named as Varicol process. In Varicol operation, although the switching period is decided a priori and kept constant,

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Nomenclature

C	liquid phase concentration (mol/l)
d	diameter of the column (m)
D	apparent axial dispersion coefficient (m^2/s)
K	reaction rate constant
K	equilibrium constant
L	length of column (m)
n	moles of TBA reacted per mole of methanol
N	number of switching
p	number of columns in section P
P	purity
q	concentration in the polymer phase (mol/l); number of columns in section Q
Q	volume flow rate (m^3/s)
r	number of columns in section R
R	reaction rate (mol/l/s)
s	number of columns in section S
S	selectivity
t	time (s)
T	temperature (K)
u	superficial velocity (m/s)
V	velocity (m/s)
X	conversion
Y	yield
z	axial coordinate (m)
Greek letters	
α	fraction of feed
β	fraction of raffinate withdrawn
γ	fraction of eluent
ε	void fraction
ϕ	section
χ	column configuration
ζ	pseudo solid phase velocity
v	stoichiometric coefficient of component
Subscripts/superscripts	
b	backward
col	column
eqm	equilibrium
f	feed, forward
i	component i
j	column number
s	solid, switching
n	exponent
N	number, switching period

a non-synchronous shift of the inlet and outlet ports is employed within a switching period. During one global switching period, there are different column configurations for the sub-time intervals due to local switching. Given the total number of columns employed in a Varicol process, the number of columns in each zone varies with time within a global switching period, but the number of columns in each zone recovers to the starting value at the end of the global switching period. The above switching process is repeated within each global switching period. Therefore, locations of input/output ports in the Varicol process are quite different from the SMB process, as the ports are not shifted concurrently. Moreover, a port may shift more than once during one global switching period, either forward or even in a backward direction. As a result, Varicol process can have several column configurations, which endow more flexibility compared to SMB process. SMB process can be regarded as the most rigid and a special case of more flexible Varicol process. It should be noted

that the Varicol process does not add any additional fixed cost.

Integration of reaction and separation is very essential to improve economics and efficiency of process industries. SMB does provide opportunity for coupling reactions that can be exploited to improve conversion and purity of many reversible reactions. Simulated moving bed reactor (SMBR) is thus a multifunctional reactor in which chemical reaction and separation of the reactants and products take place concurrently. In situ separation of the products facilitates the reversible reaction to completion beyond thermodynamic equilibrium. Although a reasonable amount of experimental and numerical studies on SMBR have been reported in literature (Ray, Tonkovich, Carr & Aris, 1990; Ray, Carr & Aris, 1994; Ray and Carr, 1995a; Ray and Carr, 1995b; Lode, Houmard, Migliorini, Mazzotti & Morbidelli, 2001), there is still no reported application of SMBR in the chemical process industry. Moreover, to date, the separation power of Varicol has not been applied to reaction systems to improve productivity and product quality. The successful implementation of SMBR and its modification, Varicol process, on an industrial scale will necessitate one to determine the optimal operating conditions and design parameters, such as length and number of columns, switching time and sequence (in Varicol) for the distribution of columns, flow rates in various sections, feed composition etc., leading to a comprehensive design of the unit. The selection of these decision (operating or design) parameters is not straightforward. Quite a few studies have been reported on the design and optimization of SMBR, but they are all based on either simulation or single objective optimization in terms of productivity, which is usually insufficient for the design of the complex SMBR process (Storti, Masi, Paludetto, Morbidelli & Carra, 1988; Storti, Baciocchi, Mazzotti & Morbidelli, 1995; Dunnebier and Klatt, 1999; Karlsson, Pettersson & Westerlund, 1999; Wu, Ma & Wang, 1999; Dunnebier, Fricke & Klatt, 2000). Operating variables and constraints often affect the performance of the SMBR system in conflicting ways that one has to necessarily opt for multi-objective optimization (Bhaskar, Gupta & Ray, 2000a).

Multi-objective optimization has been the subject of interest to engineers of different disciplines for a long time. But, only a few studies have been reported in the mainstream chemical engineering literature, which has been reviewed recently by Bhaskar et al. (2000a). In their paper, they emphasized that the complex operation of SMB would be a suitable choice to elucidate the importance of multi-objective optimization in chemical engineering. In the present work, multi-objective (two and three objective functions) optimization has been performed for the direct synthesis of methyl tertiary butyl ether (MTBE) from tertiary butyl alcohol (TBA) and methanol in SMBR and its modification, Varicol process. To the best of our knowledge, this is *the first attempt* not only to perform the three-objective optimization study on SMBR systems, but also to extend the concept of Varicol process to reacting systems and compare the optimal solutions.

A comprehensive multi-objective optimization study of SMBR is reported in this work by using a state-of-the-art AI-based robust optimization technique, non-dominated sorting genetic algorithm (NSGA). Genetic algorithm (GA) is a non-traditional search and optimization method (Holland, 1975; Goldberg, 1989; Deb, 2001) that has become quite popular in recent years in engineering optimization. There are also quite a few articles discussing the application of NSGA to chemical engineering problems (Bhaskar, Gupta & Ray, 2000b; Bhaskar, Gupta & Ray, 2001; Oh, Ray & Rangaiah, 2001; Rajesh, Gupta, Rangaiah & Ray, 2000; Rajesh, Gupta, Rangaiah & Ray, 2001; Ravi, Gupta & Ray, 2000; Ravi, Gupta, Viswanathan & Ray, 2002; Yuen, Aatmeeyata, Gupta & Ray, 2000; Zhou, Gupta & Ray, 2000). It mimics the principles of genetics and the Darwinian principle of natural selection, i.e. the survival of the fittest. Unlike the single objective function optimization, where one attempts to find the best design, which is usually the global optimum (minimum or maximum), there could exist an entire set of optimal solutions that are *equally* good for a multi-objective optimization problem. These solutions are known as *Pareto-optimal* (or non-dominated) solutions. A Pareto-set is described by a set of points such that when one moves from one point to any other, at least one objective function improves, while the other worsens. Since none of the non-dominated solutions in the Pareto set is superior to any other, any one of them is an acceptable solution.

The economical operation of SMBR and Varicol processes are governed by many factors depending on the objectives and desired product quality. One may be interested in higher productivity using minimum solvent (eluent) or may be interested in producing as high a purity product as possible while simultaneously maximizing the yield and minimizing the amount of adsorbent (catalyst). In this paper, a few two- and three-objective function optimization problems for MTBE synthesis in both SMBR and Varicol systems have been considered. A mathematical model, which predicted single column experimental results well enough (Zhang et al., 2001a) was modified for SMBR (Zhang, Hidajat & Ray, 2001b) and used in the optimization study. Thereafter, Pareto optimal curves were obtained for both SMBR and Varicol systems. It was found that performance of Varicol could be better than SMBR (due to the increased flexibility) in terms of treating more feed using less eluent or producing better product quality for fixed capacity and solvent consump-

tion. It is to be emphasized that there is no end to the variety of multi-objective optimization problems that could be formulated and studied for SMBR systems. A few examples were studied to illustrate the concepts, techniques and interpretation of the results. Furthermore, comparison of the performances of SMBR and Varicol would enable us to determine the extent to which SMBR could be improved by applying non-synchronous switching with varying zone lengths.

2. Direct synthesis of MTBE in SMBR and Varicol systems

MTBE is presently the most important high-octane blending oxygenate for gasoline as it is an effective substitute to poisonous substances, like lead compounds, to serve as an anti-knock in automobiles. Recently, Zhang et al. (2001a) reported the adsorption and kinetic data for the direct synthesis of MTBE from TBA and methanol in a fixed bed reactor-separator in which Amberlyst-15 ion exchange resin was used as both the catalyst and the adsorbent etherification reaction. The overall reaction can be described by the following equation:

$$n(CH_3)_3COH + CH_3OH(CH_3)_3COCH_3 + nH_2O + (n-1)(CH_3)_2CCH_2 \quad (1)$$

where n (usually >1) is an unknown parameter, which indicates the amount of isobutene produced. It should be noted that although methanol is one of the reactants, it also acts as a carrier solvent and is usually present in excess. Experiments were conducted at different temperatures, flow rates and feed concentrations in a single packed column and the elution (breakthrough) profiles of the various components from the exit of the column were monitored continuously. The kinetic parameters, adsorption equilibrium constants as well as the dispersion coefficients of TBA, MTBE and H_2O in methanol were obtained by minimizing the error between the experimental and model predicted results and are given Appendix A for three different temperature values. The details are described elsewhere (Zhang et al., 2001a). In this study, we have used the same kinetic data and model for the optimization study.

A schematic representation of an SMBR is illustrated in Fig. 1, which consists of a number of columns of uniform cross-section and length, L. The columns are packed with Amberlyst-15 ion exchange resin, which acts both as the catalyst and adsorbent and are arranged in a circular array. The two incoming streams (the feed and the eluent) and the two outgoing streams (the raffinate and the extract) divide the system into four sections namely P, Q, R and S, each comprising p, q, r and s columns, respectively. The flow rate in the section P, Q_P, was chosen as the reference flow rate based on which all other flow rates were described. The ratios of the feed flow rate, F, the raffinate flow rate, Ra, the eluent flow rate, E, to that in section P, Q_P, were designated as α, β and γ, respectively. By advancing the inlet and outlet ports, column by column, in the direction of the fluid flow at a pre-set switching time, t_s, it is possible to simulate the countercurrent movement of the solids with respect to the fluid flow. However, the separation of the components could be achieved only by appropriately specifying the switching time and the internal flow rates in various sections. It is worth noting that the switching time and the column configuration (the number of columns in each section) in the SMBR is decided a priori and is kept fixed for the entire operation. It should also be noted that only four of the above eight flow rates are independent, as the remaining four are determined from the mass balance at points A, B, C and D (see Fig. 1). In particular, by fixing α, β, γ and Q_P, all the other flow rates can be calculated using the following relations

$$Q_S = (1-\alpha)Q_P \quad (2)$$

$$Q_Q = (1-\beta)Q_P \quad (3)$$

$$Q_R = (1-\beta+\gamma)Q_P \quad (4)$$

$$Ex = (\alpha-\beta+\gamma)Q_P \quad (5)$$

Unlike the SMBR, the Varicol is based on a non-simultaneous and unequal shift of the inlet and outlet ports. Fig. 2(b) illustrates the principles of operation of a six-column Varicol system with a four sub-interval switching period, and also compares it with an equivalent six-column SMBR, shown in Fig. 2(a). The switching time, t_s, is still a key parameter in Varicol and is kept fixed at a pre-assigned value. However, within a global switching period, t_s, the column configuration is varied for each quarter of t_s for a four-subinterval Varicol system. For example, consider a typical sequence in a given cycle corresponding to Fig. 2 (b):

Cycle 1

First sub-interval, $0 < t < t_s/4$:	2/1/1/2
Second sub-interval, $t_s/4 < t < t_s/2$:	2/1/2/1
Third sub-interval, $t_s/2 < t < 3t_s/4$:	1/1/2/2
Last sub-interval, $3t_s/4 < t < t_s$:	1/2/1/2

The configuration 2/1/1/2 explicates that there are two columns in P section, one each in sections Q and R sections while two columns in section S, respectively. In the second sub-interval, the configuration of columns changes to 2/1/2/1 by shifting the extract port by exactly one column forward. For the next sub-interval, a forward shift of the feed port by one column changes the configuration to 1/1/2/2. Finally, in the last sub-interval, the eluent port shifts forward by one column to change the column configuration to 1/2/1/2. For the next

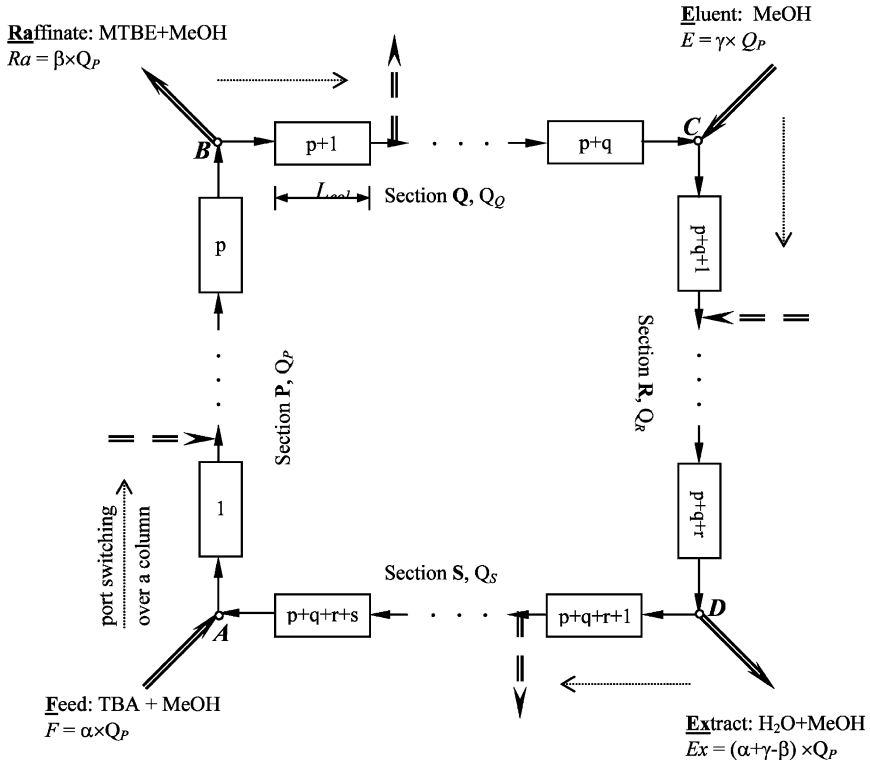

Fig. 1. Schematic flow diagram of the SMBR. The inlets and outlets divide the entire system into four sections: P, Q, R and S with, respectively, p, q, r and s as the number of columns. The flow rates in each section is given by $Q_Q = (1-\beta)\,Q_P$, $Q_R = (1-\beta+\gamma)\,Q_P$ and $Q_S = (1-\alpha)\,Q_P$, where α, β, γ are given by F/Q_P, Ra/Q_P, E/Q_P.

cycle, the column configuration gets reverted back to the original 2/1/1/2. Consequently, for a four-subinterval Varicol process, there are four different column configurations corresponding to the four subintervals, which is due to the local switching within a global switching period. Though, the number of columns in any section varied within a global switching time, the number of columns in each section returned to its initial value at the end of each cycle. For the case mentioned above, the time-averaged number of columns per section in a global switching time is equivalent to the configuration 1.5/1.25/1.5/1.75. It should be noted that it is always possible for any port to shift more than once, either forward or backward, during a global switching period. Hence, location of input and output ports in Varicol systems is quite diverse to that of SMBR. Hence, Varicol system endows more flexibility compared to the SMBR, without necessitating any additional fixed cost and SMBR can be considered the most rigid specific case of a Varicol system.

3. Mathematical model

In a four-section SMB process, as shown in Fig. 1, all input/output ports shift by one column in the direction of fluid flow after a fixed interval (switching time, t_s). In order to achieve a good separation, each section should fulfill its own role, which is decided by the length and number of columns, fluid flow rates in each section and switching time. The main task of section P is to retain strongly adsorbed component H_2O (adsorption of H_2O) so that it does not breakthrough at the raffinate port where MTBE (weakly adsorbed component) is collected as product. The possible difficulties in this section are due to large column fluid flow rate (Q_p), small section length ($L_{col} \times p$), long switching time (t_s) and axial dispersion (D). Part of MTBE flows into section Q, where the column flow rate $Q_q[\equiv(1-\beta)Q_p]$ should be small enough to prevent MTBE from breaking through into section R. The primary roles of section Q are, therefore, retention of MTBE and desorption of eluent (MeOH). Section R has the maximum flow rate, $Q_r[\equiv(1-\beta+\gamma)Q_p]$ to desorb H_2O as well as MTBE such that at least the first column of this section is clean before the next port switching is made. The difficulties for this task are due to insufficient fluid flow rate, Q_r, short switching interval, t_s and long column length, L_{col}, as well as axial dispersion and tailing effect of the desorbing concentration front. The column flow rate in section S, $Q_s[\equiv(1-\alpha)Q_p]$ is lower than Q_r after withdrawing H_2O as (extract) product at the rate of $(Q_r - Q_s)$. However, Q_s

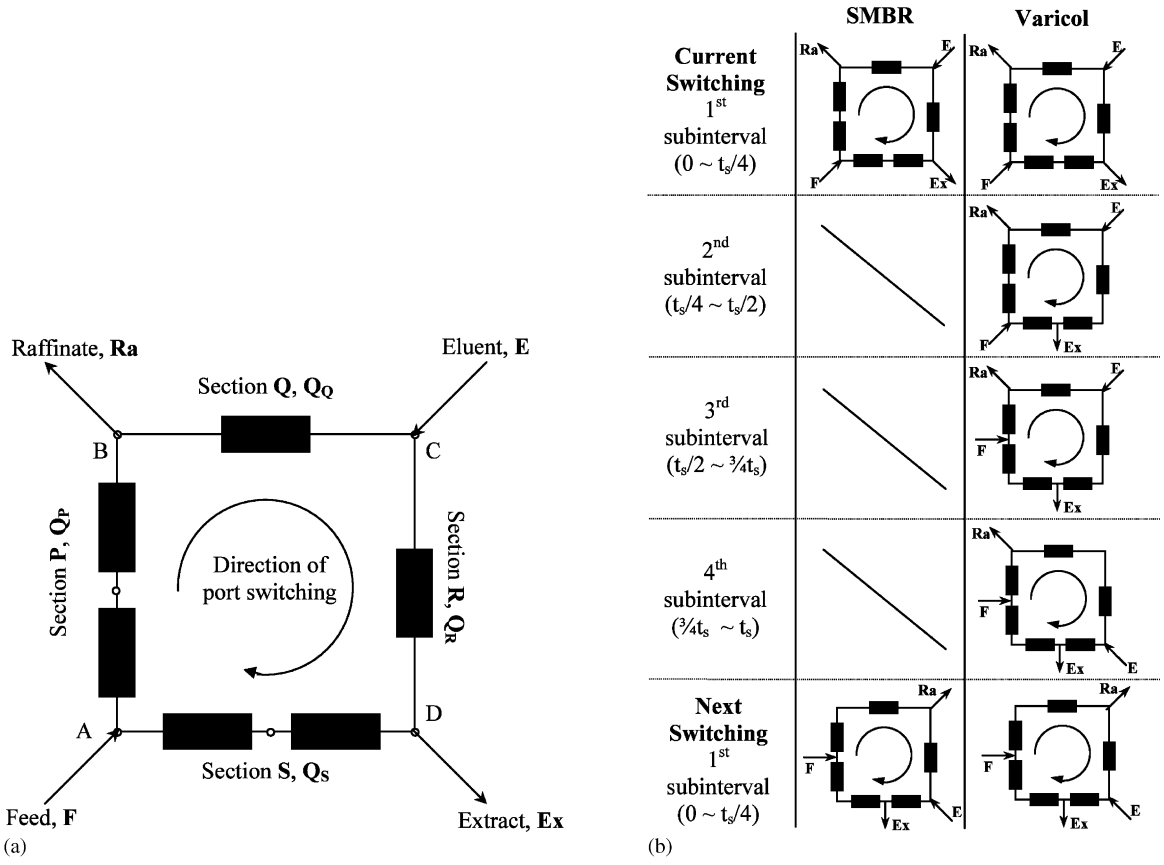

Fig. 2. (a) Schematic diagram of a six-column SMBR system. (b) Principle of operation of SMBR and four-subinterval Varicol (port switching schedule). The inlets and outlets divide the entire system into four sections: P, Q, R and S with, respectively, 2, 1, 1 and 2 number of columns. The flow rates in each section is given by $Q_Q = (1-\beta)\ Q_P$, $Q_R = (1-\beta+\gamma)\ Q_P$ and $Q_S = (1-\alpha)\ Q_P$, where α, β, γ are given by F/Q_P, Ra/Q_P, E/Q_P.

should be large enough to desorb MTBE out of the section S to be mixed with feed as recycle to section P. However, H_2O should be retained in section S. The difficulties for the task of this section is similar to those for section R, however the influence of axial dispersion is more significant due to concentration shock caused by the introduction of feed at the end of section S.

The length of sections P and S should be large enough to prevent H_2O from breaking through at the raffinate port and into section P, respectively as the primary objective for MTBE synthesis is to maximize purity and yield of MTBE. The role of sections Q and R are, respectively, to retain MTBE and desorb H_2O. However, as the primary objective in MTBE synthesis is not necessarily to achieve high purity of H_2O at the extract port, the column length of these two sections could be small and one column may be enough for each these two sections. In general, when columns are of identical length (as required in the design of SMBR), it would be advantageous if they are of smaller lengths, but larger in numbers so that columns can be distributed in each sections optimally to achieve a desired objective.

The mathematical model used is described in detail elsewhere (Zhang et al., 2001b) and is not repeated here for brevity. However, for completeness, the mass balance equations together with the initial and boundary conditions, the kinetic equation and the adsorption isotherms are given in Appendix A. These PDE equations were discretized in space using the finite difference method to convert them into a system of coupled ODE-IVPs. The resultant stiff ODEs of the initial value kind were then solved using the DIVPAG subroutine in the IMSL library. Every switching necessitates a new system of ODEs to be solved and hence, the SMBR system operates under transient conditions. However, a periodic steady state corresponding to a given switching time was eventually achieved. Since the objective is to determine the extent up to which the SMBR could improve the conversion and purity of MTBE, the design of the SMBR configuration and that of the operating conditions were set such that the conversion of the limiting reactant, TBA (X_{TBA}), the yield (Y_{MTBE}), purity (P_{MTBE}) and selectivity (S_{MTBE}) of the desired product (MTBE) were maximized at the raffinate port. The definitions of these terms are as follows:

$$X_{\mathrm{TBA}} = \frac{(\mathrm{TBA\ fed} - \mathrm{TBA\ collected\ at\ Raffinate\ and\ Extract})}{\mathrm{TBA\ fed}} = \frac{\alpha \cdot C_{\mathrm{TBA},f} \cdot t_s - \left[\beta . \int_0^{t_s} C^{(N)}_{\mathrm{TBA},p}|_{z=L} dt + (\alpha + \beta - \gamma) \int_0^{t_s} C^{(N)}_{\mathrm{TBA},p+q+r}|_{z=L} dt\right]}{\alpha \cdot C_{\mathrm{TBA},f} \cdot t_s} \quad (6)$$

$$Y_{\mathrm{MTBE}} = \frac{\mathrm{MTBE\ collected}}{\mathrm{TBA\ fed}} = \frac{\beta \cdot \left[\int_0^{t_s} C^{(N)}_{\mathrm{MTBE},p}|_{z=L} dt\right]}{\alpha \cdot C_{\mathrm{TBA},f} \cdot t_s} \quad (7)$$

$$P_{\mathrm{MTBE}} = \frac{\mathrm{MTBE\ collected}}{[\mathrm{MTBE} + \mathrm{H_2O} + \mathrm{TBA}]\ \mathrm{collected}} = \frac{\int_0^{t_s} C^{(N)}_{\mathrm{MTBE},p}|_{z=L} dt}{\int_0^{t_s} (C^{(N)}_{\mathrm{MTBE},p} + C^{(N)}_{\mathrm{H_2O},p} + C^{(N)}_{\mathrm{TBA},p})|_{z=L} dt} \quad (8)$$

$$S_{\mathrm{MTBE}} = \frac{\mathrm{MTBE\ collected}}{[\mathrm{MTBE} + \mathrm{H_2O}]\ \mathrm{collected}} = \frac{\int_0^{t_s} C^{(N)}_{\mathrm{MTBE},p}|_{z=L} dt}{\int_0^{t_s} (C^{(N)}_{\mathrm{MTBE},p} + C^{(N)}_{\mathrm{H_2O},p})|_{z=L} dt} \quad (9)$$

It is evident that there is a complex interplay of the various associated parameters (t_s, α, β, γ, p, q, r, s) on the SMBR performance. It is not possible to simultaneously improve X_{TBA}, Y_{MTBE}, S_{MTBE} and P_{MTBE}. When one is improved, the other worsened due to the conflicting effect of some of the process parameters. This cannot be attributed to a single parameter, but is due to the complex influence of many variables. This necessitates the requirement of multi-objective optimization study on SMBR configuration and its performance.

4. Optimization of SMBR performance

Comprehensive optimization studies on SMB in general, and SMBR in particular, are very sparse in the literature. There is only a couple of optimization works reported (Dunnebier et al., 2000; Zhang, Hidajat & Ray, 2002b). A staged sequential optimization algorithm, which required an excellent initial guess of the optimal solution, was used in the study of Dunnebier et al. (2000) to maximize a generalized cost function with constraints on product quality at the extract and raffinate ports. Zhang, Hidajat, Ray and Morbidelli (2002a) used a non-traditional global optimization technique, viz., non-dominated sorting genetic algorithm (NSGA), which does not require any initial guess of the optimal solution. NSGA has been found out to be quite robust and versatile and has become quite popular for handling complex engineering problems (Bhaskar et al., 2000a). It is worth noting that NSGA can converge to the global optimum even if the problem exhibits multiple local optima and it does not require the computation of the derivatives that are necessary in the case of traditional optimization techniques. The effects of the various operating parameters on the optimal solutions are reported recently by Zhang et al. (2002a). In this article, to further our understanding of the design aspects of SMBR and, in particular, the improvements the Varicol process can provide are studied in detail.

5. Formulation of the optimization problem

SMBR and Varicol systems can be optimized for a variety of objectives, which might vary from cost functions to throughput and product specifications. However, cost function is site and time specific and may not always be meaningful compared to throughput and product specifications. Unlike separation in SMB, in which both components may be desired, the attention is usually focused only to the desired product in the design of reactive SMB. The maximization of purity, yield and selectivity of the desired product, maximization of conversion of the limiting reactant, minimization of eluent consumption, minimization of volume of solid (catalyst/adsorbent) required etc. are typical objective functions that can be considered. With the aid of a powerful optimization technique like NSGA, it is possible to consider all these objective functions simultaneously. However, it would be difficult to analyze the optimal solutions when more than three objective functions are considered, as one has to consider multi-dimensional surfaces. Hence, in this work, the optimization study is limited only to two and three objective functions.

For the synthesis of MTBE in SMBR and Varicol, the decision variables can be classified into (a) fixed cost parameters—the length (N_{col}), diameter (d_{col}) and total number of columns (N_{col}); (b) operating cost parameters—the operating temperature, T and the eluent flow rate, γ and the flow rate in section P, Q_P, which is related to the pressure drop of the system; (c) throughput parameters—the feed flow rate, α and MTBE flow rate from the raffinate port, β; and (d) process parameters—the switching time, t_s, the number of columns in each section viz., p, q, r, s and the column configuration during the sub-intervals, χ, in Varicol operation. Table 1 summarizes the different column configuration (or distribution) possible for five and six columns Varicol system within a global switching period. From the above discussion it is apparent that the length and the number of columns have significant effect on the operation of the SMBR. For a fixed total length of the system, the performance efficiency of SMBR can be improved by using smaller columns but larger in numbers.

6. Triple objective functions optimization

The reported work of Zhang et al. (2002a) suggests that the operation of SMBR is considerably influenced by a large number of operating variables and one should consider optimization of more than two objective functions simultaneously to comprehend the performance of SMBR. The goal in the present study is to solve design problems of higher complexity, viz., to compare the efficiency of SMBR and Varicol for the direct synthesis of MTBE by triple objective functions' optimization.

Table 1
Possible column configuration for five and six columns Varicol within a global switching period

χ	Column distribution[a]	χ	Column distribution
$N_{col} = 5$			
A	2/1/1/1	C	1/1/2/1
B	1/2/1/1	D	1/1/1/2
$N_{col} = 6$			
E	1/1/2/2	J	2/2/1/1
F	1/2/1/2	K	3/1/1/1
G	1/2/2/1	L	1/3/1/1
H	2/1/1/2	M	1/1/3/1
I	2/1/2/1	N	1/1/1/3

[a] Column distribution 2/1/1/1 implies that there are two columns in section P while sections Q, R and S have one column each, respectively in a particular sub-interval.

7. Case I. Optimization of an existing SMBR system

The first multiobjective optimization problem solved is for an existing set-up and is described mathematically as

$$\text{Max } J_1 = P_{MTBE}[t_s,\ \beta,\ \gamma,\ p,\ q,\ r] \quad (10a)$$

$$\text{Max } J_2 = Y_{MTBE}[t_s,\ \beta,\ \gamma,\ p,\ q,\ r] \quad (10b)$$

$$\text{Min } J_3 = g[t_s,\ \beta,\ \gamma,\ p,\ q,\ r] \quad (10c)$$

$$\text{Subject to } X_{TBA} \geq 85.24\%[\equiv X_{eqm}] \quad (10d)$$

$$N_{col} = 6-8, \quad L_{col} = 0.15 \text{ m}, \quad d_{col} = 9.4 \times 10^{-3} \text{ m}, \quad T = 328 \text{ K} \quad (10e)$$

$$\alpha = 0.1, \quad Q_p = 1.667 \times 10^{-8} \text{ m}^3/\text{s}, \quad C_{TBA,in} = 1.5 \text{ kmol/m}^3 \quad (10f)$$

$$\text{Model Eqs. described in Appendix} \quad (10g)$$

The choice of the three objective functions in Eqs. (10a), (10b) and (10c) enables the simultaneous maximization of yield and purity of the desired product (MTBE) utilizing minimum solvent. These three objective functions were chosen, as the primary goal of MTBE synthesis in SMBR are to maximize yield and purity (or selectivity) of MTBE while at the same time minimizing the operating cost. Either P_{MTBE} or S_{MTBE} can be selected as one of the objective functions' since maximization of P_{MTBE} simultaneously maximizes S_{MTBE}. This is particularly true when desired conversion of TBA is high with low TBA feed concentration. Although the direct synthesis of MTBE is not severely equilibrium limited (X_{TBA} at 328 K = 85.24% in a fixed bed reactor), we have incorporated an inequality constraint Eq. (10d) to achieve even a higher value of X_{TBA}.

Six decision variables were used in this optimization study. These were switching time (t_s), number of columns in section P, Q and R, the amount of raffinate product withdrawn (β) and the eluent consumption (γ). Since we are considering an existing set-up, N_{col}, L_{col} and d_{col} were kept fixed, but sensitivity of N_{col} on the Pareto shift was studied. The flow rate in section P (Q_P) and temperature (T) in the columns were also kept fixed in order to be able to compare the optimum results at fixed operating cost. Of the two throughput parameters (α and β), we have selected β in order to determine optimum raffinate flow rate (β) for a fixed feed rate (α). Hence, these choices would usually be available for an existing set-up. The bounds of the decision variables along with the values for the other parameters are given in Table 2. The optimization problem was solved using an adaptation of genetic algorithm—the non-dominated sorting genetic algorithm (NSGA). Details of NSGA are available elsewhere (Bhaskar et al., 2000a; Deb, 2001).

Fig. 3(a, b) show the Pareto optimal solutions and compares the performance of the SMBR system for different N_{col} values. It was found out that there was no

Table 2
Description of the optimization problems solved

Case	System	Objective function	Constraint	Decision variable	Fixed parameter
I	SMBR			$240 \le t_s \le 600$ s	$\alpha = 0.1$, $Q_P = 1.667 \times 10^{-8}$ m^3/s
		Max P_{MTBE}	$X_{TBA} \ge 85.24\%$	$0.1 \le \beta \le 0.9$	$L_{col} = 0.15$, $d_{col} = 9.4 \times 10^{-3}$ m
		Min γ		$1.0 \le \gamma \le 3.0$	$N_{col} = 6$–8, $T = 328$ K
		Max Y_{MTBE}		$1 \le p, q, r \le 4$	$C_{TBA,in} = 1.5$ kmol/m^3
II	SMBR			$240 \le t_s \le 1200$ s	
		Max P_{MTBE}	$X_{TBA} \ge 85.24\%$	$0.1 \le \beta \le 0.9$	$\alpha = 0.1$, $Q_P = 1.667 \times 10^{-8}$ m^3/s
		Min γ	$P_{MTBE} \ge 90\%$	$1.0 \le \gamma \le 3.0$	$N_{col} = 5$ or 6, $q = 1$, $r = 1$
		Min V_{solid}		$1 \le p, s \le 3$	$d_{col} = 9.4 \times 10^{-3}$ m, $T = 328$ K
				$0.1 \le L_{col} \le 0.3$ m	$C_{TBA,in} = 1.5$ kmol/m^3
III				$240 \le t_s \le 600$ s	$\alpha = 0.1$, $Q_P = 1.667 \times 10^{-8}$ m^3/s
	SMBR	Max P_{MTBE}	$X_{TBA} \ge 85.24\%$	$0.1 \le \beta \le 0.9$	$L_{col} = 0.15$, $d_{col} = 9.4 \times 10^{-3}$ m
	Varicol	Min γ		$1.0 \le \gamma \le 3.0$	$N_{col} = 5$ or 6, $T = 328$ K
		Max Y_{MTBE}		? (see Table 1)	$C_{TBA,in} = 1.5$ kmol/m^3
IV			$P_{MTBE} \ge 97\%$	$240 \le t_s \le 1800$ s	$\alpha = 0.1$, $Q_P = 1.667 \times 10^{-8}$ m^3/s
	SMBR	Min γ	$Y_{MTBE} \ge 50\%$	$1.0 \le \gamma \le 3.0$	$d_{col} = 9.4 \times 10^{-3}$ m, $T = 328$ K
	Varicol	Min L_{col}	$X_{TBA} \ge 85.24\%$	$0.1 \le L_{col} \le 0.3$ m	$\beta = 0.3$, $N_{col} = 5$ or 6
				? (see Table 1)	$C_{TBA,in} = 1.5$ kmol/m^3

significant improvement in the purity and yield of MTBE when the column number was increased beyond six, eventhough the conversion improved considerably. The purity of MTBE obtained was as high as 99% while the yield obtained was as high as 90%, though both these values were not at the maximum at the same time. The yield of MTBE showed a sharp decline at very high P_{MTBE} values. The raffinate flow rate (β), which is directly related to Y_{MTBE}, also showed a similar trend, thereby explicating that higher yield required greater raffinate flows. The optimal switching time obtained was around 440 s. The optimal column distribution in each section of the SMBR unit for a given N_{col} is given in Table 3. The optimal column distribution in section Q and R was always found to be equal to one for $N_{col} = 6$, 7 or 8. It follows that the number of columns in sections P and S had a greater influence on the extent of reaction and separation.

8. Effect of feed flow rate on the five-column SMBR performance

Effect of feed flow rate (α), was studied as it is a key factor to evaluate the system's productivity. To determine the shift in the Pareto optimal solution α was increased to 0.25 and decreased to 0.055 from the reference value of 0.1. The triple objective optimization problem (case I) was solved for $N_{col} = 5$. The Pareto optimal solutions are shown in Fig. 4. As expected, Pareto shifts upward when α has a lower value. The performance of the SMBR deteriorates as α increases to 0.1 and on increasing α further to 0.25, the purity and the yield of MTBE decreases, as shown in Fig. 4(a). This is due to the incomplete cleaning of the columns in section R due to high throughputs, which results in the contamination of the raffinate stream thereby reducing the P_{MTBE} and Y_{MTBE}. This is also evident from Fig. 4(b), as it could be observed that for increasing α values, the system requires high values of γ to obtain high P_{MTBE}. The higher conversion of TBA at lower α values as illustrated in Fig. 4(e), also supports the above inference. A similar trend was observed for the raffinate flow rate (β) to achieve high Y_{MTBE}, i.e. for the same β, the SMBR unit operating with a lower α value deliver higher yields of MTBE as against the one with a higher α value. This could be seen in Fig. 4(c). While the SMBR unit operating at lower α values of 0.055 and 0.1 needed an optimal switching period of around 10–11 min, that for $\alpha = 0.25$ required an optimal t_s of 12 min. These results explicate clearly the effect of the feed flow rate on the SMBR's performance.

9. Case II. Optimization of SMBR systems at the design stage

Optimization at the *design stage* provides far more freedom than when one is constrained to optimize the performance of an *existing* system. At the design stage, several additional decision (or design) variables become available for optimization. The mathematical formulation of a meaningful optimization problem at the design stage considered is

$$\text{Max } J_1 = P_{MTBE}[t_s,\ \beta,\ \gamma,\ p,\ s,\ L_{col}] \quad (11a)$$

$$\text{Min } J_2 = \gamma[t_s,\ \beta,\ \gamma,\ p,\ s,\ L_{col}] \quad (11b)$$

$$\text{Min } J_3 = V_{solid}[t_s,\ \beta,\ \gamma,\ p,\ s,\ L_{col}] \quad (11c)$$

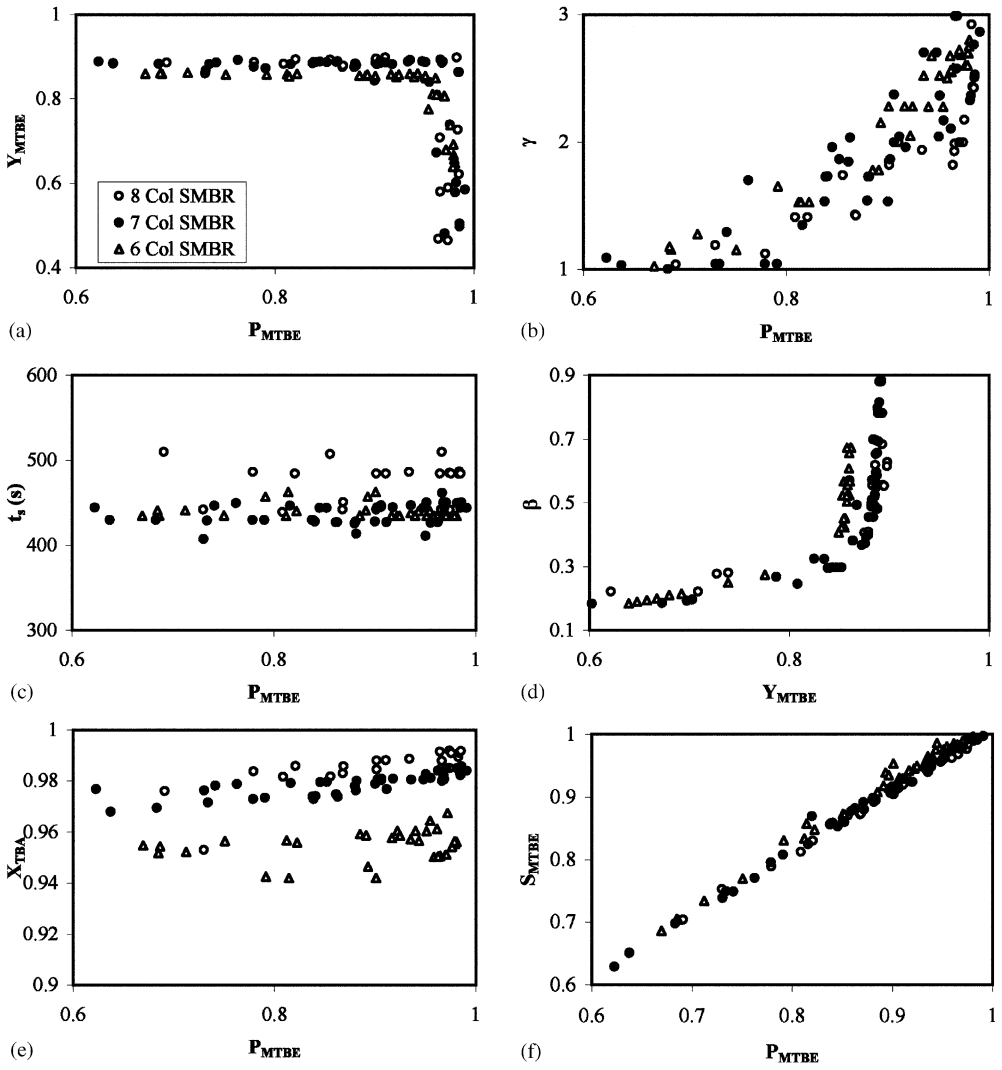

Fig. 3. Pareto optimal solutions and the corresponding decision variables for Case I optimization.

Table 3
Optimal column configuration for case I optimization study

N_{col}	Section	Optimum column configuration (χ)
6	P/Q/R/S	2/1/1/2
7	P/Q/R/S	3/1/1/2 or 2/1/1/3
8	P/Q/R/S	4/1/1/2

$$\text{Subject to } X_{TBA} \geq 85.24\%[\equiv X_{eqm}] \quad (11d)$$

$$P_{MTBE} \geq 90\% \quad (11e)$$

$$N_{col} = 5 \text{ or } 6, \quad d_{col} = 9.4 \times 10^{-3} \text{ m}, \quad T = 328 \text{ K} \quad (11f)$$

$$\alpha = 0.1, \quad Q_p = 1.667 \times 10^{-8} \text{ m}^3/\text{s}, \quad C_{TBA,in} = 1.5 \text{ kmol/m}^3 \quad (11g)$$

$$\text{Model Eqs. described in Appendix} \quad (11h)$$

The above optimization problem maximizes purity of the desired product while minimizing fixed (minimizing the total amount of adsorbent and catalyst) and operating (minimizing eluent) cost. Since the packing (adsorbent/catalyst) materials are expensive, it would be wise to determine the optimal length of each column. In this case, we have allowed N_{col} to vary between five and six as it was found in case 1 optimization that improvement in P_{MTBE} and γ is not significant when N_{col} was increased beyond 6. In addition, we have fixed q and r at 1 based on optimal solution obtained in case 1. It was found that the optimal length for the six-column SMBR is ≈ 0.15 m while that of a five-column SMBR is ≈ 0.20 m (see Fig. 5). The optimal column configuration (χ) for the five and six columns SMBR were 2/1/1/1 and 2/1/1/2, respectively.

10. Case III. Optimization of Varicol systems and its performance compared to a SMBR

Varicol process is based on non-simultaneous and unequal shift of the inlet/outlet ports. For a fixed

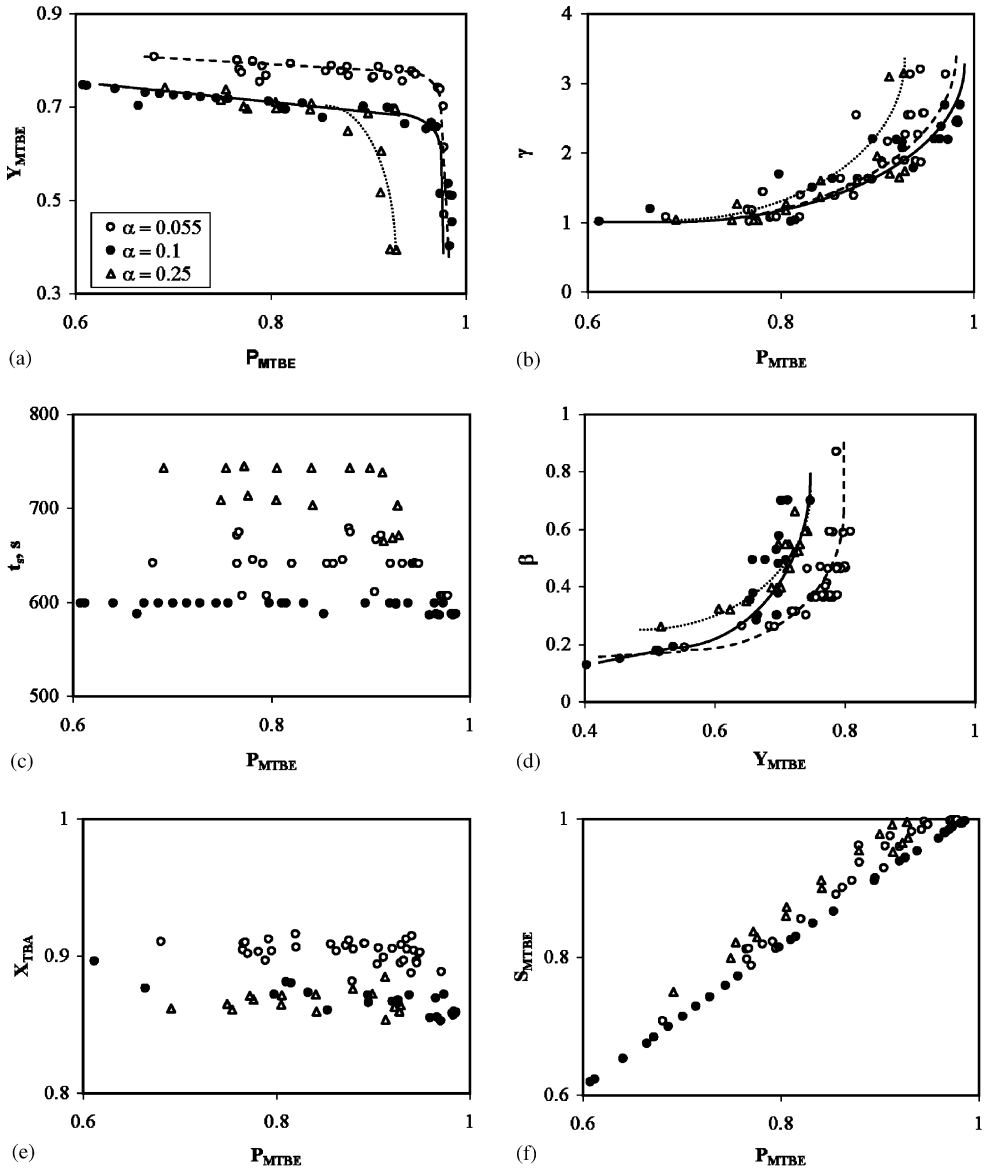

Fig. 4. Sensitivity of feed flow rat, α, on the Pareto set for the optimization of five-column SMBR.

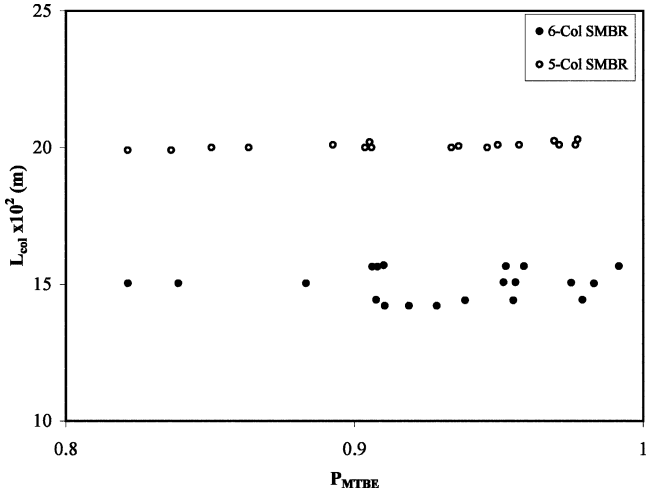

Fig. 5. Optimal column length of the SMBR for a given N_{col} (Case II).

number of total columns, for example, when $N_{col} = 5$, there exist four possible column configurations (see Table 1). In a SMBR system, there is only one column configuration, which is fixed with time is employed. However, in a Varicol process there are, in principle, infinite possible column configurations. In order to somehow restrict this variety, we consider here only four-subinterval Varicol processes assuming that in each subinterval, the unit can take any one of the configurations possible for the SMBR unit. For example, for a SMBR process, $\chi = \mathrm{B}$ indicates the column configuration 1/2/1/1. Whereas, for a four-subinterval Varicol process, $\chi = \mathrm{B–A–D–C}$ indicates that the sequence of column configurations B–A–D–C was used within the four-subinterval global switching period. In terms of time average column lengths, this corresponds to the configuration 1.25/1.25/1.25/1.25.

The optimization problem, discussed in Case I, was run for a five-column four-subinterval Varicol and its performance is compared with that of a five- and six-column SMBR. The L_{col} was chosen as 0.2 m, which was observed to be the optimal length for $N_{col} = 5$ (see Fig. 5). The mathematical formulation is described in Table 2. A detailed comparison of the optimal solutions obtained for the different SMBR and Varicol systems are illustrated in Fig. 6. The figure reveals that the performance of a five-column Varicol is far superior compared to a five-column SMBR and its performance is almost as good as that of a six-column SMBR. For the same value of P_{MTBE}, five-column Varicol results in a higher Y_{MTBE} as against the five-column SMBR. The six-column SMBR performs slightly better than the five-column Varicol, but only at the cost of an adsorbent/catalyst. The performance of the five-column Varicol system is even more startling when we look at the

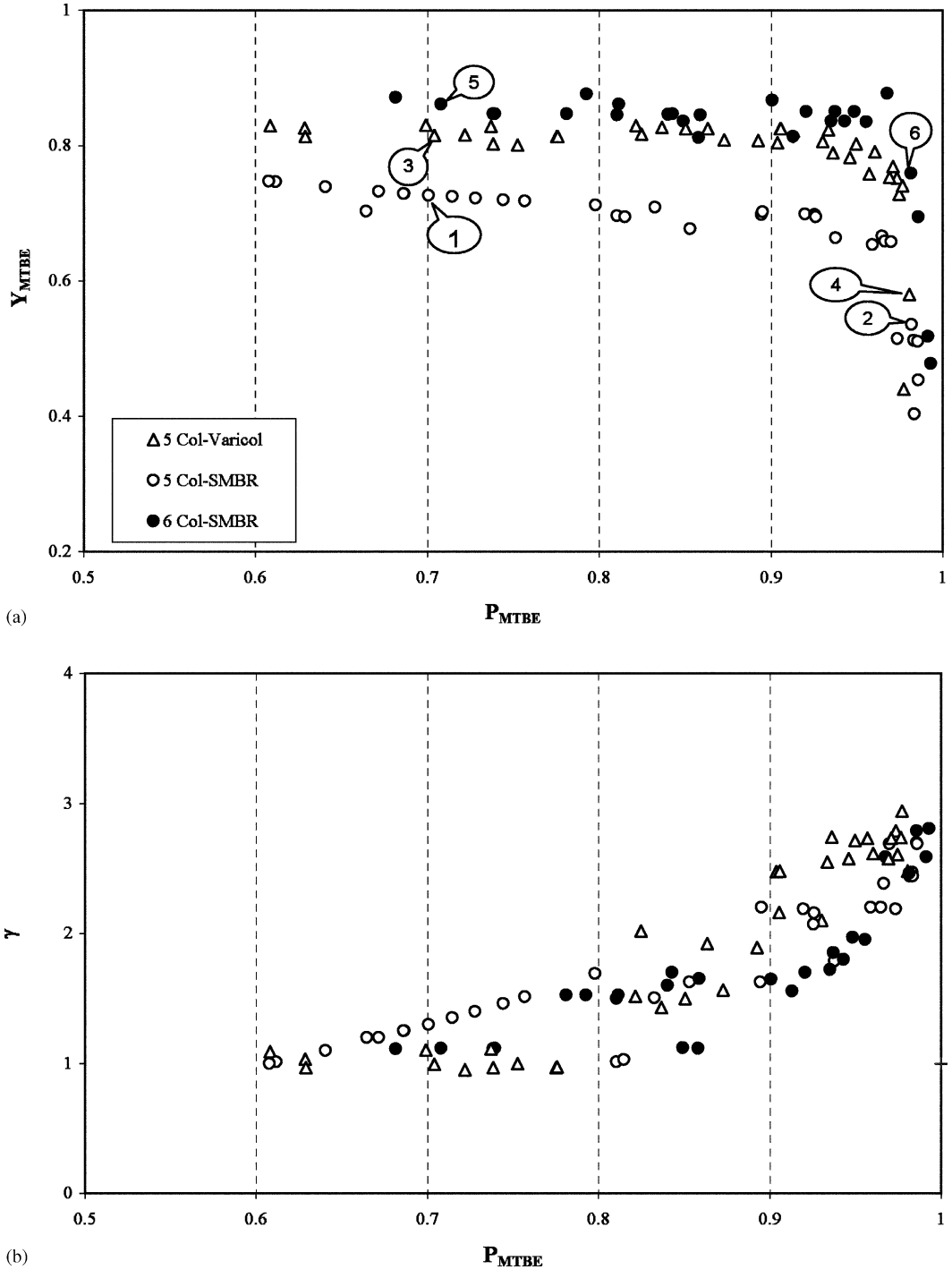

Fig. 6. Pareto sets for triple-objective functions optimization (Case III).

Table 4
Comparison of objective function and decision variable values for few chromosomes in the Pareto sets shown in Fig. 6(a)

Point in Fig. 6(a)	System	P_{MTBE} (%)	Y_{MTBE} (%)	γ (–)	t_s (s)	β (–)	χ (–)
1	5-SMBR	70.07	72.64	1.300	599	0.701	A
2	5-SMBR	98.18	53.58	2.439	588	0.192	A
3	5-Varicol	70.40	81.51	0.996	591	0.493	D–A–A–A
4	5-Varicol	98.05	58.00	2.440	553	0.178	D–A–A–A
5	6-SMBR	70.81	86.08	1.114	581	0.595	H
6	6-SMBR	98.16	75.88	2.462	555	0.295	H

objective function and the decision variable values for some selected points from Fig. 6(a) in Table 4. For example, when point three (Fig. 6(a) for 5-Varicol) is compared with point 1 (Fig. 6(a) for 5-SMBR), five-column Varicol results in higher yield using less eluent for almost the same purity of MTBE (see Table 4). When point three (5-Varicol) is compared with point five (6-SMBR), higher yield is possible in six-column SMBR, but only when eluent flow rate is increased (see Table 4). For a given raffinate flow rate, β, the five-column Varicol produces better yields of MTBE compared to five-column SMBR and almost the same as that of the six-column SMBR, as shown in Fig. 7(b). All the three systems require an optimal switching time of 9–10 min (Fig. 7a) and were able to promote the reaction beyond the equilibrium conversion of 85.24%, as depicted in Fig. 7(c). The optimal column configurations (χ) are A (2/1/1/1) for five-column SMBR, H (2/1/1/2) for six-column SMBR and D–A–A–A for five-column Varicol system.

The concentration profiles of points 1, 2, 5 and 6 (shown in Fig. 6a) are shown in Fig. 8 while the concentration profiles of points three and four are shown in Figs. 9 and 10, respectively. The additional column in the section S for the six-column SMBR increases the residence time of TBA in this section, consequently resulting in higher X_{TBA}, which in turns improves the P_{MTBE}, Y_{MTBE} and S_{MTBE} when compared

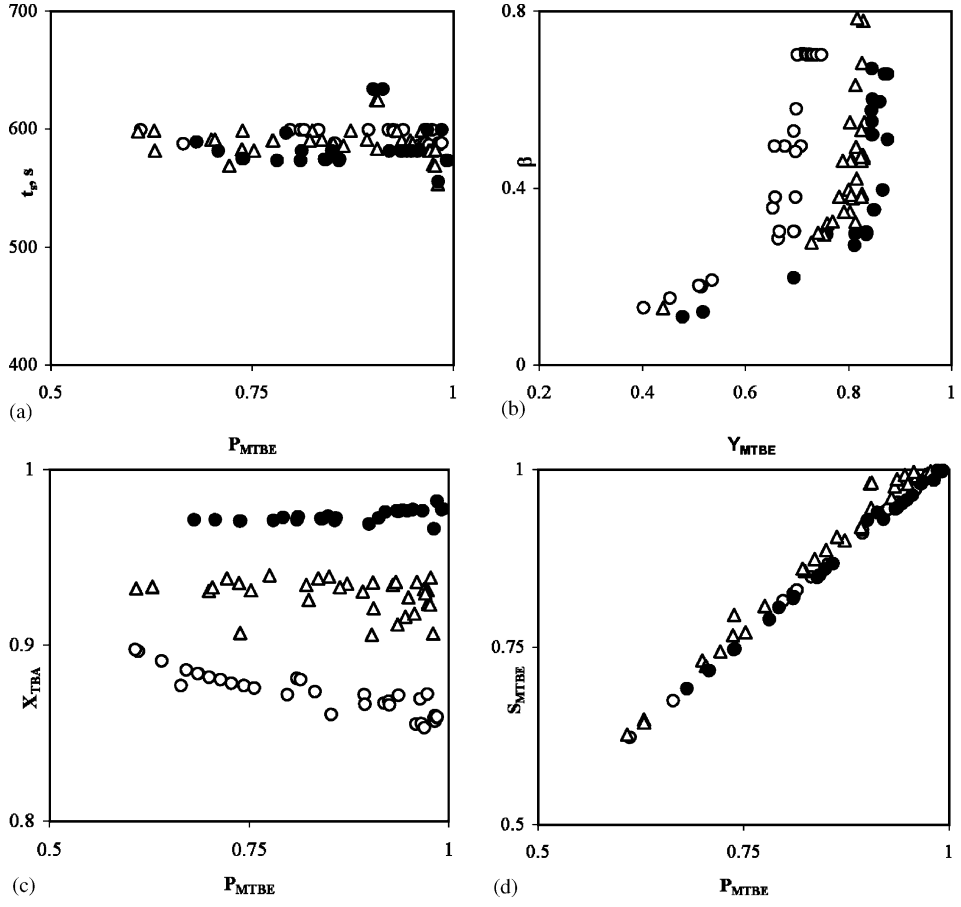

Fig. 7. Values of decision variables (t_s, β) and X_{TBA} and S_{MTBE} against P_{MTBE} corresponding to the Pareto sets in Fig. 6 (Case III).

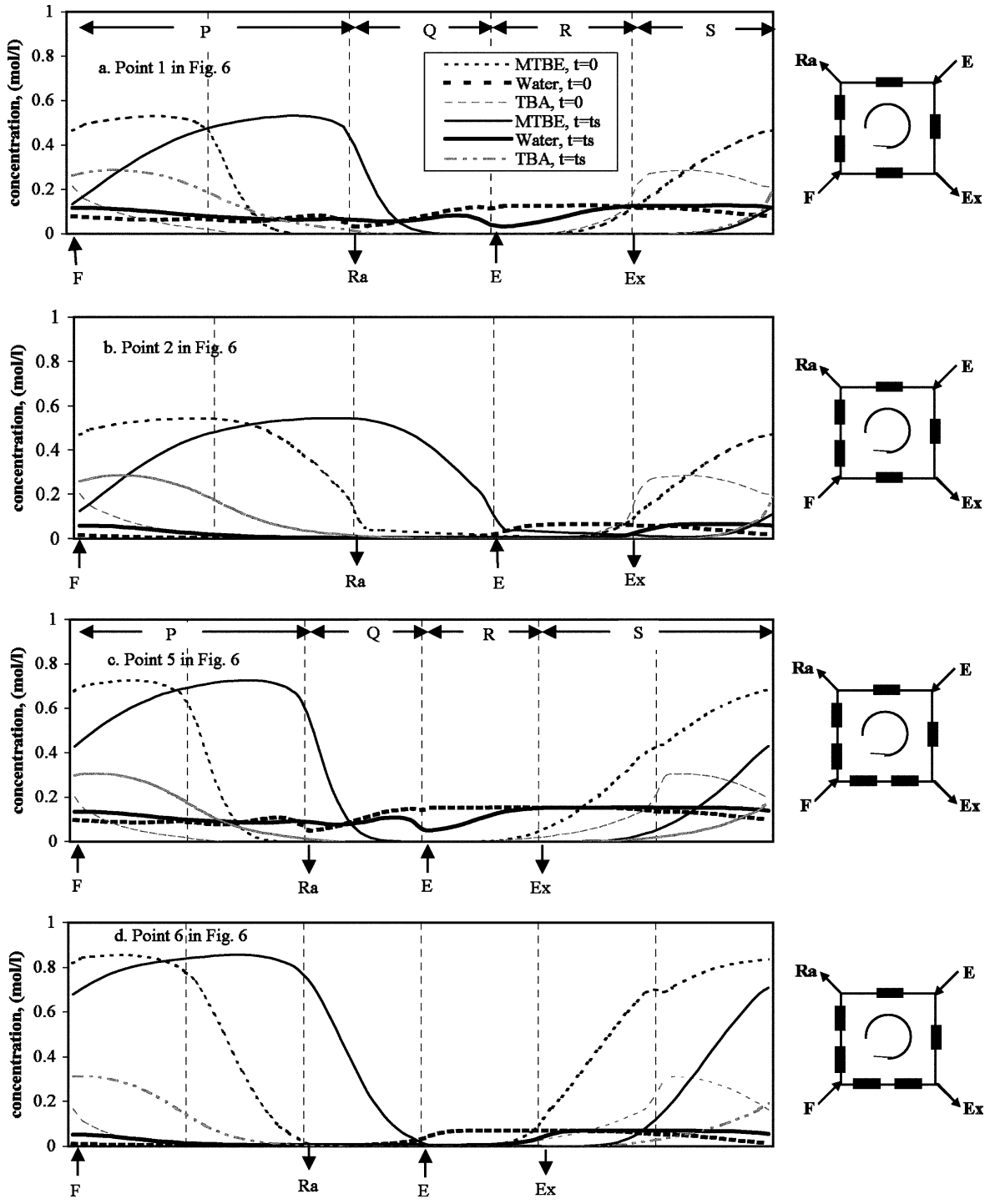

Fig. 8. Concentration profiles of MTBE–H_2O–TBA during the 100th switching period for five- and six-column SMBR systems (Case III).

to the five-column SMBR. This is evident when we compare the concentration profiles of TBA between the two points two and six shown in Fig. 8. For the five-column Varicol system, the additional column is placed either in section S or P within the global switching period, due to the influence of these two sections on the reaction progression of TBA and on the separation of MTBE and H_2O. In the first subinterval, the optimal column configuration is D (with two columns in section S) not only helps to reduce the axial dispersion from the feed port, but also aids in increasing the residence time of TBA in the section S and thereby favors high X_{TBA} and Y_{MTBE}. In the subsequent three subintervals, the optimal column configuration is A (with two columns in section P), which prevents H_2O from polluting the MTBE stream and also improves the conversion of

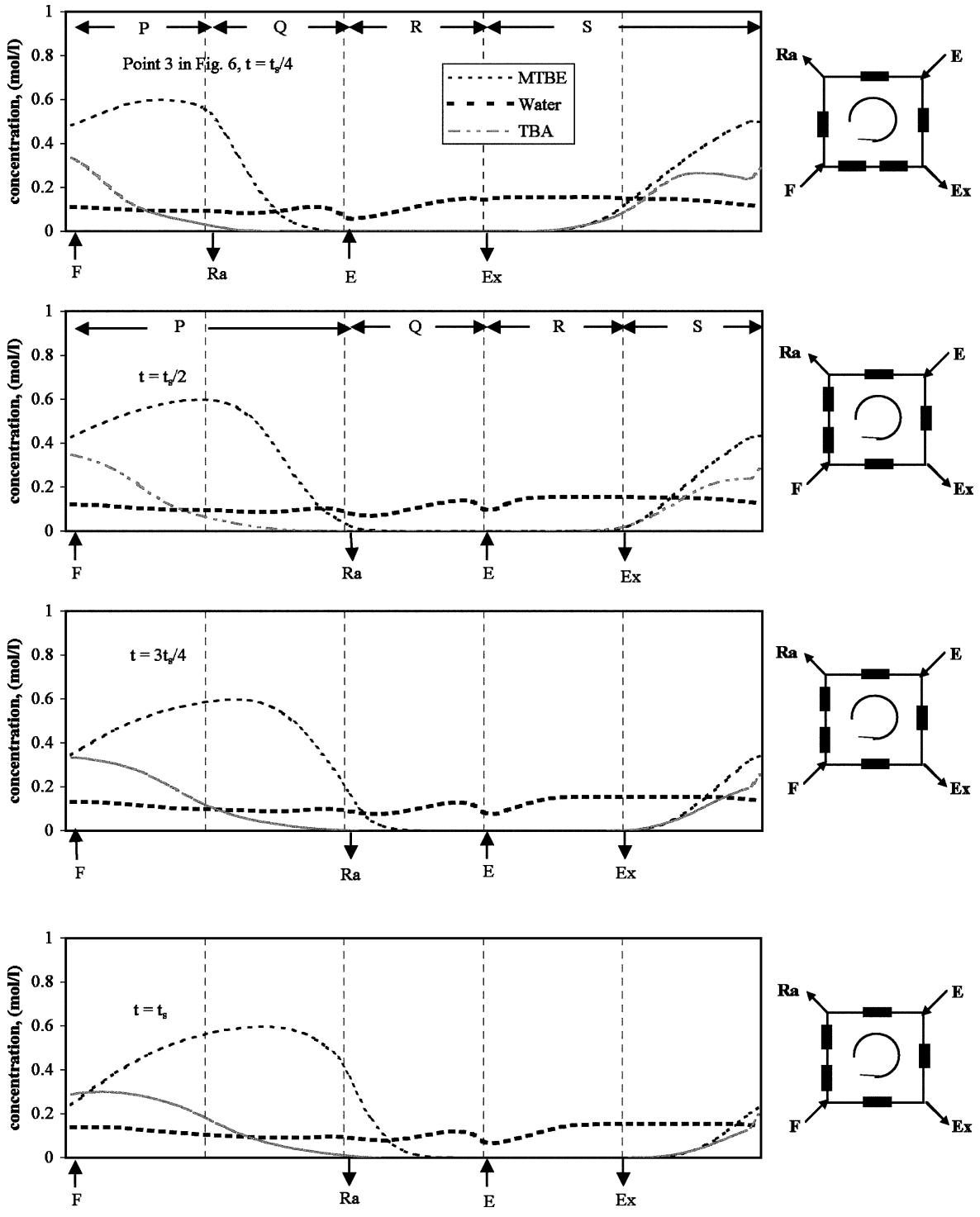

Fig. 9. Concentration profiles of MTBE-H2O-TBA at the end of the 100th switching period for a five-column Varicol system corresponding to point three in Fig. 6 (Case III).

TBA by increasing its residence time in the section P. The improvement in the performance of the five-column Varicol over the equivalent SMBR system could be elucidated by comparing the concentration profiles of the points two and four, depicted in Fig. 8(b) and Fig. 10, respectively. Because of high eluent flow rates (the value is almost the same for both the points), the section R aids in desorbing H_2O thereby enabling for a high P_{MTBE}. Also, the Varicol system improves the progression of forward reaction particularly in section S (high values of X_{TBA}) by reducing the amount of unconverted TBA contaminating the raffinate stream and this, in turn, results in high Y_{MTBE}.

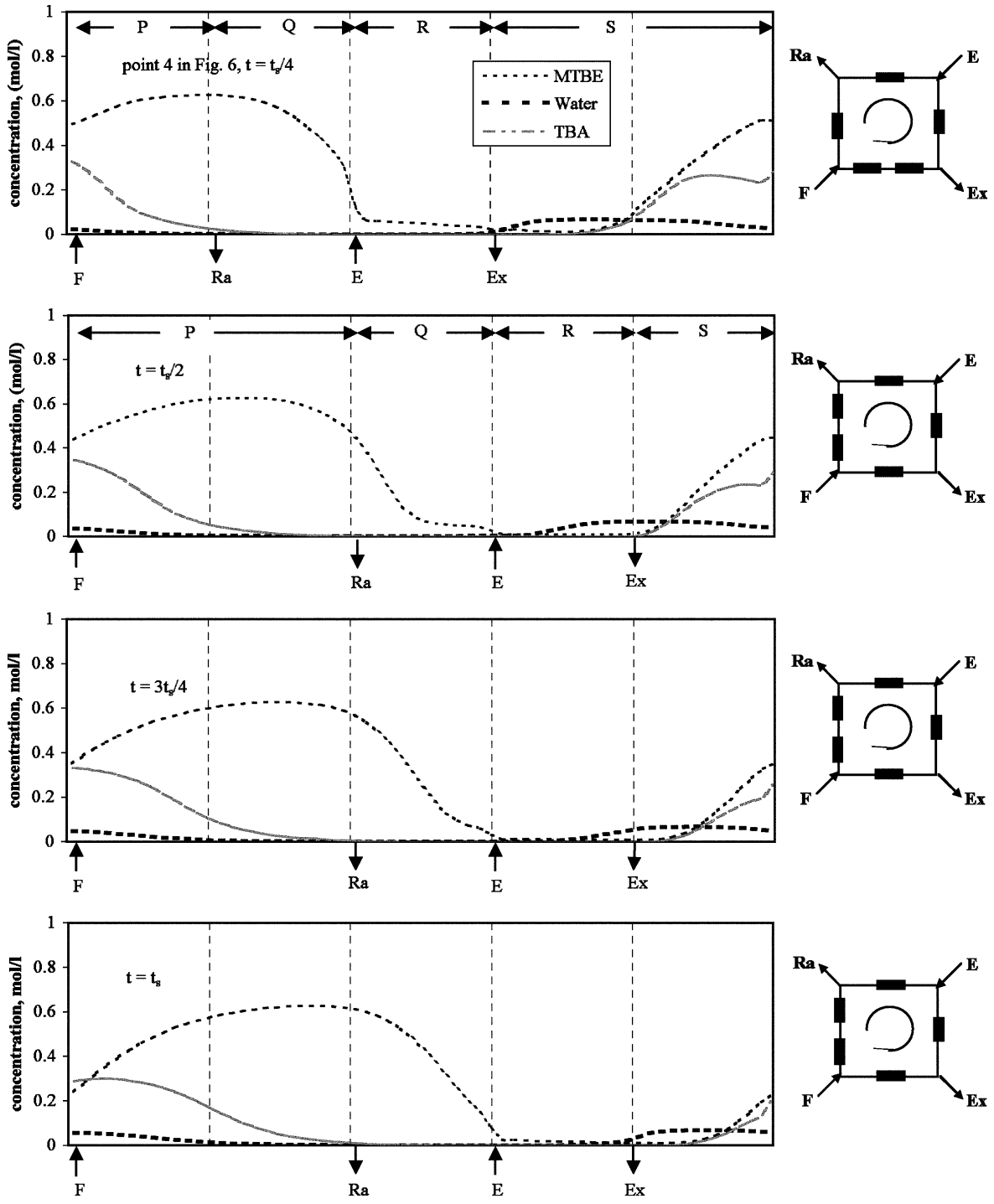

Fig. 10. Concentration profiles of MTBE-H2O-TBA at the end of the 100th switching period for a five-column Varicol system corresponding to point four in Fig. 6 (Case III).

11. Case IV. Minimization of fixed and operating cost for SMBR and Varicol systems

Having studied the performance characteristics of the five and six column SMBR and five-column Varicol system, we performed a two objective function optimization in which we minimized simultaneously the length of each column (fixed cost) and eluent requirement (operating cost) for a specified desired purity and yield of MTBE and conversion of TBA. Such a problem would enable us to evaluate the SMBR's capacity to meet a desired task. The optimization problem solved is described in Table 2.

The Pareto optimal solutions obtained are shown in Fig. 11(a). It is evident from the figure that six-column SMBR requires smaller reactor length (least amount of

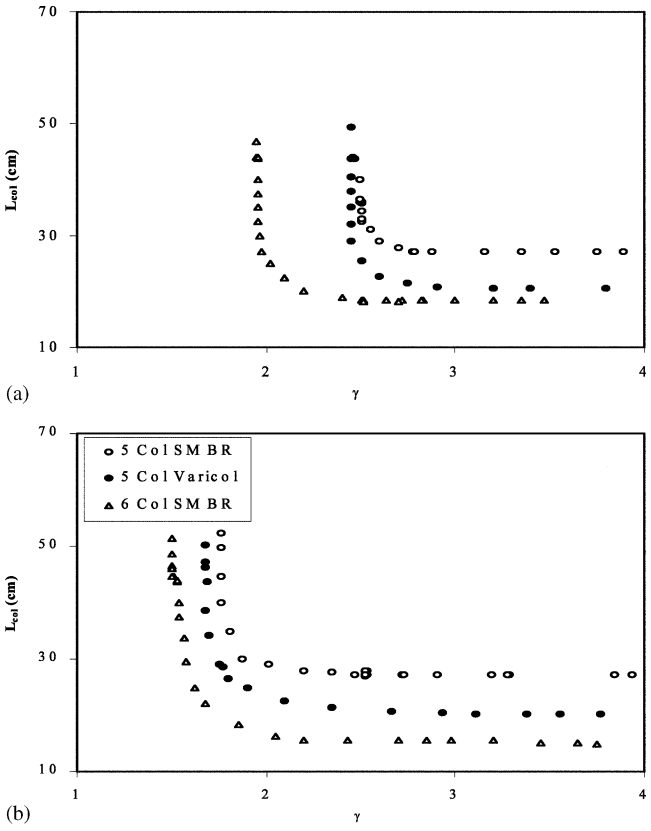

Fig. 11. Pareto-optimal sets for the simultaneous minimization of column length and eluent consumption in five-columns SMBR/Varicol and six-columns SMBR. (a) $P_{MTBE} \geq 97\%$, (b) $P_{MTBE} \geq 95\%$.

adsorbent and catalyst) and eluent for the desired task of obtaining $>97\%$ purity while at the same time having yield $>50\%$ and conversion greater than the equilibrium conversion of 85.24%. The five-column Varicol requires $\approx 24\%$ less catalyst/adsorbent performing the same task at similar eluent flow rates, when compared to an equivalent five-column SMBR system. The optimal column configuration for the five-column Varicol was found to be either D–D–A–A or D–A–A–A in the four sub-intervals within a global switching period, while for the five or six column SMBR, the optimal configuration are A or H (see Table 1), respectively. For the same eluent consumption, the six-column SMBR require less solid as against the five-column SMBR and Varicol. This is simply because increase in the number of columns in SMB set-up leads to greater flexibility and towards the true moving bed behavior and hence the improvement in performance. For the same column length, the eluent consumption for the six-column SMBR was $\approx 20\%$ less compared to the five-column SMBR or Varicol due to the additional column in section S. The X_{TBA}, Y_{MTBE} and P_{MTBE} achieved were as high as 95–98, 60–80 and $\approx 98\%$, respectively, for all the three different reactive SMB systems.

The Pareto optimal set in Fig. 11(a) shows an asymptotic behavior elucidating that if one of these objectives (L_{col} or γ) is chosen at the lowest possible optimal value, the other one had to be selected at considerably high value to achieve the specified reaction and separation task. This behavior due to the extreme restrictions imposed through constraints prompted us to relax the constraint on P_{MTBE} to 95% (reduced from 97%) and the optimization problem was once again solved for the optimal values and the Pareto optimal solution is shown in Fig. 11(b). The optimal column configuration during the four different sub-intervals for the five-column Varicol was found to be D–D–A–A. The figure reveals that for a given eluent consumption, the six-column SMBR require 33% less solid volume compared to the five-column SMBR and $\approx 8.4\%$ less solid than that of the five-column Varicol system. Likewise, for a given solid volume, six-column SMBR necessitates ≈ 14 and 10% less eluent to perform the same task compared to the five-column SMBR and Varicol, respectively. It also follows that five-column Varicol showed marked improvement over the equivalent five-column SMBR, requiring nearly 27% less adsorbent at a given eluent flow rate to perform the same specified task of achieving $>95\%$ in purity 50% in yield of MTBE, while at the same time achieving more than equilibrium conversion of the limiting reactant, TBA. Moreover, X_{TBA}, Y_{MTBE} and P_{MTBE} achieved were more than 95, 70 and 96%, respectively, for five and six-column reactive SMB and five-column reactive Varicol systems.

12. Conclusions

Simulated moving bed (SMB) systems have received greater attention these days, particularly in the specialty chemicals sector and separation of chiral drugs. Researchers worldwide have been fascinated by the enormous advantages that SMB offers for the production of pure compounds that are difficult or nearly impossible to separate otherwise into pure forms. Recent developments have improved the SMB technology, thereby utilizing its potentials for in situ reaction and separation. Research is still at the early stages for the comprehensive design and scale-up of such novel reactor-separators. In this work, we have performed multi-objective optimization studies (two and three objective functions) for the design of reactive SMB system for direct synthesis of MTBE from TBA and methanol. Recently, a modification of SMB system has been reported, named as Varicol process, which is based on non-synchronous switching of inlet and outlet ports instead of synchronous switching applied in SMB systems. In this paper, multi-objective optimization study was also performed on Varicol systems and its performance is compared with that of SMBR. This is

the first ever attempt to apply multiobjective optimization to the complicated Varicol system.

Triple objective function optimization was performed using a robust, state-of-the-art AI-based technique, Non-dominated sorting genetic algorithm (NSGA). The goal was to obtain the optimal operating conditions that provide both for the improvement of an existing as well as for the design of new SMB systems. Pareto optimal curves, which provide a set of optimal solutions that are equally good, were obtained. These curves explicate the complexity involved in the operation of SMB systems and helps in better understanding the effect of each of the numerous parameters that influence the performance of the SMBR and reactive Varicol systems. It was observed that a five-column Varicol performs better than an equivalent five-column SMBR and its performance is nearly equal to that of a six-column SMBR in terms of purity and yield of MTBE and minimal eluent consumption. This is an important inference as it enables to reduce fixed and operating costs while at the same time helps to achieve high purity and yield of the desired product and conversion of the limiting reactant. It is to be emphasized that there is no end to the variety of multi-objective optimization problems, which could be formulated and studied, and we have presented here, only a few simple examples, to illustrate the concepts, techniques and interpretation of results. It is also to be noted that this is the first time that not only the separating potential of Varicol has been extended to reaction systems, but also optimized for multiple objectives.

Appendix A: Complete set of equations for the mathematical model of SMBR used in this work and described in detail in Zhang et al. (2001b)

Material balance:

$$\frac{\partial C_{ij}^{(N)}}{\partial t}+\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q_{ij}^{(N)}}{\partial t}+\frac{u_\phi}{\varepsilon}\frac{\partial C_{ij}^{(N)}}{\partial z}-\left(\frac{1-\varepsilon}{\varepsilon}\right)v_i R_j^{(N)}=D_i\frac{\partial^2 C_{ij}^{(N)}}{\partial z^2} \tag{A1}$$

for the component i in the jth column during the Nth switching period, where $i=$ TBA, MTBE or H_2O, u_ϕ designate superficial flow rate in section ϕ (where $\phi = P, Q, R, S$) and the reaction rate expression and adsorption isotherms are given by

$$R_j^{(N)}=k_f\left[q_{\mathrm{TBA},j}^{n(N)}-\frac{q_{\mathrm{MTBE},j}^{(N)}\cdot q_{\mathrm{H_2O},j}^{n(N)}}{K_e}\right] \tag{A2}$$

$$q_{ij}^{(N)}=K_i C_{ij}^{(N)} \tag{A3}$$

The initial and boundary conditions are given by

Initial condition

$$\text{When } N=0,\quad C_{ij}^{(0)}=C_{ij}^{\mathrm{Initial}}=0 \tag{A4}$$

When $N\geq 1$,

$$\begin{aligned} C_{ij}^{(N)}&=C_{i,j+1}^{(N-1)} && \text{for } j=1\sim(N_{\mathrm{col}}-1)\\ C_{ij}^{(N)}&=C_{i,j+1}^{(N-1)} && \text{for } j=1-(N_{\mathrm{col}}-1)\\ C_{ij}^{(N)}&=_{i1}^{(N-1)} && \text{for } j=N_{\mathrm{col}}\end{aligned} \tag{A5}$$

Boundary conditions:

Feed point (point A)

$$C_{i1}^{(N)}|_{z=0}=(1-\alpha)C_{i,N_{\mathrm{col}}}^{(N)}|_{z=L}+\alpha C_{i,\mathrm{f}} \tag{A6}$$

Raffinate withdrawal point (point B)

$$C_{i,p+1}^{(N)}|_{z=0}=C_{i,p}^{(N)}|_{z=L} \tag{A7}$$

Eluent inlet point (point C)

$$C_{i,p+q+1}^{(N)}|_{z=0}=\left[\frac{1-\beta}{1-\beta+\gamma}\right]C_{i,p+q}^{(N)}|_{z=L} \tag{A8}$$

Extract withdrawal point (point D)

$$C_{i,p+q+r+1}^{(N)}|_{z=0}=C_{i,p+q+r}^{(N)}|_{z=L} \tag{A9}$$

The mass balance equation (Eq. (A1)), initial (Eq. (A4) and Eq. (A5)) and boundary conditions (Eqs. (A6), (A7), (A8) and (A9)), kinetic equation (Eq. (A2)) and adsorption isotherm (Eq. (A3)) completely defines the SMBR system. After each switching, column numbering was redefined according to Eq. (A10) so that feed is always introduced into the first column.

Before switching	*After switching*
Column 1	Column N_{col}
Column j	Column $j-1$ $\quad j=2,3,\ldots,N_{\mathrm{col}}$

(A10)

Adsorption constant, K_i, kinetic parameters, k_f, K_e and n, and dispersion coefficients, D_i (Zhang et al. (2001a)).

T/K	K_{MTBE} (−)	K_{H2O} (−)	K_{TBA}	k_f (mol$^{(1-n)}\cdot$l$^{(n-1)}$/min)	K_e (mol/l)	n (−)	10^6 D_{MTBE} (m^2/s)	10^6 D_{H2O} (m^2/s)
318	0.375	2.846	0.460	0.025	24.682	1.018	1.948	7.092
323	0.330	2.800	0.440	0.060	20.943	1.092	2.333	7.708
328	0.300	2.750	0.460	0.112	18.202	1.120	2.350	8.167

References

Bhaskar, V., Gupta, S. K., & Ray, A. K. (2000a). Applications of multiobjective optimization in chemical engineering. *Reviews in Chemical Engineering 16*, 1.

Bhaskar, V., Gupta, S. K., & Ray, A. K. (2000b). Multiobjective optimization of an industrial wiped film poly(ethylene terephthalate) reactor. *American Institute of Chemical Engineers Journal 46* (5), 1046.

Bhaskar, V., Gupta, S. K., & Ray, A. K. (2001). Multiobjective optimization of an industrial wiped film poly (ethylene terephthalate) reactor: some further insights. *Computers and Chemical Engineering 25*, 391.

Deb, K. (2001). *Multi-Objective Optimization Using Evolutionary Algorithms*. Chichester: Wiley.

Dunnebier, G., & Klatt, K. U. (1999). Optimal operation of simulated moving bed chromatographic processes. *Computers and Chemical Engineering 23*, S195.

Dunnebier, G., Fricke, J., & Klatt, K. U. (2000). Optimal design and operation of simulated moving bed chromatographic reactors. *Industrial and Engineering Chemistry Research 39*, 2290.

Goldberg, D. E. (1989). *Genetic Algorithms in Search, Optimization, and Machine Learning*. Reading, MA: Addision-Wesley.

Holland, J. H. (1975). *Adaptation in Natural and Artificial Systems: An Introductory Analysis with Applications to Biology, Control and Artificial Intelligence*. Ann Arbor: University of Michigan Press.

Karlsson, S., Pettersson, F., & Westerlund, T. (1999). A MILP-method for optimizing a preparative simulated moving bed chromatographic separation process. *Computers and Chemical Engineering 23*, S487.

Lode, F., Houmard, M., Migliorini, C., Mazzotti, M., & Morbidelli, M. (2001). Continuous reactive chromatography. *Chemical Engineering Science 56*, 269.

Ludemann-Hombourger, O., Nicoud, R. M., & Bailly, M. (2000). The 'VARICOL' process: a new multicolumn continuous chromatographic process. *Separation Science and Technology 35*, 1829.

Ludemann-Hombourger, O., Pigorini, G., Nicoud, R. M., Ross, D. S., & Terfloth, G. (2002). Application of the 'VARICOL' process to the separation of the isomers of the SB-553261 racemate. *Journal of Chromatography A 947*, 59.

Mazzotti, M., Storti, G., & Morbidelli, M. (1994). Robust design of countercurrent adsorption separation processes: 2. Multicomponent systems. *American Institute of Chemical Engineers Journal 40*, 1825.

Mazzotti, M., Storti, G., & Morbidelli, M. (1996a). Robust design of countercurrent adsorption separation: 3. Nonstoichiometric systems. *American Institute of Chemical Engineers Journal 42*, 2784.

Mazzotti, M., Baciocchi, R., Storti, G., & Morbidelli, M. (1996b). Vapor-phase SMB adsorptive separation of linear/nonlinear paraffins. *Industrial and Engineering Chemistry Research 35*, 2313.

Mazzotti, M., Kruglov, A., Neri, B., Gelosa, D., & Morbidelli, M. (1996c). A continuous chromatographic reactor: SMBR. *Chemical Engineering Science 51*, 1827.

Mazzotti, M., Storti, G., & Morbidelli, M. (1997a). Optimal operation of simulated moving bed units for nonlinear chromatographic separations. *Journal of Chromatography A 769*, 3.

Mazzotti, M., Storti, G., & Morbidelli, M. (1997b). Robust design of countercurrent adsorption separation processes: 4. Desorbent in the feed. *American Institute of Chemical Engineers Journal 43* (1), 64.

Mazzotti, M., Neri, B., Gelosa, D., Kruglov, A., & Morbidelli, M. (1997c). Kinetics of liquid-phase esterification catalyzed by acidic resins. *Industrial and Engineering Chemistry Research 36*, 3.

Oh, P. P., Ray, A. K., & Rangaiah, G. P. (2001). Triple objective optimization of industrial hydrogen plants. *Journal of Chemical Engineering of Japan 34*, 1341.

Rajesh, J. K., Gupta, S. K., Rangaiah, G. P., & Ray, A. K. (2000). Multiobjective optimization of steam reformer performance using genetic algorithm. *Industrial and Engineering Chemistry Research 39* (3), 706.

Rajesh, J. K., Gupta, S. K., Rangaiah, G. P., & Ray, A. K. (2001). Multi-objective optimization of industrial hydrogen plants. *Chemical Engineering Science 56* (3), 999.

Ravi, G., Gupta, S. K., & Ray, M. B. (2000). Multiobjective optimization of cyclone separators. *Industrial and Engineering Chemistry Research 39* (11), 4272.

Ravi, G., Gupta, S. K., Viswanathan, S., & Ray, M. B. (2002). Optimization of Venturi scrubbers using genetic algorithm. *Industrial and Engineering Chemistry Research 41*, 2988–3002.

Ray, A. K., & Carr, R. W. (1995a). Experimental study of a laboratory scale simulated countercurrent moving bed chromatographic reactor. *Chemical Engineering Science 50*, 2195.

Ray, A. K., & Carr, R. W. (1995b). Numerical simulation of a simulated countercurrent moving bed chromatographic reactor. *Chemical Engineering Science 50*, 3033.

Ray, A. K., Tonkovich, A., Carr, R. W., & Aris, R. (1990). The simulated countercurrent moving bed chromatographic reactor: a novel reactor-separator. *Chemical Engineering Science 45*, 2431.

Ray, A. K., Carr, R. W., & Aris, R. (1994). The simulated countercurrent moving-bed chromatographic reactor—a novel reactor separator. *Chemical Engineering Science 49*, 469.

Ruthven, D. M., & Ching, C. B. (1989). Counter-current and simulated counter-current adsorption separation processes. *Chemical Engineering Science 44*, 1011.

Storti, G., Masi, M., Paludetto, R., Morbidelli, M., & Carra, S. (1988). Adsorption separation processes: countercurrent and simulated countercurrent operations. *Computers and Chemical Engineering 12*, 475.

Storti, G., Mazzotti, M., Morbidelli, M., & Carra, S. (1993). Robust design of binary countercurrent adsorption separation processes. *American Institute of Chemical Engineers Journal 39*, 471.

Storti, G., Baciocchi, R., Mazzotti, M., & Morbidelli, M. (1995). Design of optimal operating conditions of simulated moving bed adsorptive separation units. *Industrial and Engineering Chemistry Research 34*, 288.

Wu, D. J., Ma, Z., & Wang, N. H. L. (1999). Optimization of throughput and desorbent consumption in simulated moving-bed chromatograph for Paclitaxel purification. *Journal of Chromatography A 855*, 71.

Yuen, C. C., Aatmeeyata, Gupta, S. K., & Ray, A. K. (2000). Multiobjective optimization of membrane separation modules using genetic algorithm. *Journal of Membrane Science 176* (2), 177.

Zhang, Z., Hidajat, K., & Ray, A. K. (2001a). Determination of adsorption and kinetic parameters for methyl tert-butyl ether synthesis from tert-butyl alcohol and methanol. *Journal of Catalysis 200*, 209.

Zhang, Z., Hidajat, K., & Ray, A. K. (2001b). Application of simulated countercurrent moving bed chromatographic reactor for MTBE synthesis. *Industrial and Engineering Chemistry Research 40*, 5305.

Zhang, Z., Hidajat, K., Ray, A. K., & Morbidelli, M. (2002a). Multiobjective optimization of simulated moving bed system and Varicol process for chiral separation. *American Institute of Chemical Engineers Journal 48* (12), 2800.

Zhang, Z., Hidajat, K., & Ray, A. K. (2002b). Multiobjective optimization of simulated countercurrent moving bed chromatographic reactor (SMBR) for MTBE synthesis. *Industrial and Engineering Chemistry Research 41*, 3213.

Zhou, F., Gupta, S. K., & Ray, A. K. (2000). Multiobjective optimization of the continuous casting process for poly(methyl methacrylate) using adapted genetic algorithm. *Journal of Applied Polymer Science 78*, 1439.