Conceptual design of reactive distillation for selectivity improvement in multiple reactant systems

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A B S T R A C T

Reactive distillation (RD) can be effectively used to improve selectivity by manipulating the composition profiles of reactants and products inside the reactive zone of a RD column. One can obtain close to quantitative yields if the azeotropes, if any, do not limit the separation. As against the single reactant systems (e.g. condensation, dimerization), more design options are available in the case of multiple reactants (e.g. esterification, cross aldol condensation) and we propose design guidelines for such systems in this work. The parametric studies for the representative hypothetical reaction systems, involving both reversible and irreversible reactions, form the basis of these guidelines. The cases associated with non-ideality through formation of azeotropes are also discussed. The analysis is further extended to real processes involving reactions such as cross aldol condensation, esterification and transesterification.

Keywords: Chemical reactors; Conceptual design; Design; Reactive distillation; Selectivity; Azeotrope

1. Introduction

Integration of reaction with separation in a single unit offers distinct advantages over conventional sequential approach of reaction followed by separation. Reactive distillation (RD) is a combination of chemical reaction with distillation in a single unit. Various advantages of RD include increased conversion in case of equilibrium reactions, improved selectivity, heat integration, avoidance of azeotropes, etc. Various commercial applications of RD have been reviewed elsewhere (e.g. see Sharma and Mahajani, 2002; Hiwale et al., 2004). While, most of the studies in the past target equilibrium controlled reactions, selectivity engineering is also emerging as a promising application of RD. Aldol condensation of acetone to diacetone alcohol (Podrebarac et al., 1998; Thotia et al., 2007) and dimerization of isobutene (Talwalkar et al., 2007) are the processes in which use of RD to improve selectivity towards the intermediate product has been demonstrated successfully through experimental studies and theoretical analysis.

Reactive distillation can be effectively used to improve the selectivity of a reaction especially when an intermediate product is desired in the series or combination of series and parallel reactions. Removing one of the products from the reaction mixture or maintaining low concentration of one of the reactants can lead to reduction in the rates of side reactions. In our earlier work on single reactant system (Agarwal et al., 2008a,b), we showed that RD can be used as a promising tool to improve the selectivity of the desired product in a single reactant system. For a non-azeotropic reacting system with series (A → B → C) and series-parallel (2A → B; A + B → C) reactions, Damköhler number can be manipulated such that maximum possible selectivity close to 100% can be achieved at any conversion. As a general rule, for a non-azeotropic system, it has been recommended that if the reactant (A) is more volatile than the desired product then the reactive section of RD should be placed in the rectifying zone of the reactive distillation column and if it is less volatile than the desired product the reactive section should be placed in the stripping section. The Damköhler number per stage should be as small as possible and the column should be operated at sufficiently high reboiler duty. Essentially the choice of parameters is governed by distillation requirements, and any decision that favors distillative separation of the intermediate product (B) from the reactive zone is recommended for the improvement in the performance. The separation of the intermediate product (B) from the reactive zone helps maintain low concentration of this component on the catalyst thereby suppressing its further side reaction(s). In all these configurations the column is
operated either in total reflux or in total re-boil mode depending on the volatility of the reactant. The proposed reactive distillation column thus has a single feed stream and single product stream (Fig. 1a and b). In particular cases however, when the reactant is intermediate boiling (i.e. a saddle node in the residue curve map), a multi-product hybrid configuration that is capable of maintaining the saddle node composition in the middle reactive zone is recommended (Fig. 1c and d). The theory developed for a single reactant system by Agarwal et al. (2008a,b) has been validated through the experimental studies by Thotla et al. (2007) and Talwalkar et al. (2007).

The reactions with multiple reactants (i.e. two reactants) such as hydration, alkylation, trans-esterification, esterification, cross aldol condensation, etherification etc. form a class of systems which often suffer from selectivity issues due to side reactions. Table 1 lists various potentially important industrial reactions which fall in this category. A properly designed RD column can improve the performance significantly. The conventional reactors, e.g. batch reactors or PFR with side injection, fail short in producing desired products with 100% yield because the product formed is always present in the reaction mixture, which is prone to either limit the conversion level due to reversibility or decrease the selectivity of the desired product under the operating conditions of interest. Though theoretically it is also possible to achieve 100% selectivity in these conventional reactors, the design and operation requirements at times, are unfavorable, e.g. extremely low feed rate of one of the reactants in the semi-batch reactor leading to very long reaction times. On the other hand, with continuous removal of the desired product from the reaction mixture through reactive distillation, one can reach close to 100% yield of the desired product and enhance the performance. In the reactions involving two reactants, the presence of the second reactant has a considerable influence on the selectivity in these conventional reactors, the design and operation requirements at times, are unfavorable, e.g. extremely low feed rate of one of the reactants in the semi-batch reactor leading to very long reaction times. On the other hand, with continuous removal of the desired product from the reaction mixture through reactive distillation, one can reach close to 100% yield of the desired product and enhance the performance. In the reactions involving two reactants, the presence of the second reactant has a considerable influence on the design as its presence also opens up new design options. A better understanding of such cases and a systematic conceptual design method is not evident in the existing literature on this subject.

In the present work, we consider three different illustrative examples of multiple reactant systems involving side reactions and propose design guidelines so as to obtain a RD configuration capable of offering close to 100% yield. The analysis is performed for a semi-batch reactive distillation (SBRD) configuration and later the corresponding continuous versions are suggested. The methodology developed for hypothetical reactions has been further extended to selected commercially important processes from Table 1, such as cross aldol condensation of acetaldehyde with methyl ethyl ketone, esterification of glutaric acid, acetalization of glyoxal and transesterification of cyclohexyl acetate with n-butanol.

The first illustrative example considers the multiple reactant systems when simultaneous product removal from SBRD is not necessary whereas in the second example simultaneous product removal of the product enhances the performance significantly. In the last example we consider azetotropic systems and demonstrate the effect of azeotrope on the attainable yields.

### 2. Example 1: SBRD without simultaneous product removal

A reacting system involving following irreversible liquid phase reactions is considered as the first illustrative example:

- **desired reaction:** \( A + B \rightarrow C \)
- **undesired reaction:** \( B + C \rightarrow D \)
The reactions are assumed to be elementary and the kinetics is given by the following equations:

\[ r_1 = k_1 x_A x_B \]  
\[ r_2 = k_2 x_C x_B \]  

The ratio of rate constants \( k_1/k_2 = 1 \).

The conversion is defined as moles of reactant \( A \) consumed per moles of reactant \( A \) fed and selectivity as moles of reactant \( B \) used in forming desired product to the total moles of \( B \) reacted. Yield is defined as the multiplication of conversion and selectivity. The main objective is to increase the selectivity (or yield) of the intermediate product \( C \). The selectivity parameter is defined as the ratio of rates of the desired reaction to that of the undesired reaction and in the present case it is given by \( k_1 x_A / k_2 x_C \). Conventionally, a semi-batch reactor with addition of \( B \) in the pool of \( A \) as shown in Fig. 2a is the recommended option to obtain high selectivity (Levenspiel, 2002). A continuous version of this configuration is PFR with side injection of the feed. The idea is to maintain as high concentration of \( A \) in the reactor as possible. In RD, a relatively higher selectivity can be obtained by maintaining high concentration of \( A \) and low concentration of \( B \) on the reactive stages. For instance, if \( A \) is the most volatile component

Fig. 1 – (a) Reactive rectification \((A > B, C)\), (b) reactive stripping \((A < B, C)\), (c) Hybrid configuration-1 \((B > A > C)\) and (d) hybrid configuration-2 \((B < A < C)\) (Agarwal et al., 2008a).

Fig. 2 – (a) Semi-batch reactor, (b) hybrid semi-batch reactive rectification (HSRR) and (c) hybrid semi-batch reactive stripping (HSRS).
<table>
<thead>
<tr>
<th>Reactions</th>
<th>Desired product(s)</th>
<th>Reaction conditions/volatility order</th>
<th>References</th>
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<tr>
<td><strong>Esterifications</strong></td>
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<tr>
<td>(1) Adipic acid (A) + methanol (B) → monomethyl adipate (C) + water (D)</td>
<td>Dimethyl adipate</td>
<td>Ion exchange resin, 60–120 °C/B &gt; A &gt; C &gt; D</td>
<td>Hung et al. (2007)</td>
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<td></td>
<td>Monomethyl adipate (C) + methanol (B) → dimethyl adipate + water (D)</td>
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<td>(2) Oxalic acid (A) + n-butanol (B) → monobutyl oxalate (C) + water (D)</td>
<td>Dibutyl oxalate</td>
<td>PTSA on granular active carbon/D &gt; B &gt; C &gt; E &gt; A</td>
<td>Sheng-wen and Ji-zhong (2005)</td>
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<td></td>
<td>Monobutyl oxalate (C) + n-butanol (B) → dibutyl oxalate (E) + water (D)</td>
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<td>(3) Glyoxalic acid (A) + n-butanol (B) → butyl glyoxalate (C) + water (D)</td>
<td>Dibutoxy butyl glyoxalate</td>
<td>Ion exchange resin, 100–120 °C/D &gt; B &gt; C &gt; E &gt; A</td>
<td>Mahajani (2000)</td>
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<td>Butyl glyoxalate (C)(C) + n-butanol (B) → dibutoxy butyl glyoxalate (E) + water (D)</td>
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<td>(4) Glyoxalic acid (A) + isoamyl alcohol (B) → isoamyl glyoxalate (C) + water (D)</td>
<td>Diisooxy isooamyl glyoxalate</td>
<td>Ion exchange resin, 100–120 °C/D &gt; B &gt; C &gt; E &gt; A</td>
<td>Mahajani (2000)</td>
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<td>Isoamyl glyoxalate (C) + isoamyl alcohol (B) → diisooxy isooamyl glyoxalate (E) + water (D)</td>
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<tr>
<td>(5) Glutaric acid (A) + methanol (B) → monomethyl glutarate (C) + water (D)</td>
<td>Dimethyl glutarate</td>
<td>Ion exchange resin, 90–180 °C/B &gt; A &gt; C &gt; D</td>
<td>Hung et al. (2007)</td>
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<td>Monomethyl glutarate (C) + methanol (B) → dimethyl glutarate (E) + water (D)</td>
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<td>(6) Maleic acid (A) + ethanol (B) → monoethyl maleate (C) + water (D)</td>
<td>Diethyl maleate</td>
<td>Ion exchange resin, 50–80 °C/B &gt; A &gt; C &gt; D</td>
<td>Yadav and Thathagar (2002)</td>
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<td>Monoethyl maleate (C) + ethanol (B) → diethyl maleate (E) + water (D)</td>
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<td>(7) Ethylene glycol (A) + acetic acid (B) → ethylene glycol diacetae (C) + water (D)</td>
<td>Ethylene glycol diacetae</td>
<td>Ion exchange resin, 25–40 °C/B &gt; A &gt; C &gt; D</td>
<td>Schmid et al. (2008)</td>
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<td>Ethylene glycol monoacetate (C) + Acetic acid (B) → Ethylene glycol diacetae (F) + Water (D)</td>
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<td>(8) Glycerol (A) + acetic acid (B) → monoacetine (C) + water (D)</td>
<td>Triacetine</td>
<td>Ion exchange resin, 60–100 °C/B &gt; D &gt; A &gt; C &gt; E &gt; F</td>
<td>Gelosa et al. (2003)</td>
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<td>Monoacetine (C) + acetic acid (B) → diacetine (E) + water (D)</td>
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<tr>
<td>Diacetine (E) + acetic acid (B) → triacetine (F) + water (D)</td>
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<td>(9) Citric acid (A) + ethanol (B) → monoethyl citrate (C) + water (D)</td>
<td>Triethyl citrate</td>
<td>Ion exchange resin, 78–120 °C/B &gt; D &gt; A &gt; C &gt; E &gt; F</td>
<td>Kolah et al. (2007)</td>
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<td>Monoethyl citrate (C) + ethanol (B) → diethyl citrate (E) + water (D)</td>
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<tr>
<td>Diethyl citrate (E) + ethanol (B) → triethyl citrate (F) + water (D)</td>
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<td><strong>Acetalizations</strong></td>
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<tr>
<td>(1) Glyoxal (A) + alcohol* (B) → monoacetal (C) + water (D)</td>
<td>Diacetal</td>
<td>Resin, 60–85 °C/B &gt; D &gt; C &gt; E &gt; A (for methanol) D &gt; B &gt; C &gt; E &gt; A (for other alcohols)</td>
<td>Mahajani and Sharma (1997)</td>
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<tr>
<td>Monoacetal (C) + alcohol* (B) → diacetal (E) + water (D)</td>
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<td><strong>Trans-vinylation</strong></td>
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<td>(1) Vinyl acetate (A) + stearic acid (B) → vinyl stearate (C) + acetic acid (D)</td>
<td>Vinyl stearate</td>
<td>Mercuric acetate and sulphuric acid, 70–95 °C/D &gt; A &gt; C &gt; E &gt; B</td>
<td>Geelen and Wijffels (1965)</td>
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<tr>
<td>Vinyl acetate (A) + acetic acid (D) → ethylidenic acid (E)</td>
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<td><strong>Etherifications</strong></td>
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<tr>
<td>(1) Ethylene glycol (EG) (A) + isobutylene (B) = mono-tert-butyl ether of EG (C)</td>
<td>Diethers of ethylene glycol</td>
<td>Ion exchange resin, 50–90 °C/B &gt; E &gt; F &gt; C &gt; D &gt; A</td>
<td>Klepacova et al. (2007)</td>
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<td>Mono-tert-butyl ether of EG (C) + isobutylene (B) = Di-tert-butyl ether of EG (D)</td>
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### Table 1 (Continued)

<table>
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</table>
| Isobutylene (B) + isobutylene (B) → diisobutylene (F)  
Diisobutylene (E) + isobutylene (B) → triisobutylene (F) |  |  |  |
| (2) Propylene glycol (PG) (A) + isobutylene  
(B) → mono-tert-butyl ether of PG (C)  
Mono-tert-butyl ether of PG (C) + isobutylene  
(B) → di-tert-butyl ether of PG (D)  
Isobutylene (B) + isobutylene (B) → diisobutylene (F)  
Diisobutylene (E) + isobutylene (B) → triisobutylene (F) | Di ethers of propylene glycol | Ion exchange resin, 50–70 °C/B > E > F > C > D > A | Jayadeokar and Sharma (1993) |
| (3) Glycerol (A) + isobutylene (B) → mono-tert-butyl ether of glycerol (MTBG) (C)  
MTBG (C) + isobutylene (B) → di-tert-butyl ether of glycerol (DTBG) (D)  
DTBG (D) + isobutylene (B) → tri-tert-butyl ether of glycerol (TTBG) (E)  
Isobutylene (B) + isobutylene (B) → diisobutylene (F)  
Diisobutylene (E) + isobutylene (B) → triisobutylene (G) | Tri-tert-butyl ether of glycerol | Ion exchange resin, 50–90 °C/B > F > G > C > D > E > A | Klepacova et al. (2007) |
| Trans-esterifications  
(1) Dimethyl carbonate (A) + ethanol (B) → monomethyl ethyl carbonate (C) + methanol (D)  
Monomethyl ethyl carbonate (C) + ethanol (B) → diethyl carbonate (E) + methanol (D) | Diethyl carbonate | Ion exchange resin, 75 °C/D > B > A > C > E | Luo and Xiao (2001) |
| (2) Dimethyl oxalate (A) + phenol (B) → monomethyl phenyl oxalate (C) + methanol (D)  
Monomethyl phenyl oxalate (C) + phenol (B) → diphenyl oxalate (E) + methanol (D) | Mmethyl phenyl oxalate | Homogeneous organotin compounds, 120–220 °C/D > B > C > A > E | Nishihira et al. (2000) |
| (3) Cyclohexyl acetate (A) + n-butanol (B) → cyclohexanol (C) + n-butyl acetate (D)  
Cyclohexanol (C) + n-butanol (B) → butyl cyclohexyl ether (E) + water (F) | Cyclohexanol | Ion exchange resin, 120–160 °C/F > B > D > C > A > E | Chakraborti and Sharma (1992a) |
| (4) Triacetine (A) + methanol (B) → diacetine (C) + methyl acetate (D)  
Diacetine (C) + methanol (B) → monoaetine (E) + methyl acetate (D)  
Monoaetine (E) + methanol (B) → glycerol (F) + methyl acetate (D) | Glycerol | Ion exchange resin, 60 °C/B > D > F > E > C > A | Lopez et al. (2005) |
| (5) Ethylene carbonate (A) + methanol (B) → 2-hydroxy methyl carbonate (C)  
2-Hydroxy methyl carbonate (C) + methanol (B) → dimethyl carbonate (D) + ethylene glycol (E) | Dimethyl carbonate | Ion exchange resin/B > A > C > D > E | Scott et al. (2003) |
| Hydrations  
(1) Propene (A) + water (B) → isopropyl alcohol (C)  
Isopropyl alcohol (C) + propene (A) → diisopropyl ether (D) | Isopropyl alcohol | Ion exchange resin, 130 °C/A > C > B > D | Petrus et al. (1984) |
| (2) Ethylene oxide (A) + water (B) → ethylene glycol (C)  
Ethylene glycol (C) + ethylene oxide (A) → diethylene glycol (D) | Ethylene glycol | Ion exchange resin, 200–300 °C/A > B > C > D | Reed et al. (1956) |
| (3) Isobutene (A) + water (B) → tert-butyl alcohol (C)  
Isobutene (A) + isobutene (A) → diisobutylene (D)  
Isobutene (A) + tert-butyl alcohol (C) + water (B) | tert-Butyl alcohol | Ion exchange resin, 50–80 °C/A > B > C > D | Zhang et al. (2003) |
| Aminations  
(1) Methanol (A) + urea (B) → monomethyl amine (C) + water (D)  
Methanol (A) + monomethyl amine (C) → dimethyl amine (E) + water (D) | Dimethyl amine | Dibutyltin dimethoxide, Tetraphenethinyl, 145–191 °C/A > D > C > E > B | Ryu and Gelbein (2002) |
then a semi-batch RD configuration shown in Fig. 2b, called as hybrid semi-batch reactive rectification (HSRR), may be used. The reboiler is charged with A, and B is fed continuously to the column at an appropriate location. Further, by using a hybrid column configuration with reactive and non reactive stages placed at the appropriate locations one can maintain sufficiently low concentration of product (C) in the reactive zone to suppress the side reaction. Hence, the non-reactive stages serve the purpose of improving the selectivity of a desired product. Similarly if A is the least volatile component, configuration shown in Fig. 2c, called as hybrid semi-batch reactive stripping (HSRS) may be used. Hence, we introduce two new configurations for multiple reactants-single product systems, viz. hybrid semi-batch reactive rectification (HSRR) and hybrid semi-batch reactive stripping (HSRS) with continuous feed of one of the reactants that participates in both the reactions (i.e. B). Like semi-batch reactors, these configurations are also capable of offering selectivity close to 100%, if perfect separation is possible. The difference between semi-batch reactor and HSRR (or HSRS) is the removal of desired product from the reactive zone. Hence, HSRR (or HSRS) is expected to offer better yield than the conventional semi-batch reactor under otherwise similar conditions. In the following section, we present a detailed analysis of the performances of these RD units and suggest the design methodology. First we formulate general models for HSRR and HSRS. The models are then solved for a hypothetical case and the performance is analyzed through the effects of different parameters to devise a design methodology at conceptual level.

### 2.1 Hybrid semi-batch reactive rectification (HSRR) and hybrid semi-batch reactive stripping (HSRS)

Hybrid semi-batch reactive rectification (Fig. 2b) is similar to the reactive rectification unit (Fig. 1a and c) except that HSRR has non-reactive stages below the reactive zone and one of the reactants that is participating in both the reactions is continuously fed to the column at an appropriate location. The re-boiler is non-reactive and the reaction takes place only in the reactive zone placed between the condenser and the non-reactive zone. On the other hand, in hybrid semi-batch reactive stripping (HSRS), condenser is non-reactive and the reactive zone is placed between the reboiler and the non-reactive zone. The assumptions made in our earlier work (Agarwal et al., 2008a,b), while developing the reactive condenser and reactive re-boiler models apply here as well and are given below:

(a) In the reactive rectification (HSRR) model, condenser is considered as a total condenser and re-boiler as a non-reactive equilibrium stage. On the other hand, in the reactive stripping (HSRS) model, re-boiler is a total re-boiler and the condenser acts as a non-reactive equilibrium stage.

(b) The molar holdup of a stage on which reaction takes place is assumed to be negligible. This assumption enables us to conveniently calculate the conversion and selectivity based on the holdup in the reboiler alone, in the case of HSRR, and condenser alone, in the case of HSRS.

### Table 1 (Continued)

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<tr>
<th>Reactions</th>
<th>Desired product(s)</th>
<th>Reaction conditions/volatility order</th>
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</tr>
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<tbody>
<tr>
<td>(2) Ethylene oxide (A) + ammonia (B) → monoethanol amine (C) + water (D)</td>
<td>Diethanol amine</td>
<td>Absence of catalyst</td>
<td>DiGulio and McKinney (2000)</td>
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<tr>
<td>Ethylene oxide (A) + monoethanol amine (C) → diethanol amine (E) + water (D)</td>
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<tr>
<td>Ethylene oxide (A) + diethanol amine (E) → triethanol amine (F) + water (D)</td>
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<tr>
<td>Ethylene oxide (A) + water (D) → ethylene glycol (G)</td>
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<tr>
<td>Ethylene oxide (A) + ethylene glycol (G) → diethylene glycol (H)</td>
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<tr>
<td>Alkylation</td>
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<tr>
<td>(1) p-Cresol (A) + isobutene (B) = 2-tert-butyl-p-cresol (C)</td>
<td>2-tert-Butyl-p-cresol</td>
<td>Ion exchange resin, 30–45°C</td>
<td>Santacesaria et al. (1988)</td>
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<td>2,4-di-tert-butyl-p-cresol (D)</td>
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<tr>
<td>Isobutylene (B) + isobutylene (B) = diisobutylene (E)</td>
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<td>Diisobutylene (E) + isobutylene (B) = trisobutylene (F)</td>
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<tr>
<td>(2) Phenol (A) + cyclohexane (B) → cyclohexylphenyl ether (C)</td>
<td>o- and p-cyclohexylphenol</td>
<td>Ion exchange resin, 45–80°C</td>
<td>Chakrabarti and Sharma (1992b)</td>
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<tr>
<td>Phenol (A) + cyclohexane (B) → ortho/para-cyclohexylphenol (D)</td>
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<tr>
<td>Cyclohexylphenyl ether (C) → ortho/para-cyclohexylphenol (D)</td>
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<tr>
<td>ortho/para-Cyclohexylphenol (D) + cyclohexane</td>
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<tr>
<td>(3) Phenol (A) + alpha methyl styrene</td>
<td>o- and p-cumylphenol</td>
<td>Ion exchange resin, 60–100°C</td>
<td>Chaudari and Sharma (1991)</td>
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<td>(B) = ortho/para-cumylphenol (C)</td>
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<tr>
<td>2 ortho/para-Cumylphenol (C) → Dicumylphenol (D)</td>
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<td>2 Alpha methyl styrene (B) → dimethyl styrene (F)</td>
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*a Methanol/n-butanol/isopropyl alcohol/2-ethyl hexanol.*
(c) The extent of the reaction on the reactive stage is dependent on Damköhler number (Da) which is based on the catalyst weight and not on the volume or molar holdup. The reaction takes place in liquid phase and in the presence of catalyst only.

\[ Da = \frac{k_{\text{ref}} H_{\text{cat}}^2}{V} \]  
(3)

(d) The heat duty is adjusted such that the vapor flow rate with respect to time is constant for the HSRR model. This allows us to club the vapor flow rate in Da. Similarly the liquid flow rate is assumed to be constant for the HSRS model.

(e) The energy balances on both reactive and non-reactive stages are ignored for simplicity. The liquid flow rate in HSRR and vapor flow rate in HSRS, however, may change with respect to time in the case of a non-eqimolar reaction.

As against reactive rectification and stripping (Fig. 1a and b), two additional parameters, viz., the number of non-reactive stages and the feed flow rate are introduced in the present models. Following are the model equations applicable to HSRR shown in Fig. 2b.

(a) Overall and component material balances on the re-boiler (stage 1)

\[
\frac{1}{H_1} \frac{d(H_1)}{dt} = -1 + \frac{L_2 + F}{V_1} \]  
(4)

\[
\frac{d(x_{i,1})}{dt} = (x_{i,1} - y_{i,1}) + \frac{L_2 + F}{V_1} (x_{i,2} - x_{i,1}) \]

for \( i = 1, 2, \ldots, NC - 1 \)  
(5)

where \( dt = (V_1/H_1) \, dt \).

(b) Overall and component material balances on feed stage (for \( j = m \))

\[
F + L_{j+1} - L_j + V_{j-1} - V_j + \sum_{k=1}^{k=R} v_{j,k} x_k(x_j) H_{\text{cat}}^j = 0 \]  
(6)

\[
F x_F + L_{j+1} x_{i,j+1} - L_j x_{i,j} + V_{j-1} y_{i,j-1} - V_j y_{i,j} + \sum_{k=1}^{k=R} v_{j,k} x_k(x_j) H_{\text{cat}}^j = 0 \quad \text{for} \quad i = 1, 2, \ldots, NC - 1 \]  
(7)

Assuming \( V_{j-1} = V_j = V \), we get

\[
F - L_j + L_{j+1} + \sum_{k=1}^{k=R} v_{j,k} x_k(x_j) H_{\text{cat}}^j = 0 \]  
(8)

\[
F x_F + L_{j+1} x_{i,j+1} - L_j x_{i,j} + V(y_{i,j-1} - y_{i,j}) + \sum_{k=1}^{k=R} v_{j,k} x_k(x_j) H_{\text{cat}}^j = 0 \quad \text{for} \quad i = 1, 2, \ldots, NC - 1 \]  
(9)

Assuming catalyst loading on each stage to be same, we get

\[
H_{\text{cat}}^j = \frac{H_{\text{cat}}^1}{N - 1} \]

Dividing by \( V \), we get

\[
f_j - l_j + l_{j+1} + \frac{Da}{N - 1} \sum_{k=1}^{k=R} v_{j,k} x_k(x_j) = 0 \]  
(10)

\[
f x_F + l_{j+1} x_{i,j+1} - l_j x_{i,j} + y_{i,j-1} - y_{i,j} + \frac{Da}{N - 1} \sum_{k=1}^{k=R} v_{j,k} x_k(x_j) = 0 \quad \text{for} \quad i = 1, 2, \ldots, NC - 1 \]  
(11)

where \( f_j = F/V, l_j = L_j/V, l_{j+1} = (F + L_{j+1})/V \) and \( Da = k_{\text{cat}} H_{\text{cat}}^2/V \).

(c) Overall and component material balances below the feed stage (\( j = 1 \) to \( j = m - 1 \)) in non-dimensionalized form

\[
-l_j + l_{j+1} + \frac{Da}{N - 1} \sum_{k=1}^{k=R} v_{j,k} x_k(x_j) = 0 \]  
(12)

\[
l_{j+1} x_{i,j+1} - l_j x_{i,j} + y_{i,j-1} - y_{i,j} + \frac{Da}{N - 1} \sum_{k=1}^{k=R} v_{j,k} x_k(x_j) = 0 \quad \text{for} \quad i = 1, 2, \ldots, NC - 1 \]  
(13)

where \( l_j = L_j/V, l_{j+1} = L_{j+1}/V \) and \( Da = k_{\text{cat}} H_{\text{cat}}^2/V \).

All the above equations without reaction term are applicable to the stages in the non-reactive section for stages \( j = 2 \) to \( p \).

(d) Overall and component material balance on the \( m + 1 \)th stage (total condenser)

\[
1 = l_m + \frac{D}{V} \]  
(14)

\[
y_{i,m} = l_m x_{i,m} + \frac{D x_{i,D}}{V_m} \]  
(15)

As condenser is the total condenser, we can write

\[
y_{i,m} = x_{i,m} = x_{i,D} \]  
(16)

Along with these equations, the VLE equations are also valid for each stage except the total condenser. Similarly the corresponding model equations can be written for hybrid semi-batch reactive stripping (HSRS).

2.1.1. Case 1: volatility order \( C, D < A, B \)

In this case, both the products, \( C \) and \( D \), are less volatile than the reactants \( A \) and \( B \). Hence, we choose hybrid semi-batch reactive rectification unit operated under total reflux condition. The choice of changing the reactant in continuous mode or batch mode to HSR is governed by the selectivity parameter (S). For the liquid phase reacting system of interest \( A + B \rightarrow C; B + C \rightarrow D \), selectivity parameter is equal to \( k_{1A}/k_{2C} \). From the selectivity parameter, selectivity of \( C \) for a given ratio of \( k_1/k_2 \) is proportional to the ratio \( x_A/x_C \) in the reactive zone. To improve selectivity of \( C \), either we need to maintain high concentration of \( A \) or less concentration of \( C \) in the reactive zone. Hence, reboiler is initially charged with \( A \) and continuous feed of \( B \) is given to semi-batch reactive rectification column. The controlled addition of \( B \) would ensure large concentration of \( A \) in the reactive zone. If we have sufficiently tall rectifier, the concentration of \( C \) in the reactive zone would be minimal due to its less volatility and in situ separation.
Fig. 3 – Comparison of performance of SRR with SBR under similar conditions of \( F_B = 5 \text{ mol/h}; \) total catalyst loading = 50 g ms; total batch time = 10 h.

The relative volatility of A, B and C with respect to D used for simulations for this case are 4.4, 2.5 and 1.6, respectively.

2.1.2. Effect of various parameters on yield vs conversion

From the model equations, we have six independent parameters which influence the selectivity of the desired product, i.e. feed location and flow rate, location and number of non-reactive stages, \( D_a \) per stage and vapor flow rate (i.e. reboiler duty). Fig. 3 shows the conversion vs yield plot for a base case that corresponds to semi-batch reactive rectification with continuous feed of B under total reflux condition (i.e. distillate rate = 0), and with one reactive stage and without a non-reactive section. The plot is obtained by solving both HSRR and conventional semi-batch reactor (SBR) models from time = 0 to the time till 100% conversion is obtained in HSRR.

It can be seen that due to product (C) removal from the reactive zone HSRR outperforms SBR over the entire conversion range. Another important observation is that the conversion obtained in HSRR in a given time is also higher than that in SBR. For example HSRR conversion in 15 h is 100% against 92% in SBR in the same period. This is because removal of C results in an increase in the concentration of A in the reactive zone. On the other hand, accumulation of C in SBR results in dilution thereby slowing down the reaction as time proceeds.

2.1.2.1. Feed location.

For the given elementary reaction kinetics the choice of feed location primarily depends on the volatility of B with respect to A. Fig. 4 shows the results when B is less volatile than A. The selectivity of C increases if the feed location moves from reboiler to the condenser under otherwise similar conditions. Since B is less volatile than A, it should be fed at the top of the reactive zone. Similarly if B is more volatile then it should be fed below the reactive zone. Also, as expected, it was observed that the quantity of B required for 100% conversion of A reduces as B feed location shifts from reboiler to condenser.

2.1.2.2. Effect of feed flow rate.

Fig. 5 shows the effect of feed flow rate of B on selectivity parameter, calculated on the reactive stage, for different conversion levels. Under given operating conditions, by increasing the feed flow rate of B, concentration of B on the reactive stage increases with negligible change in the concentration of C leading to formation of undesired product (D). Conditions thus favor the second reaction thereby resulting in a decrease in selectivity of C as shown in Fig. 6. Hence, to obtain a better selectivity under similar operating conditions, lower feed rate of B is recommended.

These results are similar to that recommended in the case of conventional semi-batch reactor (SBR). However, as explained later due to simultaneous removal of the desired product from the reactive zone, the feed flow rate of B in absolute terms,
Fig. 7 – Effect of location of non-reactive stage on reactive stage on selectivity parameter for $F_B = 5$ mol/h, $Da$ per stage = 0.4.

required to attain same yield is much less than that in SBR. In other words, for the same feed flow rate of $B$, the yield obtained in a given time period is higher in SBRD than that in SBR.

2.1.2.3. Effect of the location of non-reactive zone. The non-reactive zone may be introduced in the column to effectively separate the desired product $C$ and keep it away from the reactive zone. It should be noted that $C$ in the present case is less volatile than $A$ and $B$. Fig. 7 shows the effect of location of non-reactive stage(s) on selectivity parameter at different conversion levels. By placing non-reactive zone above the reactive zone, concentration of $C$ for a given conversion increases with negligible change in the concentration of $B$ on the reactive stage leading to formation of the undesired product $D$, and hence a decrease in selectivity of $C$. By placing non-reactive stages below the reactive stage, amount of $C$ present on the reactive stage decreases to give higher selectivity. Hence, placing non-reactive stages below the reactive zone for HSRR serves the purpose of improving the selectivity of a desired intermediate product ($C$). Similarly in the case of HSRS by placing non-reactive stages above the reactive zone one can improve the selectivity of a desired intermediate product ($C$).

2.1.2.4. Effect of number of non-reactive stages. As shown in Fig. 8, as the number of non-reactive stages increases, selectiv-

Fig. 8 – Effect of non-reactive stages below the reactive stages on selectivity of $C$ for number of reactive stages = 1; $F_B = 5$ mol/h; $Da$ per stage = 0.4.

ity of the desired product increases up to a particular point for the given feed flow rate and $Da$ per stage. Thereafter with a further increase in the number of non-reactive stages, there is no effect on the selectivity of the desired product. This is because selectivity parameter, which depends on volatility of components and kinetic parameters, becomes almost constant over the entire conversion range as shown in Fig. 9, i.e. the compositions of $A$ and $C$ on the reactive stages are insensitive to further change in number of non-reactive stages.

2.1.2.5. Effect of number of reactive stages. The extent of side reaction is proportional to \( \int_0^W x_A x_C \, dW \) evaluated over the entire reactive zone. If one can maintain relatively large concentration of $A$ in the reactive zone ($x_A \sim 1$) then the selectivity is mainly determined by $\int_0^W x_C \, dW$. Fig. 10 shows the plot of mole fraction of $C$ vs. catalyst loading as one travels from the top of the reactive zone to the bottom of it. It should be noted that the total catalyst loading in each case is constant and only the number of reactive stages has been varied. The amount of side product formed in each case is proportional to the area under the corresponding profile in Fig. 10. For a given feed flow rate of $B$, by increasing the number of reactive stages, the area under the curve decreases and the selectivity of $C$ increases. This is because, with increase in number of reactive stages and for the same catalyst loading, the distillation
Fig. 11 – Effect of vapor flow rate on composition of (a) B and (b) C for number of reactive stages = 1; \( F_B = 5 \) mol/h; total catalyst loading = 50 g ms; reactive stage: stage 2 (→ indicates change due to increase in vapor flow rate).

Effect of vapor flow rate (reboiler duty). Da per stage can be reduced either by increasing the vapor flow rate (i.e., reboiler duty) for the same catalyst loading per stage or by increasing the number of reactive stages for the given total catalyst loading and the vapor flow rate. For a given feed flow rate of B, under total reflux condition an increase in the vapor flow rate pulls the desired product down from the reactive zone making it rich in reactant A and deficient in C as shown in Fig. 11a and b for a base case configuration with one reactive stage (stage number 2). Similar behavior is observed with multiple reactive stages. This results in an increase in the selectivity.

2.1.2.6. Effect of vapor flow rate (reboiler duty). Da per stage can be reduced either by increasing the vapor flow rate (i.e., reboiler duty) for the same catalyst loading per stage or by increasing the number of reactive stages for the given total catalyst loading and the vapor flow rate. For a given feed flow rate of B, under total reflux condition an increase in the vapor flow rate pulls the desired product down from the reactive zone making it rich in reactant A and deficient in C as shown in Fig. 11a and b for a base case configuration with one reactive stage (stage number 2). Similar behavior is observed with multiple reactive stages. This results in an increase in the selectivity.

Fig. 12 – Effect of distributed feed of B on reactive stages on selectivity of C for number of reactive stages = 5; \( F_B = 7 \) mol/h; Da per stage = 0.8.
2.1.3. Design methodology

Based on the parametric studies, a methodology has been suggested to conceptually design a reactive distillation column for the reactions falling in the above class of systems, i.e., $A + B \rightarrow C + D$, where $C$ is the desired product. The steps to be followed are as follows:

1. The choice between HSRR or HSRS depends on the volatility of the desired product (i.e., $C$) with respect to the reactant (i.e., $B$) which is involved in both the reactions. If the product is less volatile than the reactants then use HSRR else, use HSRS. If the desired product (i.e., $C$) is less volatile than the reactant then charge the reboiler with reactant (i.e., $A$) that is involved only in the desired reaction.

2. The reactant which is common in both the reactions (i.e., $B$) is fed in a continuous manner at an appropriate location in the column, i.e., above the reactive stages if it is less volatile than the other reactant (i.e., $A$). Set the feed flow rate to a value as low as possible.

3. Adjust the total catalyst loading ($D_a$) in the column such that desired conversion can be obtained. It should be noted that if the feed flow rate is high, a large catalyst loading is required and a suitable combination of feed flow rate and catalyst loading may be decided based on the economic considerations.

4. Add non-reactive stages below the reactive zone for HSRR and above the reactive zone for HSRS until selectivity is insensitive to the change in number of non-reactive stages.

5. Increase the number of reactive stages by keeping the total catalyst loading ($D_a$) constant. The selectivity will improve.

6. If the attainable yield is not same as the maximum achievable yield defined by the reaction stoichiometry or in other words, if the selectivity is not close to 100%, then the effect of re-boiler duty may be examined. Increase in re-boiler duty will further expand the feasible region and stretch it to its maximum limit defined by the stoichiometry of the desired reaction if there are no separation limitations imposed by azeotropes, if any.

By following this methodology, higher selectivity is achieved at higher conversion and the feasible region for the given reaction system is much larger than that offered by a conventional semi-batch reactor operated under similar conditions.

The same methodology is applicable to the following reaction systems:

1. Multiple reactants-multiple products irreversible reactions $A + B \rightarrow C + D; A + C \rightarrow E + D$, with $C$ as the desired product.

2. Multiple reactants-single product reversible reactions $A + B \rightleftharpoons C; C + A \rightleftharpoons D$, when the objective is to increase the selectivity of $C$. In this case an added advantage of using RD is that it shifts the equilibrium of the reaction allowing one to obtain 100% conversion which is otherwise not possible with SBR or any conventional reactor.

3. Multiple reactants-multiple products reversible reactions $A + B \rightleftharpoons C + D; A + C \rightleftharpoons E + D$, with $C$ as the desired product. The removal of one of the products ($D$) strongly influences the performance. The advantage of using RD is that it shifts the equilibrium of the reaction allowing one to obtain 100% conversion which otherwise is not possible with SBR or any conventional reactor.

In the following section we extend the design methodology developed above to real reaction system involving multiple reactants and single or multiple products.

2.1.4. Esterification of glutaric acid

Glutaric acid (GA) on esterification with methanol gives monomethyl glutarate (MMG) and water. Further, the esterification of MMG produces dimethyl glutarate (DMG). As both the reactions are reversible, the conversion in conventional
reactors is limited so it is impossible to get pure DMG from GA. The reaction scheme falls in the category of $A + B = C + D$, $A + C = E + D$ and is given by Eqs. (17) and (18). MMG (i.e. monobasic ester) has a wide range of applications in pharmaceutical industry. The objective is to improve the selectivity for MMG.

\[
\text{glutaric acid} + \text{methanol} \overset{k_1}{\underset{k_3}{\rightleftharpoons}} \text{monomethyl glutarate} + \text{water}
\]

(17)

\[
\text{monomethyl glutarate} + \text{methanol} \overset{k_1}{\underset{k_3}{\rightleftharpoons}} \text{dimethyl glutarate} + \text{water}
\]

(18)

Thermodynamics is modeled using NRTL equation with binary interaction parameters estimated by UNIFAC model from ASPEN PROPERTY PLUS (Aspen Technology Inc., 2001). Concentration based kinetic model (Eqs. (19) and (20)) used for the simulations is taken from Hung et al. (2007). The VLE and kinetic parameters are given in the Appendix A (Tables A1a and A1b):

\[
r_1 = k_1 C_{GA} C_{MeOH} - k_3 C_{MMG} C_{water}
\]

(19)

\[
r_2 = k_3 C_{MMG} C_{MeOH} - k_4 C_{DMG} C_{water}
\]

(20)

\[
S = \frac{k_1 C_{GA} + (k_4 C_{DMG} C_{water}/C_{MeOH})}{(k_2 C_{MMG} C_{water}/C_{MeOH}) + k_3 C_{MMG} C_{MeOH}}
\]

(21)

This is a non-azeotropic system and desired product, i.e. MMG is less volatile than glutaric acid which is fed to the reboiler. The expression for the selectivity parameter (Eq. (21)) suggests that MMG needs to be removed from the reactive zone so as to achieve selectivity close to 100%. Based on the proposed design guidelines it is expected that hybrid semi-batch reactive rectification (HSRR), shown in Fig. 2b, would offer the best performance in terms of selectivity to MMG. The objective of using RD in this case is to improve the conversion of reactants and hence the yield by simultaneous removal of product from the reactive zone even with close to stoichiometric mole ratios of the reactants. Table 2 shows the operating conditions and comparison of SBR with SBRD. It can be seen that SBRD performance is superior to that of SBR under otherwise similar conditions.

### 3. Example 2: SBRD with simultaneous product removal

In all the previous cases, the product(s) formed are not removed continuously from the column during the reaction. In some cases, this may be desired and is possible to implement if volatilities are right. In this section, we consider such examples wherein each reaction is associated with formation of multiple products one of which can be separated in situ from either top or bottom depending on its volatility. In most of the cases the second reaction is the desired one. It is a special case of the series parallel reactions, and the first reaction is also necessary for the second reaction to take place. The substrate 'B' is a bifunctional molecule. The reaction of interest is given below:

\[
A + B = C + D
\]

\[
A + C = E + D
\]

It should be noted that the example of glutaric acid esterification discussed in the earlier section does not fall in this category through it follows the same stoichiometry. Since methanol (B) is more volatile than water (D), the simultaneous removal of water from the system is not recommended. Moreover, in the present case the product of interest is D and not C. The reaction is assumed to be elementary. The kinetics and the selectivity parameter are given by the following equations:

\[
r_1 = k_2 x_A x_B - k_4 x_A x_D
\]

(22)

\[
r_2 = k_3 x_A x_C - k_4 x_A x_D
\]

(23)

\[
S = \frac{x_A (k_3 x_B + k_3 x_C)}{k_4 x_A x_D + k_3 x_A x_D}
\]

(24)

1, 2, 3 and 4 are assumed to be equal and unity. The conversion is defined as moles of reactant A consumed per mole of reactant A fed, and selectivity as moles of reactant used in forming desired product to total moles reacted. The selectivity parameter is defined by the Eq. (24). When the main objective is to increase the selectivity of the desired product E, separation of D from the reactive stages is crucial as it limits the conversion of reactant A and governs the selectivity of the desired product E. Hence for such cases, we propose two additional basic RD units, viz., hybrid semi-batch reactive rectification with product removal (HSRRP) and hybrid semi-batch reactive stripping with product removal (HSSRP). These configurations facilitate the separation of D from the reactive stages by removing desired product either from the top (if it is more volatile) or from the bottom (if it is less volatile) as shown in Fig. 15. In the following example, one of the products is more volatile (D) and the other products C and E are less volatile than the reactants. In such case, it is advisable to use HSSRP shown in Fig. 15a. When the desired product is E, either of A and B is charged to the reboiler and the other reactant is fed continuously.

### 3.1. Semi-batch reactive rectification with product removal (HSRRP)

HSRRP is similar to the hybrid semi-batch reactive rectification (Fig. 2b) used for the multiple reactant-single product systems explained in the previous section, except that HSRRP is associated with continuous overhead product removal. Hence, in multiple reactant- multiple product reaction system, we add one of the reactants continuously, the other reactant is charged to the reboiler and the product which controls the selectivity of the desired component is withdrawn.

![Table 2 – Comparison of SBRD and SBR for the given operating parameters](image-url)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SBRD</th>
<th>SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total glutaric acid charged (mol)</td>
<td>6.36</td>
<td>6.36</td>
</tr>
<tr>
<td>Feed flow rate of methanol (mol/h)</td>
<td>0.051</td>
<td>0.051</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>148</td>
<td>80/105/145</td>
</tr>
<tr>
<td>Total catalyst loading (g)</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Reactive stages</td>
<td>20</td>
<td>–</td>
</tr>
<tr>
<td>Non-reactive stages (below reactive stages)</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>Conversion</td>
<td>99.9</td>
<td>60/73/85</td>
</tr>
<tr>
<td>Yield of MMG</td>
<td>99.9</td>
<td>40/52.7/64.5</td>
</tr>
<tr>
<td>Time of operation (h)</td>
<td>55</td>
<td>55</td>
</tr>
</tbody>
</table>
Fig. 15 – (a) Hybrid semi-batch reactive rectification with product removal (HSRRP) and (b) hybrid semi-batch reactive stripping with product removal (HSRSP).

continuously. As explained in the previous section, the choice of reactant to be charged in continuous or batch mode depends on the selectivity parameter \( S \). The selectivity parameter given by Eq. (24) indicates that the selectivity of \( E \) can be enhanced by maintaining high concentration of \( A \) and/or low concentration of \( B \) in the reactive zone. Hence, reboiler is initially charged with \( A \) and continuous feed of \( B \) is given to HSRRP. All the model equations and assumptions made in the previous section for HSRR apply here as well. The only difference is in the equation for the condenser wherein, distillate flow rate is finite and not equal to zero.

3.1.1. Effect of various parameters on yield vs. conversion

From the model equations, we have eight independent parameters which influence the selectivity of the desired product, i.e. distillate rate, the location of the feed, feed flow rate, overall \( Da \), location of non-reactive zone, number of reactive stages, number of non reactive stages and vapor flow rate (i.e. reboiler duty). As expected, if the intermediate product \( C \) is desired, the column should operate at low feed flow rate and at high vapor flow rate. On the other hand, if the main objective is to increase the selectivity of \( E \), the conditions are reversed and the column should operate at a relatively higher feed flow rate of \( B \) and lower vapor flow rate under otherwise similar conditions. Other parameters such as number of reactive stages, location of non-reactive stages and distillate rate mainly influence the removal of \( D \) and hence these effects are analyzed here. Fig. 16 shows a base case conversion vs. yield plot of HSRRP with continuous feed of \( B \) at specific distillate rate and vapor flow rate. The unit has single reactive stage and no non-reactive section. As can be seen, in both the cases the conversion level is not 100%. In SBR the limit is imposed by the equilibrium constraint, whereas for HSRRP, with a limited number of stages, the efficiency of removal of product is not good enough to avoid the loss of reactant loss in the distillate. At higher conversion, the yield towards \( E \) is higher than that of SBR. This is because of the simultaneous removal of \( B \) from the reactive stage.

3.1.1.1. Effect of distillate rate. As explained before the objective is to remove the volatile \( D \) as the overhead product. Ideally the distillate flow rate should be equal to the \( D \) formed by assuming conversion of \( A \rightarrow E \) only, with formation of the intermediate component \( C \) to be negligible. However, it is possible that if the distillate stream is not pure \( D \), some amount of the reactant may be lost through distillate and conversion close to 100% may not be realized. Hence the reaction and distillation parameters should be manipulated such the distillate is pure \( D \).

3.1.1.2. Location and number of non-reactive stages. It is obvious that by providing the non reactive zone above the reactive section serves the purpose of removing relatively pure \( D \) from the reactive zone and enriching the reactive zone with relatively less volatile reactants such as \( A \). Hence, the reaction shifts in forward direction and also an increase in the selectivity to \( E \) is realized. By providing the non-reactive zone below the reactive zone, selectivity of \( E \) decreases under otherwise similar conditions because of the relatively high concentration of \( D \) on the reactive stages. As explained in the previous section, on increasing the non-reactive stages, the selectivity of \( E \) increases up to a point and thereafter, there is no further increase with increase in the number of non-reactive stages. This is because, the distillate composition of \( D \) becomes insensitive to further change in non-reactive stages. As the distillate rate of \( D \) is fixed based upon the stoichiometry of reaction, purity of distillate mainly depends on the number of non-reactive stages and vapor flow rate. An optimum combination of these two parameters that offers desired conversion, 100% selectivity towards the desired product and minimum cost needs to be worked out for a given problem and

Fig. 16 – Comparison of performance of HSRRP with SBR under similar conditions of \( F_B = 0.1 \text{ mol/h}; \text{ total catalyst loading} = 60 \text{ g}. \)
Fig. 17 – (a) Effect of number of reactive stages on mole fraction of $D$ for $F_B = 5$ mol/h; $Da$ (over all) = 1; distillate rate = 0.1 mol/h for conversion of $A$ = 40% and (b) effect of reactive stages on $E$ selectivity for $k_1/k_3 = 1$, $k_1 = k_2 = k_4$; $FA = 0.1$ mol/h; $Da$ (over all) = 1; distillate rate = 0.1 mol/h.

is out of the scope of the conceptual design work presented here.

### 3.1.1.3. Effect of number of reactive stages

An effective separation of common product, i.e. $D$, from the reactive zone results in an increase in the selectivity of $E$ instead of intermediate product $C$. Fig. 17a shows composition of $D$ along the reactive zone for different number of stages. The area under each curve quantitatively represents the adverse effect of $D$ present on the reactive stages which in turn controls the selectivity of $E$ due to equilibrium limitations. As shown in Fig. 17b, the selectivity of $E$ increases with an increase in the number of reactive stages for the given total catalyst loading.

### 3.1.1.4. Effect of catalyst loading ($Da$ per stage)

In the present case we are interested in the product of the second reaction and not the intermediate one. As mentioned before, in a sense, both the reactions are desired and expediting the first reaction would help the second reaction indirectly. Fig. 18 shows the effect of total catalyst loading on the selectivity of $E$. Increase in the total catalyst loading for a given number of reactive stages increases the selectivity of $E$. On the contrary, in example 1, discussed in the previous section, when our objective was to improve selectivity for the intermediate product, $Da$ per stage was recommended to be as small as possible.

From the foregoing discussion on the effects of various parameters, the feasible region can be stretched to its maximum limit of 100% selectivity to $E$ by adopting one or more of the following design strategies: (1) increasing catalyst loading or number of reactive stages; (2) placing non-reactive zone in the upper section of the column, i.e. above the reactive zone if the product to be removed is most volatile or in the lower section of the column, i.e. below the reactive zone if the product to be removed is less volatile, and increasing the number of non-reactive stages; (3) decreasing the vapor flow rate (i.e. reboiler duty), and if possible introducing $B$ in a distributed manner.

### 3.1.2. Design methodology for multiple reactant-single/multiple product reaction systems with continuous removal of common product

Based on the parametric studies, design guidelines have been developed to design a reactive distillation column for the reaction system $A + B \rightarrow C + D$, $A + C \rightarrow E + D$ when $E$ is the desired product. The steps to be followed are given below:

1. Use the HSRRP with distillate withdrawal or HSRSP with bottom withdrawal depending upon the volatility of the common product with respect to the reactant which is involved in both the reactions. HSRRP is used if the common product is more volatile and HSRSP is used when the common product is less volatile than the reactants. Charge the reboiler with reactant that is involved in both the reactions (i.e. $A$).

2. The reactant which is involved in the single reaction is added in a continuous manner at an appropriate location in the column. If it is more volatile than the other reactant, continuous feed is introduced below reactive zone and if it is less volatile, the feed is given above the reactive zone.

3. Adjust the total catalyst loading ($Da$) in the column such that desired conversion can be obtained. Conversion increases with the catalyst loading.

4. Based on the reaction stoichiometry and desired conversion, fix the distillate rate/bottom rate to remove common product from top/bottom. This flow rate is set equal to the rate of $E$ formed.

5. Add non-reactive stages above the reactive stages for HSRRP and below reactive stages for HSRSP until the increase in selectivity is independent of number of non-reactive stages.
reactive stages for a given vapor flow rate (i.e. reboiler duty) and distillate/bottom rate.
6. Manipulate the vapor flow rate (i.e. reboiler duty) and number of non-reactive stages to obtain the pure common product as a distillate or as a bottom product. Reduction in vapor flow rate (i.e. reboiler duty) and increase in number of non-reactive stages lead to increase in selectivity.
7. Increase the number of reactive stages and/or increase the total catalyst loading. The feasible region will expand.

By following this methodology, higher selectivity is achieved at higher conversion and the feasible region for the given reaction system expands. Fig. 19 shows the composition profiles of components obtained by simulation for a case in which conversion and selectivity close to 100% are achieved by adjusting the parameters using the design guidelines mentioned before. Fig. 20 shows a comparison between semi-batch reactor and SBRD under otherwise similar conditions. It can be seen that for the suitable design and operating parameters, the desirable 100% selectivity is achieved over the entire conversion range using reactive distillation. For the case if the volatility order is $C \lor D > B \lor A$, HSRSP shown in Fig. 12b can give the desired attainable region.

In the following section we extend this design methodology to real reaction systems involving multiple reactants and single or multiple products.

3.1.3. Esterification of ethylene glycol with acetic acid
Ethylene glycol (EG) on esterification with acetic acid gives monoacetate ethylene glycol (MAEG) and water. Further, the esterification of MAEG produces diacetate of ethylene glycol (DAEG). As both the reactions are reversible, the conversion in conventional reactors is limited so it is impossible to get pure MAEG or DAEG from EG. The reaction scheme falls in the category of $A + B \rightleftharpoons C + D$, $A + C \rightleftharpoons E + D$ and is given by Eqs. (17) and (18). DAEG and MAEG are used in thermoplastic acrylic coatings and specialty chemical industry. The objective is to improve the selectivity for DAEG.

diethylene glycol
$$+\text{acetic acid} \xrightleftharpoons[k_2]{k_1} \text{monoacetate ethylene glycol} + \text{water} \quad (25)$$
monoacetate ethylene glycol
$$+\text{acetic acid} \xrightleftharpoons[k_4]{k_3} \text{diacetate ethylene glycol} + \text{water} \quad (26)$$

The activity based kinetic model used for the simulations is taken from Schmid et al. (2008). The UNIQUAC interaction parameters and the kinetic parameters are given in the Appendix A (Tables A2a and A2b):

Table 3 – Comparison of SBRD and SBR for the given operating parameters

<table>
<thead>
<tr>
<th></th>
<th>SBRD (HSRRP)</th>
<th>SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total acetic acid charged (mol)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Feed flow rate of ethylene glycol (mol/h)</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Distillate rate (mol/h)</td>
<td>0.836</td>
<td>–</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>116</td>
<td>116</td>
</tr>
<tr>
<td>Total catalyst loading (kg)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Reactive stages</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>Non-reactive stages (above reactive stages)</td>
<td>60</td>
<td>–</td>
</tr>
<tr>
<td>% Conversion of acetic acid</td>
<td>95.4</td>
<td>43</td>
</tr>
<tr>
<td>% Yield of DAEG</td>
<td>95.4</td>
<td>17.3</td>
</tr>
<tr>
<td>Time of operation (h)</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Fig. 20 – Comparison of attainable region for $E$ between hybrid semi-batch reactive distillation with product removal and semi-batch reactor.
This is a non-azeotropic system and water—the common product in both the reactions, is more volatile than acetic acid which is charged to the reboiler. From selectivity parameter given in Eq. (29), to achieve significant conversion and selectivity, water needs to be removed from the reactive zone. Hence, based on the proposed design guidelines, it is expected that hybrid semi-batch reactive rectification with continuous removal of product (HSRRP), as shown in Fig. 15a, will give the best performance in terms of selectivity to DAEG. As mentioned before, SBR is also likely to offer significant yield with excess acetic acid. Objective of using RD in this case is to improve the conversion of reactants and hence the yield by simultaneous removal of products from the reactive zone even with close to stoichiometric mole ratios of the reactants. However, the separation of water and acetic acid requires large number of non-reactive stages. Table 3 shows the operating conditions and comparison of SBR and SBRD performances.

4. Continuous models

In this section, we describe the continuous versions of the hybrid models analyzed before. It is well known that for every batch/semi-batch operation there is a continuous counterpart that offers similar performance. Fig. 21 shows the continuous models capable of giving close to 100% selectivity over the entire range of conversion if the system is ideal. Similar guidelines can be used for design of these continuous versions. In the continuous version, the reactant which is charged to the reboiler of HSRR or HSRRP is fed continuously below or above the reactive zone depending on the volatility of the reactant, and also the bottom product is continuously removed in the continuous version. The same logic may be applied to derive the continuous version of HSRS and HSRSP units.

The generalized model equations for continuous hybrid reactive rectification are given below:
there exists a minimum boiling azeotrope at 
same illustrative example 1 discussed before. In this example, 
ical azeotropic case.

In our earlier work (Agarwal et al., 2008b), we showed that for a 
system of interest. In the following section, we extend the 
design methodology developed for ideal system to a hypothet-
ical (for j=1) of Fig. 11c gives:

\[
l_j + \frac{D}{V} = 0 \tag{30}
\]

\[
l_jx_{i-1} + \left(\frac{D}{V}\right)x_{i-1} - y_{i-1} = 0 \quad \text{for } i=1, 2, \ldots, NC - 1 \tag{31}
\]

where \( l_j = L_j/V \).

(b) Overall and component material balances on feed stage 

\[
l_{j-1} - b + f_j + \frac{D}{N-1} \sum_{k=1}^{R} \nu_k r_k'(x_j) = 0 \tag{32}
\]

\[
l_{j-1}x_{j-1} - \left(\frac{V}{N}\right)x_{j-1} - y_{j-1} = 0 \quad \text{for } i=1, 2, \ldots, NC - 1 \tag{33}
\]

for \( i = 1, 2, \ldots, NC - 1 \).

(c) For the stages other than feed stages (\( j \neq N_f1 \) and \( N_f2 \)):

If the stage is reactive, \( f_j = 0 \) in Eqs. (32) and (33) and if the 
stage is non-reactive, both \( f_j \) and reaction term are 
removed from Eqs. (32) and (33).

(d) Overall and Component Material Balance on reboiler (for 

\[
l_{N-1} - b = 0 \tag{34}
\]

\[
l_{N-1}x_{N-1} - \left(\frac{V}{N}\right)x_{N-1} - y_{N-1} = 0 \quad \text{for } i=1, 2, \ldots, NC - 1 \tag{35}
\]

Similar to continuous hybrid reactive rectification, continuous 
hybrid reactive stripping can also be modeled. Fig. 22 
shows the column profiles of components for 100% selectivity 
and for 100% conversion of reactants obtained in a continu-
ous hybrid reactive rectification unit for the hypothetical case 
discussed in Example 2.

5. Example 3: systems with azeotropes

In our earlier work (Agarwal et al., 2008b), we showed that for a 
single reactant system the presence of azeotrope between the 
reactant and the desired product limits the selectivity and it 
has been concluded that when there is no azeotrope between 
reactant and desired product then 100% selectivity can be 
obtained for the entire range of conversion. Similarly, in the 
multiple reactant systems the selectivity may be influenced 
by the azeotrope between reactant(s) and the desired prod-
uct(s). In such case a complex configuration may be designed 
based on the complete knowledge of the VLE behavior of the 
system of interest. In the following section, we extend the 
design methodology developed for ideal system to a hypothet-
ical azeotropic case.

To demonstrate the effect of azeotrope, we consider the 
same illustrative example 1 discussed before. In this example, 
there exists a minimum boiling azeotrope at \( x_C = 0.5 \) between 
desired product (C) and reactant (A). Extended antoine’s con-
stants and the binary interaction parameters are given in the 
Table 4. In this case, both the products C and D are less 
volatile than the reactants A and B. Hence, we choose hybrid 
semi-batch reactive rectification (HSRR) configuration under 

total reflux condition. The choice of reactant to be charged 
in continuous mode or batch mode to HSRR depends on 
the selectivity parameter (S). For the liquid phase reaction 
of interest \( A + B \rightarrow C; B + C \rightarrow D \), selectivity parameter is equal 
to \( k_1 x_A/k_2 x_C \) up to azeotropic composition. At higher conver-

\[
\begin{array}{cccccc}
\text{Component} & A & B & C & D \\
A & 0 & -43.45 & -38 & 55 \\
B & 37.36 & 0 & 10 & 54.51 \\
C & 30 & 240 & 0 & 60 \\
D & -69 & -60 & 2 & 0 \\
\end{array}
\]

\[
\begin{array}{cccccc}
\text{Component} & A & B & C & D \\
1 & 57 & 104.65 & 103 & 56.1 \\
2 & -966.04 & -699.55 & -1259.1 & -9.64E+03 \\
3 & 0 & 0 & 0.00E+00 & 0.00E+00 \\
4 & 0 & 0 & 0.00E+00 & 0.00E+00 \\
6 & 1.47E-06 & 1.24E-05 & 3.81E-06 & 1.47E-06 \\
7 & 2 & 2 & 2.00E+00 & 2.00E+00 \\
\end{array}
\]
because the composition in the reactive zone is equal to the azeotropic composition. Hence, the selectivity of C depends on the ratio of \( x_A/x_C \) or \( x_{BA}/x_{CH} \) in the reactive zone for a given ratio \( k_1/k_2 \). The definitions of Conversion, selectivity and yield are same as that in example 1. To improve selectivity of C, we need to maintain either high concentration of A or less concentration of C in the reactive zone. Hence, reboiler is initially charged with A and continuous feed of B is given to the semi-batch reactive rectification column. The design methodology developed for HSRR in the previous section is used to compare the performance with that of SBR. Fig. 23 shows the performance of a HSRR against a SBR when azeotrope is present between B and C. It can be seen that there is a decrease in the performance of HSRR beyond the azeotropic composition. At higher conversions, the selectivity obtained in HSRR is much lower than that in SBR. This is because reactive zone is in such case is enriched with respect to product C leading to formation of D, thus lowering the selectivity. From Fig. 23, it can be seen that the presence of azeotrope between C and A drastically affects the performance of HSRR when compared to SBR at composition higher than the azeotropic composition. Hence, when azeotrope is present between the desired product and the reactant that is involved in single reaction, it limits the selectivity in RD which in turn depends on azeotropic composition.

In the multiple reactant systems, only the presence of azeotrope between desired product and the reactant that is involved in single reaction limits the selectivity of desired product and all other azeotropes do not influence the attainable selectivity of the desired product. In the following sections we analyze real examples involving formation of azeotropes.

### 5.1. Case 1: azeotrope between desired product and reactant

#### 5.1.1. Transesterification of cyclohexyl acetate

Cyclohexyl acetate (CHA) on transesterification with n-butanol (BuOH) gives cyclohexanol (CH) and butyl acetate (BA). Cyclohexanol is used in the manufacture of plasticizers and adipic acid. Cyclohexanol reacts with n-butanol in a side reaction to give butyl cyclohexyl ether (BCHE) and water. In conventional reactors, it is impossible to obtain pure CH from CHA. The reaction scheme falls in the category of \( A + B \rightarrow C + D \), \( A + C \rightarrow E + F \) and is given by Eqs. (36) and (37):

\[
\begin{align*}
\text{cyclohexyl acetate} + \text{butanol} & \rightarrow k_1 \text{cyclohexanol} + \text{butyl acetate} \\
\text{cyclohexanol} + \text{butanol} & \rightarrow k_2 \text{butyl cyclohexyl ether} + \text{water}
\end{align*}
\]

Thermodynamics is modeled using UNIQUAC equation with binary interaction parameters determined by UNIFAC method from ASPE PROPERTY PLUS (Aspen Technology Inc., 2001). Concentration based kinetic model used for the simulations (Eqs. (38) and (39)) is taken from Chakrabarti and Sharma (1992a,b). The binary interaction and kinetic parameters are given in the Appendix A (Tables A3a and A3b):

\[
\begin{align*}
\tau_1 &= k_1 \text{C}_{\text{CHA}} \text{C}_{\text{BuOH}} \\
\tau_2 &= k_2 \text{C}_{\text{CH}} \text{C}_{\text{BuOH}} \\
S &= \frac{k_1 \text{C}_{\text{CHA}}}{k_2 \text{C}_{\text{CH}}}
\end{align*}
\]

Various azeotropes present in this reaction system are given in Table 5. The desired product (i.e. cyclohexanol) is intermediate boiling compared to the reactants, i.e. n-butanol and cyclohexyl acetate. Its volatility is close to the less volatile reactant and hence, based on the proposed design guidelines, it is expected that hybrid semi-batch reactive rectification (HSRR), shown in Fig. 2b, would offer the best performance in terms of selectivity for cyclohexanol. Based on the expression of selectivity parameter (Eq. (40)), the reboiler is charged with cyclohexyl acetate, and n-butanol is fed continuously below the reactive stages. As the objective is to improve the selectivity for cyclohexanol, the azeotropes between water or butyl cyclohexyl ether with any other component are not relevant here. However, the azeotrope between cyclohexyl acetate (reactant) and cyclohexanol (desired product) is of relevance in HSRR as the reactive zone consists of cyclohexanol along...
Fig. 24 – Comparison of SBR and SBRD for transesterification of cyclohexyl acetate.

Table 6 – Comparison of SBRD and SBR for the given operating parameters

<table>
<thead>
<tr>
<th></th>
<th>SBRD</th>
<th>SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total CH charged (mol)</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Feed flow rate of 2-butanol (mol/h)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>120–140</td>
<td>130</td>
</tr>
<tr>
<td>Total catalyst loading (g)</td>
<td>560</td>
<td>560</td>
</tr>
<tr>
<td>Reactive stages</td>
<td>14 –</td>
<td>–</td>
</tr>
<tr>
<td>Non-reactive stages (below reactive stages)</td>
<td>4 –</td>
<td>–</td>
</tr>
<tr>
<td>Reboiler duty (kW)</td>
<td>4 –</td>
<td>–</td>
</tr>
<tr>
<td>Yield of CH</td>
<td>96 –</td>
<td>80</td>
</tr>
<tr>
<td>Time of operation (h)</td>
<td>33</td>
<td>33</td>
</tr>
</tbody>
</table>

Table 7 – Comparison of HSRR and SBR for the given operating parameters

<table>
<thead>
<tr>
<th></th>
<th>HSRR</th>
<th>SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total MEK charged (mol)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Feed flow rate of acetaldehyde (mol/h)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>70–75</td>
<td>75, 90 and 105</td>
</tr>
<tr>
<td>Total catalyst loading (g)</td>
<td>416</td>
<td>416</td>
</tr>
<tr>
<td>Reactive stages</td>
<td>28 –</td>
<td>–</td>
</tr>
<tr>
<td>Non-reactive stages (below reactive stages)</td>
<td>6 –</td>
<td>–</td>
</tr>
<tr>
<td>Reboiler duty (kW)</td>
<td>2 –</td>
<td>–</td>
</tr>
<tr>
<td>% Conversion</td>
<td>99.9</td>
<td>85/90/90</td>
</tr>
<tr>
<td>% Yield of MPO</td>
<td>97</td>
<td>54/58/60</td>
</tr>
<tr>
<td>Time</td>
<td>60.5</td>
<td>60.5</td>
</tr>
</tbody>
</table>

With cyclohexyl acetate. Fig. 24 shows the comparison of HSRR and SBR for the operating conditions given in Table 6. It is not possible to obtain 100% selectivity due to azeotrope formed between the reactant and the desired product.

5.2. Case 2: azeotrope between reactant and product

5.2.1. Cross aldol condensation of acetaldehyde and methyl ethyl ketone

The aldol condensation of acetaldehyde with methyl ethyl ketone (MEK) yields an unstable aldol which rapidly dehydrates to the desired product, i.e., 3-methyl-3-pentene-2-one (MPO). However, MPO further reacts with acetaldehyde in a side reaction to give undesired heavier products. It is also possible that acetaldehyde on self-condensation gives crotonaldehyde. The reaction scheme given by Eqs. (41)–(43), falls in the category of \( A + B \rightarrow C + D, A + C \rightarrow E + D, 2A \rightarrow E \). Aim is to improve selectivity toward MPO (C) as it is an important intermediate in perfumery industry:

\[
\text{acetaldehyde} + \text{MEK} \rightarrow \text{3-methyl-3-pentene-2-one (MPO)} + \text{water} \tag{41}
\]

\[
\text{MPO} + \text{acetaldehyde} \rightarrow \text{heavier products} + \text{water} \tag{42}
\]

\[
2\text{acetaldehyde} \rightarrow \text{crotonaldehyde} + \text{water} \tag{43}
\]

Kinetic model (Eqs. (44)–(46)) based on a modified Langmuir–Hinselwood mechanism proposed by Mahajan (2007), is used for the simulations. The kinetic parameters are given in the Appendix A (Tables A4a and A4b):

\[
r_1 = \frac{k_1 a_A a_B}{(1 + K_W a_W)^2} \tag{44}
\]

\[
r_2 = \frac{k_2 a_A a_C}{(1 + K_W a_W)^2} \tag{45}
\]

\[
r_3 = \frac{k_3 a_A^2}{(1 + K_W a_W)^2} \tag{46}
\]

\[
S = \frac{k_1 a_{\text{MEK}} a_{\text{MEK}}}{k_2 a_{\text{Heavies}} a_{\text{Heavies}} + k_3 a_{\text{Ace}} a_{\text{Ace}}} \tag{47}
\]

VLE of the reaction system is non-ideal, i.e., MEK and water form binary azeotrope at \( x_w = 0.35 \). Water, in this case, is not a desired product. The volatility order of reactant and products is acetaldehyde > azeotrope of MEK and water > MPO > crotonaldehyde > heavies. As MPO is less volatile than the reactants, as per the guidelines given before, hybrid semi-batch reactive rectification (HSRR) would offer the best performance in terms of selectivity toward MPO. Based on the expression of selectivity parameter (Eq. (47)), MEK is fed to the reboiler and acetaldehyde is introduced continuously below the reactive stages. As the objective is to improve the selectivity for MPO, the presence of intermediate boiling azeotrope between MEK and water is responsible for an increase in water concentration in the reactive zone. However, it does not influence the performance of HSRR as water is not involved in any of the reactions and does not affect the reaction rates significantly though it inhibits the

Table 8 – Comparison of SBRD and SBR for the given operating parameters

<table>
<thead>
<tr>
<th></th>
<th>SBRD</th>
<th>SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total methanol charged (mol)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Feed flow rate of glyoxal (40%, w/w, aqueous solution) (g/h)</td>
<td>0.105</td>
<td>0.105</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>65–66</td>
<td>65</td>
</tr>
<tr>
<td>Total catalyst loading (g)</td>
<td>475</td>
<td>475</td>
</tr>
<tr>
<td>Reactive stages</td>
<td>19 –</td>
<td>–</td>
</tr>
<tr>
<td>Non-reactive stages (below reactive stages)</td>
<td>9 –</td>
<td>–</td>
</tr>
<tr>
<td>Reboiler duty (kW)</td>
<td>3 –</td>
<td>–</td>
</tr>
<tr>
<td>% Conversion</td>
<td>99.9</td>
<td>45</td>
</tr>
<tr>
<td>% Yield of DAG</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>Time of operation (h)</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>
reaction to some extent given by the Eqs. (44)–(46). It is possible to obtain higher yields toward MPO in SBR under extreme conditions such as very small feed flow rate of acetaldehyde. HSRR is designed based on the guidelines mentioned before. HSRR gives a better performance than SBR for the given operating conditions mentioned in Table 7. The presence of azeotrope does not influence the attainable yields/selectivity of MPO. It should be noted that unlike HSRR, in SBR, one has a choice of operating temperature and hence the results on SBR at three different temperatures are reported for better comparison.

5.3. Case 3: azeotrope between products

5.3.1. Acetalization of glyoxal

Glyoxal (G) on acetalization with methanol gives monocetal of glyoxal (MAG) and water. Further, MAG on acetalization produces diacetal of glyoxal (DAG). As both the reactions are reversible, it is impossible to get pure DAG from glyoxal in conventional reactors. The reaction scheme falls in the category of $A + B = C + D$, $A + C = E + D$ and is given by eqs (48)–(49). MAG and DMG (i.e. mono and diacetal of glyoxal) find applications as substitutes of glyoxal in the various non-aqueous reactions. The objective is to improve the selectivity to DAG:

$$\text{glyoxal} + \text{methanol} \rightleftharpoons \text{monoacetal} + \text{water} \quad (48)$$

$$\text{monoacetal} + \text{methanol} \rightleftharpoons \text{diacetal} + \text{water} \quad (49)$$

Vapor–liquid equilibrium is modeled using UNIQUAC equation with binary interaction parameters estimated by UNIFAC method from ASPEN PROPERTY PLUS (Aspen Technology Inc., 2001). Concentration based kinetic model (Eqs. (50) and (51)) used for the simulations is taken from Mahajani and Sharma (1997). The binary interaction and kinetic parameters are given in the Appendix A (Tables A5a and A5b):

$$r_1 = k_1 C_G C_{MEOH} - k_2 C_{MAG} C_{water} \quad (50)$$

$$r_2 = k_3 C_{MAG} C_{MEOH} - k_4 C_{DMAG} C_{water} \quad (51)$$

$$S = C_{MEOH} (k_1 C_G + k_2 C_{MAG}) / C_{water}(k_3 C_{MAG} + k_4 C_{DMAG}) \quad (52)$$

VLE of the reaction system is non-ideal, i.e. monocetal of glyoxal and water form azeotrope at $x_w = 0.975$. The volatility order of reactants and products is methanol > azeotrope of MAG and water > azeotrope > MAG > DAG. Water, the common product in both the reactions, is less volatile than methanol which is fed to the reboiler. Water needs to be removed from the reactive zone so as to achieve significant conversion and selectivity. Based on the proposed design guidelines it is expected that hybrid semi-batch reactive rectification (HSRR) (Fig. 2b) will offer the best performance in terms of selectivity to DAG. The expression for the selectivity parameter (Eq. (52)) indicates that reboiler should be charged with methanol and glyoxal should be continuously fed above the reactive stages. As the objective is to improve the selectivity for DAG, the presence of intermediate boiling azeotrope between monocetal of glyoxal and water does not influence the performance of HSRR as the azeotrope ($x_w = 0.975$) is not relevant here. As mentioned before, SBR is also likely to offer significant yield with excess methanol. The advantage of using RD in this case is to improve the conversion of reactants and hence the yield by simultaneous removal of products from the reactive zone even with close to stoichiometric mole ratios of the reactants. Table 8 shows the operating conditions and comparison of the performances of SBR and SBRD.

6. Conclusion

For series or series-parallel reactions involving multiple reactants, when no azeotrope is present in between reactant and desired product, 100% selectivity can be obtained for the entire range of conversion using reactive distillation. Semi-batch reactive distillation offers better performance than the conventional semi-batch reactor under identical operating conditions. However, when an azeotrope is present between reactant and the desired product, there is a limit on the selectivity and the performance of RD depends on azotropic composition. Based on the volatility order of reactants and products, the design guidelines have been developed to obtain the improved selectivity for the desired product using various configurations of RD.

Appendix A. Binary interaction parameters and kinetic parameters used as input for various simulations

<table>
<thead>
<tr>
<th>Component</th>
<th>GA</th>
<th>MeOH</th>
<th>MMG</th>
<th>DMG</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA</td>
<td>0</td>
<td>1322.397</td>
<td>−381.858</td>
<td>901.943</td>
<td>−319.112</td>
</tr>
<tr>
<td>MeOH</td>
<td>−708.714</td>
<td>0</td>
<td>306.754</td>
<td>300.238</td>
<td>838.5936</td>
</tr>
<tr>
<td>MMG</td>
<td>1029.935</td>
<td>−17.448</td>
<td>0</td>
<td>422.863</td>
<td>129.646</td>
</tr>
<tr>
<td>DMG</td>
<td>−459.037</td>
<td>−334.455</td>
<td>−215.938</td>
<td>0</td>
<td>48.026</td>
</tr>
<tr>
<td>Water</td>
<td>1010.6</td>
<td>−1347.527</td>
<td>129.646</td>
<td>1698.559</td>
<td>0</td>
</tr>
</tbody>
</table>

Table A2a – Temperature dependent binary interaction parameters (cal/mol) (Schmid et al., 2008)

<table>
<thead>
<tr>
<th>Component</th>
<th>DEG</th>
<th>AA</th>
<th>MAEG</th>
<th>DAEG</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEG</td>
<td>0</td>
<td>−214.98</td>
<td>−12.65</td>
<td>141.62</td>
<td>−606.48</td>
</tr>
<tr>
<td>AA</td>
<td>288.43</td>
<td>0</td>
<td>−219.36</td>
<td>−521.77</td>
<td>300.68</td>
</tr>
<tr>
<td>MAEG</td>
<td>236.84</td>
<td>224.50</td>
<td>0</td>
<td>278.52</td>
<td>567.78</td>
</tr>
<tr>
<td>DAEG</td>
<td>360.94</td>
<td>1101.82</td>
<td>−156.03</td>
<td>0</td>
<td>812.11</td>
</tr>
<tr>
<td>Water</td>
<td>722.44</td>
<td>−180.16</td>
<td>−344.69</td>
<td>−113.52</td>
<td>0</td>
</tr>
</tbody>
</table>
### Table A2b – Kinetic parameters for MG system (Schmid et al., 2008)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{10}$ (mol/(g s))</td>
<td>539.14</td>
</tr>
<tr>
<td>$k_{20}$ (mol/(g s))</td>
<td>114.41</td>
</tr>
<tr>
<td>$k_{30}$ (mol/(g s))</td>
<td>156.43</td>
</tr>
<tr>
<td>$k_{40}$ (mol/(g s))</td>
<td>95.68</td>
</tr>
<tr>
<td>$E_1$ (kJ/mol)</td>
<td>39.84</td>
</tr>
<tr>
<td>$E_2$ (kJ/mol)</td>
<td>39.85</td>
</tr>
<tr>
<td>$E_3$ (kJ/mol)</td>
<td>39.9</td>
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<td>$E_4$ (kJ/mol)</td>
<td>39.86</td>
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</tbody>
</table>

### Table A3a – Binary interaction parameters (Aspen Technology Inc.)

<table>
<thead>
<tr>
<th>Component</th>
<th>CHA</th>
<th>BuOH</th>
<th>BA</th>
<th>CH</th>
<th>BCHE</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHA</td>
<td>0</td>
<td>−146.63</td>
<td>82.01</td>
<td>−111.08</td>
<td>95.82</td>
<td>−393.37</td>
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<tr>
<td>BuOH</td>
<td>35.69</td>
<td>0</td>
<td>−39.79</td>
<td>−411.24</td>
<td>265.73</td>
<td>−34.22</td>
</tr>
<tr>
<td>BA</td>
<td>−90.28</td>
<td>−32.05</td>
<td>0</td>
<td>−252.63</td>
<td>37.509</td>
<td>−345.06</td>
</tr>
<tr>
<td>CH</td>
<td>27.96</td>
<td>273.66</td>
<td>169.15</td>
<td>0</td>
<td>287.34</td>
<td>−515.15</td>
</tr>
<tr>
<td>BCHE</td>
<td>−107.51</td>
<td>−558.40</td>
<td>−50.47</td>
<td>−536.12</td>
<td>0</td>
<td>−1343.45</td>
</tr>
<tr>
<td>Water</td>
<td>−135.24</td>
<td>−292.44</td>
<td>−232.22</td>
<td>144.35</td>
<td>−266.55</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table A3b – Kinetic parameters for CH system (Chakrabarti and Sharma, 1992a)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ (m³/(kmol s))</td>
<td>$4.814 \times 10^{-5}$</td>
</tr>
<tr>
<td>$k_2$ (m³/(kmol s))</td>
<td>$4.985 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

### Table A4a – Binary interaction parameters (Mahajan, 2007)

<table>
<thead>
<tr>
<th>Component</th>
<th>Acet.</th>
<th>MEK</th>
<th>MPO</th>
<th>Crotonaldehyde</th>
<th>Water</th>
<th>HiB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acet.</td>
<td>0</td>
<td>−19.85</td>
<td>67.83</td>
<td>114.35</td>
<td>−539.28</td>
<td>113.81</td>
</tr>
<tr>
<td>MEK</td>
<td>5.18</td>
<td>0</td>
<td>32.23</td>
<td>−15.34</td>
<td>−408.65</td>
<td>1.82</td>
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<tr>
<td>MPO</td>
<td>−99.06</td>
<td>−38.09</td>
<td>0</td>
<td>22.36</td>
<td>−298.39</td>
<td>27.71</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>−139.56</td>
<td>0.11</td>
<td>−37.35</td>
<td>0</td>
<td>−233.86</td>
<td>0.60</td>
</tr>
<tr>
<td>Water</td>
<td>69.85</td>
<td>−4.54</td>
<td>−139.44</td>
<td>−165.61</td>
<td>0</td>
<td>−263.63</td>
</tr>
<tr>
<td>HiB</td>
<td>−182.79</td>
<td>−18.24</td>
<td>−33.64</td>
<td>−21.78</td>
<td>−255.97</td>
<td>0</td>
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</tbody>
</table>

### Table A4b – Kinetic parameters for MPO system (Mahajan, 2007)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>$\ln(k_{10})$ (g mol/(h g))</td>
<td>18.57</td>
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<tr>
<td>$\ln(k_{20})$ (g mol/(h g))</td>
<td>10.34</td>
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<td>$\ln(k_{30})$ (g mol/(h g))</td>
<td>16.31</td>
</tr>
<tr>
<td>$E_1$ (kJ/g mol)</td>
<td>57.894</td>
</tr>
<tr>
<td>$E_2$ (kJ/g mol)</td>
<td>37.894</td>
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<tr>
<td>$E_3$ (kJ/g mol)</td>
<td>49.911</td>
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<tr>
<td>$K_W$</td>
<td>1.179</td>
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</table>

### Table A5a – Binary interaction parameters (Aspen Technology Inc.)

<table>
<thead>
<tr>
<th>Component</th>
<th>Glyoxal</th>
<th>MeOH</th>
<th>MAG</th>
<th>DAG</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyoxal</td>
<td>0</td>
<td>340.19</td>
<td>−839.05</td>
<td>−464.23</td>
<td>−480.81</td>
</tr>
<tr>
<td>MeOH</td>
<td>−306.39</td>
<td>0</td>
<td>−7.37</td>
<td>−366.75</td>
<td>165.26</td>
</tr>
<tr>
<td>MAG</td>
<td>313.01</td>
<td>−41.4</td>
<td>0</td>
<td>110.35</td>
<td>219.62</td>
</tr>
<tr>
<td>DAG</td>
<td>78.87</td>
<td>248.46</td>
<td>−129.82</td>
<td>0</td>
<td>574.70</td>
</tr>
<tr>
<td>Water</td>
<td>116.01</td>
<td>−254.73</td>
<td>−394.57</td>
<td>−1770.17</td>
<td>0</td>
</tr>
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Table A5b – Kinetic parameters for DAG system
(Mahajani and Sharma, 1997)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>$k_1$ (kmol$^{-2}$/kg s)</td>
<td>0.034</td>
</tr>
<tr>
<td>$k_2$ (kmol/(kg s))</td>
<td>0.044</td>
</tr>
<tr>
<td>$k_3$ (kmol$^{-2}$/kg s)</td>
<td>0.0085</td>
</tr>
<tr>
<td>$k_4$ (kmol/(kg s))</td>
<td>0.14</td>
</tr>
</tbody>
</table>

References


