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Review

# Modelling reactive distillation

R. Taylor[a,b], R. Krishna[c,*]

[a] *Department of Chemical Engineering, Clarkson University, Potsdam, NY 13699-5705, USA*
[b] *Department of Chemical Technology, University of Twente, 7500 AE Enschede, The Netherlands*
[c] *Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

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## Abstract

The design and operation issues for reactive distillation systems are considerably more complex than those involved for either conventional reactors or conventional distillation columns. The introduction of an in situ separation function within the reaction zone leads to complex interactions between vapor–liquid equilibrium, vapor–liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes) and chemical kinetics. Such interactions have been shown to lead to the phenomenon of multiple steady-states and complex dynamics, which have been verified in experimental laboratory and pilot plant units. We trace the development of models that have been used for design of reactive distillation columns and suggest future research directions. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Reactive distillation; Equilibrium stage model; Non-equilibrium stage model; Multiple steady-states; Maxwell–Stefan equations

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[*] Corresponding author. Tel.: + 31-20-525-7007; fax: + 31-20-525-5604.
*E-mail address:* krishna@its.chem.uva.nl (R. Krishna).

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## 1. Introduction

> The versatility of the fractionating column in the dual role of continuous reactor and separator as applied to chemical processing is well established.
> Berman, Isbenjian, Sedoff and Othmer (1948a)

The quote with which we begin this review appeared in print more than five decades ago! It provides an interesting historical perspective because in more recent times we have seen an explosion of interest in the subject of reactive distillation, and a veritable plethora of papers have appeared in the last 12 years alone. The recent interest in this process can be attributed in part to the growing commercial importance of reactive distillation, and in part to a keynote paper by Doherty and Buzad (1992), who reviewed the literature to that time. More than half of the over 300 references cited in this review have appeared after 1992. Thus, one of the objectives of this article is to provide an up-date to their work with a review of more recent developments in reactive distillation.

The term catalytic distillation is also used for such systems where a catalyst (homogeneous or heterogeneous) is used to accelerate the reaction. In this review we use the generic name reactive distillation, with the acronym RD, to cover both catalysed or uncatalysed reactions systems.

The first patents date back to the 1920s (Backhaus, 1921, 1922, 1923a,b). Early journal articles are by Keyes (1932), Leyes and Othmer (1945a,b), Schniep, Dunning and Lathrop (1945), Berman, Melnychuk & Othmer (1948b) and Berman et al. (1948a). The first publications deal mainly with homogeneous self-catalysed reactions such as esterifications, trans-esterifications, and hydrolysis. Heterogeneous catalysis in RD is a more recent development and was first described by Spes (1966).

The main focus of this review is on the modelling of RD processes. We have tried to be comprehensive in our coverage, but it would be nearly impossible to cite every paper even in this fairly well-defined niche. This review does not attempt quite such comprehensive coverage of the literature devoted more to RD catalysis and kinetics studies, although some of the works in these sub-fields necessarily are included in our review to some extent.

Descriptions of specific RD processes also are largely beyond our scope (see, for example, Sharma (1985), Stichlmair and Frey (1999) for reviews and Bart and Resil (1997) discuss an unusual application). Introductory overviews of RD and RD design and equipment are by

Fair (1998), Hauan and Hildebrandt (1999), and by Towler and Frey (2000). The non-English language literature also is less well served here. Fortunately, many of the papers in the German and Russian literature have been translated into English. Overviews of parts of the extensive Russian literature on RD (in English) are by Serafimov, Pisarenko and Timofeev (1993), Serafimov, Pisarenko and Kardona (1999a), and Timofeev, Serafimov and Solokhin (1994).

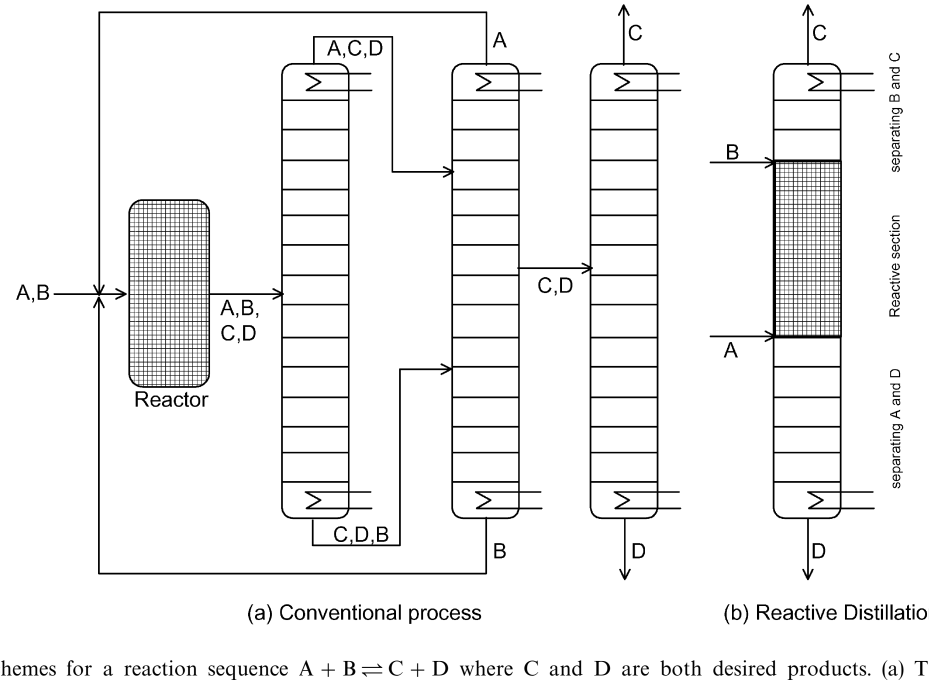
A short section on RD thermodynamics is followed by a much longer one on equilibrium (EQ) stage modelling. A brief discussion on efficiencies in RD leads to an outline of mass transfer considerations and an overview of non-equilibrium (NEQ) modelling of RD processes. We end with some comments on RD design methods. We begin, however, with an appreciation of the benefits of RD.

### 1.1. Why RD?

Let us begin by considering a reversible reaction scheme: $A + B \rightleftharpoons C + D$ where the boiling points of the components follow the sequence A, C, D and B. The traditional flow-sheet for this process consists of a reactor followed by a sequence of distillation columns; see Fig. 1(a). The mixture of A and B is fed to the reactor, where the reaction takes place in the presence of a catalyst and reaches equilibrium. A distillation train is required to produce pure products C and D. The unreacted components, A and B, are recycled back to the reactor. In practice the distillation train could be much more complex than the one portrayed in Fig. 1(a) if one or more azeotropes are formed in the mixture. The alternative RD configuration is shown in Fig. 1(b). The RD column consists of a reactive section in the middle with non-reactive rectifying and stripping sections at the top and bottom. The task of the rectifying section is to recover reactant B from the product stream C. In the stripping section, the reactant A is stripped from the product stream D. In the reactive section the products are separated in situ, driving the equilibrium to the right and preventing any undesired side reactions between the reactants A (or B) with the product C (or D). For a properly designed RD column, virtually 100% conversion can be achieved.

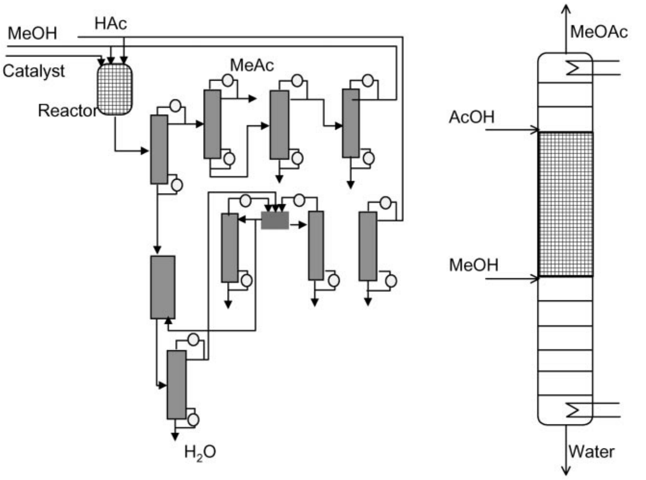
The most spectacular example of the benefits of RD is in the production of methyl acetate. The acid catalysed reaction $MeOH + AcOH \rightleftharpoons MeOAc + H_2O$ was traditionally carried out using the processing scheme shown in Fig. 2(a), which consists of one reactor and a train of nine distillation columns. In the RD implementation (see Fig. 2(b)) only one column is required and nearly 100% conversion of the reactant is achieved. The capital and operating costs are significantly reduced (Siirola, 1995).

For the acid catalysed reaction between *iso*-butene and methanol to form methyl *tert*-butyl ether: *iso*-butene + $MeOH \rightleftharpoons$ MTBE, the traditional reactor-followed-by-distillation concept is particularly complex for this case because the reaction mixture leaving the reactor forms three minimum boiling azeotropes. The RD implementation requires only one column to which the butenes feed (consisting of a mixture of *n*-butene, which is



(a) Conventional process (b) Reactive Distillation

Fig. 1. Processing schemes for a reaction sequence $A + B \rightleftharpoons C + D$ where C and D are both desired products. (a) Typical configuration of a conventional process consisting of a reactor followed by a distillation train. (b) The reactive distillation configuration. The components A, C, D and B have increasing boiling points. The reactive sections are indicated by grid lines. Adapted from Stichlmair and Frey (1999).



(a) Conventional process (b) Reactive Distillation

Fig. 2. Processing schemes for the esterification reaction $MeOH + AcOH \rightleftharpoons MeOAc + H_2O$. (a) Conventional processing scheme consisting of one reactor followed by nine distillation columns. (b) The reactive distillation configuration. The reactive sections are indicated by grid lines. Adapted from Siirola (1995).

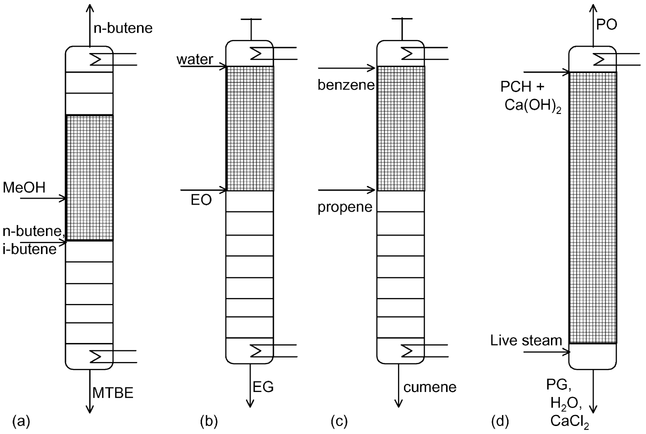


Fig. 3. (a) Reactive distillation concept for synthesis of MTBE from the acid-catalysed reaction between MeOH and iso-butene. The butene feed is a mixture of reactive iso-butene and non-reactive *n*-butene. (b) Reactive distillation concept for the hydration of ethylene oxide to ethylene glycol. (c) Reactive distillation concept for reaction between benzene and propene to form cumene. (d) Reactive distillation concept for reaction production of propylene oxide from propylene chlorohydrin and lime. The reactive sections are indicated by grid lines.

non-reactive, and *iso*-butene which is reactive) and methanol are fed near the bottom of the reactive section. The RD concept shown in Fig. 3(a) is capable of achieving close to 100% conversion of *iso*-butene and methanol, along with suppression of the formation of the unwanted dimethyl ether (Sundmacher, 1995). Also, some of the azeotropes in the mixture are "reacted away" (Doherty & Buzad, 1992).

For the hydration of ethylene oxide to mono-ethylene glycol: $EO + H_2O \rightarrow EG$, the RD concept, shown in Fig. 3(b) is advantageous for two reasons (Ciric & Gu, 1994). Firstly, the side reaction $EO + EG \rightarrow DEG$ is suppressed because the concentration of EO in the liquid-phase is kept low because of its high volatility. Secondly, the high heat of reaction is utilised to vaporise the liquid-phase mixtures on the trays. To achieve the same selectivity to EG in a conventional liquid-phase plug-flow reactor would require the use of 60% excess water (Ciric & Gu, 1994). Similar benefits are also realised for the hydration of *iso*-butene to *tert*-butanol (Velo, Puigjaner & Recasens, 1988) and hydration of 2-methyl-2-butene to *tert*-amyl alcohol (Gonzalez & Fair, 1997).

Several alkylation reactions, aromatic + olefin $\rightleftharpoons$ alkyl aromatic, are best carried out using the RD concept not only because of the shift in the reaction equilibrium due to in situ separation but also due to the fact that the undesirable side reaction, alkyl aromatic + olefin $\rightleftharpoons$ dialkyl aromatic, is suppressed. The reaction of propene with benzene to form cumene, benzene + propene $\rightleftharpoons$ Cumene (Shoemaker & Jones, 1987; see Fig. 3(c)), is advantageously carried out in a RD column because not only is the formation of the undesirable di-isopropylbenzene suppressed, but also the problems posed by high exothermicity of the reaction for operation in a conventional packed-bed reactor are avoided. Hot spots and runaway problems are alleviated in the RD concept where liquid vaporisation acts as a thermal flywheel. The alkylation of *iso*-butane to *iso*-octane, *iso*-butane + *n*-butene $\rightleftharpoons$ *iso*-octane, is another reaction that benefits from a RD implementation because in situ separation of the product prevents further alkylation: *iso*-octane + *n*-butene $\rightleftharpoons C_{12}H_{24}$ (Doherty & Buzad, 1992).

The reaction between propylene chlorohydrin (PCH) and $Ca(OH)_2$ to produce propylene oxide (PO) is best implemented in an RD column, see Fig. 3(d). Here the desired product PO is stripped from the liquid-phase by use of live steam, suppressing hydrolysis to propylene glycol (Bezzo, Bertucco, Forlin & Barolo, 1999).

Co-current gas–liquid downflow trickle-bed reactors are widely applied for hydroprocessing of heavy oils. This co-current mode of operation is disadvantageous in most hydroprocesses (Krishna & Sie, 1994), and counter-current flow of gas and liquid would be much more desirable (cf. Fig. 4). This is because reactions such as hydrodesulphurisation and hydrogenation are inhibited by hydrogen sulphide formed, even when using the so-called sulphur-tolerant catalyst of the mixed sulphide type. The removal of sulphur from heavy oil generally follows second-order kinetics in sulphur concentration, which is a reflection of the presence of a variety of sulphur containing compounds with different reactivities. The second-order kinetics imply that a relatively large proportion of sulphur is removed in an early stage of the process (due to conversion of the bulk of reactive

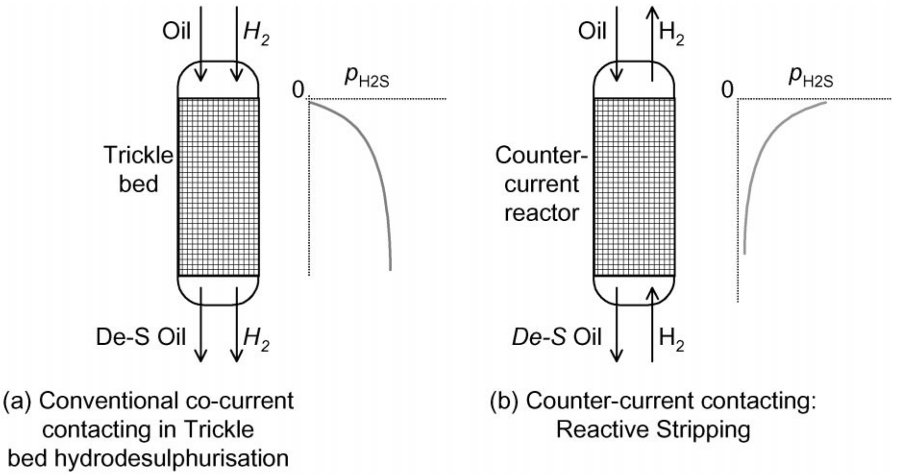


Fig. 4. Hydrodesulphurisation of gas oil carried out in (a) co-current trickle-bed reactor and (b) counter-current RD unit.

molecules) while removal of the remaining sulphur takes place much more slowly in later stages. This means that the bulk of the $H_2S$ is generated in a small inlet part of the bed and that this $H_2S$ exerts its inhibiting influence in the remaining part of the bed. Fig. 4(a) shows the partial pressure of $H_2S$ in the gas phase. It can be seen that in co-current operation the larger part of the bed operates under a $H_2S$-rich regime. The situation is clearly more favourable in the counter-current mode of operation since in this case the major part of the bed operates in the $H_2S$ lean regime. The co-current mode of operation is particularly unfavourable since the inhibiting effect is strongest in the region where the refractory compounds have to be converted, which calls for the highest activity. A similar situation exists in hydrocracking. The by-product of conversion of nitrogen containing organic compounds, viz., ammonia, is a very strong inhibitor for hydrogenation and particularly for hydrocracking reactions. For the hydrogenation of aromatics too the co-current operation is unfavourable. This is not only so from a kinetic point of view (inhibition by $H_2S$ and $NH_3$), but also because of thermodynamics (Trambouze, 1990). Deep removal of aromatics from an oil fraction generally is limited by thermodynamic equilibrium. In the co-current mode of operation the partial pressure of $H_2$ at the exit end of the reactor is lowest because of the combined effects of pressure drop, hydrogen consumption and build up of gaseous components other than $H_2$ ($H_2S$, $NH_3$, $H_2O$, light hydrocarbons).

The counter-current reactor shown in Fig. 4(b) is essentially a RD column wherein the $H_2S$ is *stripped* from the liquid-phase at the bottom and carried to the top. The quantitative advantages of the RD implementation for hydroprocessing are brought out in a design study carried out by Van Hasselt (1999). For a 20,000 bbl/d hydrodesulphurisation unit with a target conversion of 98% conversion of sulphur compounds, the catalyst volume required for a conventional trickle-bed reactor is about 600 $m^3$. For counter-current RD implementation the catalyst volume is reduced to about 450 $m^3$.

From the foregoing examples, the benefits of RD can be summarised as follows:

(a) Simplification or elimination of the separation system can lead to significant capital savings.
(b) Improved conversion of reactant approaching 100%. This increase in conversion gives a benefit in reduced recycle costs.
(c) Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.
(d) Significantly reduced catalyst requirement for the same degree of conversion.
(e) Avoidance of azeotropes. RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other. RD conditions can allow the azeotropes to be “reacted away” in a single vessel.
(f) Reduced by-product formation.
(g) Heat integration benefits. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporisation and reduce the reboiler duty.
(h) Avoidance of hot spots and runaways using liquid vaporisation as thermal fly wheel.

### 1.2. The constraints and difficulties in RD implementation

Against the above-mentioned advantages of RD, there are several constraints and foreseen difficulties (Towler & Frey, 2000):

(a) Volatility constraints. The reagents and products must have suitable volatility to maintain high concentrations of reactants and low concentrations of products in the reaction zone.

(b) Residence time requirement. If the residence time for the reaction is long, a large column size and large tray hold-ups will be needed and it may be more economic to use a reactor-separator arrangement.
(c) Scale up to large flows. It is difficult to design RD processes for very large flow rates because of liquid distribution problems in packed RD columns.
(d) Process conditions mismatch. In some processes the optimum conditions of temperature and pressure for distillation may be far from optimal for reaction and vice versa.

### *1.3. The complexity of RD*

The design and operation issues for RD systems are considerably more complex than those involved for either conventional reactors or conventional distillation columns. The introduction of an in situ separation function within the reaction zone leads to complex interactions between vapor–liquid equilibrium, vapor–liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes) and chemical kinetics. Fig. 5 shows the various transfer processes in homogeneous and heterogeneous RD. In heterogeneous RD the problem is exacerbated by the fact that these transfer processes occur at length scales varying from 1 nm (pore diameter in gels, say) to say a few meters (column dimensions); see Fig. 6. The time scales vary from 1 ms (diffusion within gels) to say a few hours (column dynamics). The phenomena at different scales interact with each other. Such interactions, along with the strong nonlinearities introduced by the coupling between diffusion and chemical kinetics in counter-current contacting, have been shown to lead to the phenomenon of multiple steady-states and complex dynamics, which have been verified in experimental laboratory and pilot plant units (Bravo, Pyhalathi & Jaervelin, 1993; Mohl et al., 1999; Rapmund, Sundmacher & Hoffmann, 1998). Successful commercialisation of RD technology requires careful attention to the modelling aspects, including column dynamics, even at the conceptual design stage (Doherty & Buzad, 1992; Roat, Downs, Vogel & Doss, 1986). As will be shown later many of the reactor and distillation paradigms do not translate easily to RD. The potential advantages of RD could be nullified by improper choice of feed stage, reflux, amount of catalyst, boilup rate, etc. Thus, it is possible to decrease conversion by increasing the amount of catalyst under certain circumstances (Higler, Taylor & Krishna, 1999b). Increased separation capability could decrease process performance (Sneesby, Tadé, Datta & Smith, 1998a).

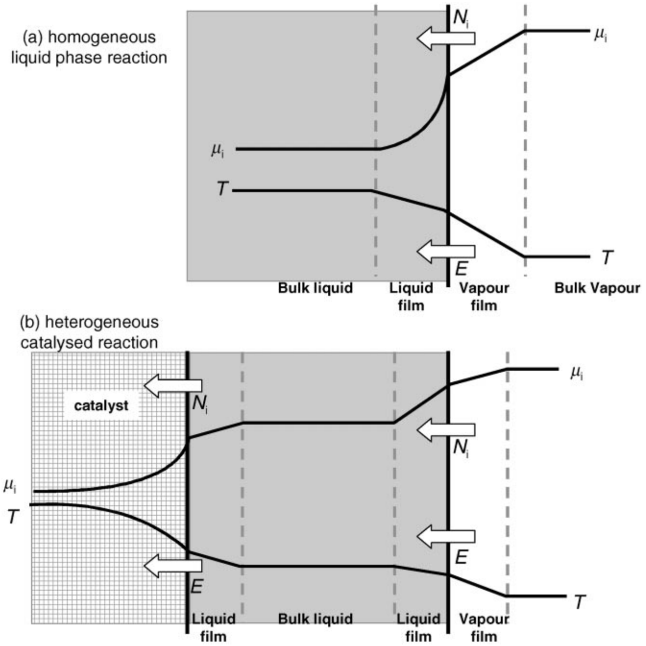


Fig. 5. Transport processes in RD. (a) homogeneous liquid-phase reaction, and (b) heterogeneous catalysed reactions. Adapted from Sundmacher (1995).

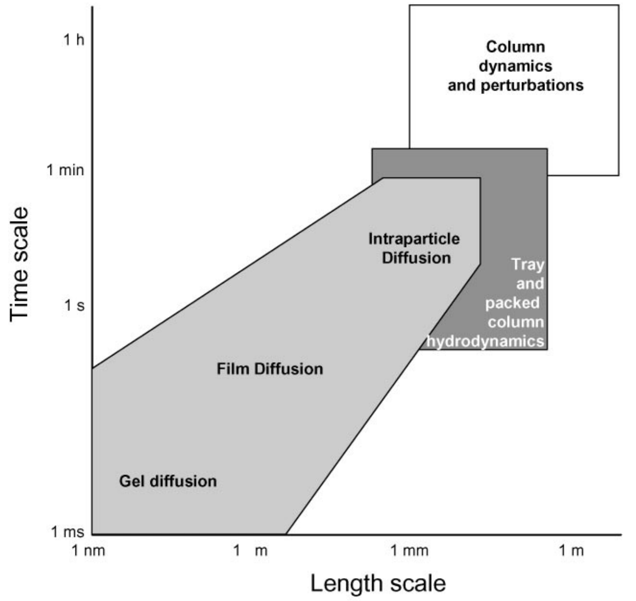


Fig. 6. Length and time scales in RD. Adapted from Sundmacher (1995).

### *1.4. Practical design considerations*

Towler and Frey (2000) have highlighted some of the practical issues in implementing a large-scale RD application. These are discussed below.

#### *1.4.1. Installation, containment and removal of the catalyst*

It is important to allow easy installation and removal of the RD equipment and catalyst. If the catalyst undergoes deactivation, the regeneration is most conveniently done ex situ and so there must be provision for easy removal and installation of catalyst particles. Reactive distillation is often passed over as a processing option because the catalyst life would require frequent shutdowns. An RD device that allowed on-stream removal of catalyst would answer this concern.

### 1.4.2. *Efficient contacting of liquid with catalyst particles*

The hardware design must ensure that the following "wish-list" is met.

(a) Good liquid distribution and avoidance of channelling. Liquid maldistribution can be expected to have a more severe effect in RD than in conventional distillation (Podrebarac, Ng & Rempel, 1998a,b).
(b) Good radial dispersion of liquid through the catalyst bed. This is required in order to avoid reactor hot-spots and runaways and allow even catalyst ageing. The requirement of good radial mixing has an impact on the choice of the packing configuration and geometry. For example, frequent criss-crossing mixing patterns may be desirable, as is realised in some hardware configurations discussed in Section 1.5.

### 1.4.3. *Good vapor/liquid contacting in the reactive zone*

If the reaction rate is fast and the reaction is equilibrium-limited then the required size of the reactive zone is strongly influenced by the effectiveness of the vapor–liquid contacting. Vapor–liquid contacting becomes less important for slower reactions. Commonly used devices for good vapor–liquid contacting are the same as for conventional distillation and include structured packing, random packing and distillation trays.

### 1.4.4. *"Low" pressure drop through the catalytically packed reactive section*

This problem arises because of the need to use small catalyst particles in the 1–3 mm range in order to avoid intra-particle diffusional limitations. Counter-current operation in catalyst beds packed with such small-sized particles has to be specially configured in order to avoid problems of excessive pressure drop and "flooding". These configurations are discussed in Section 1.5.

### 1.4.5. *Sufficient liquid hold-up in the reactive section*

The liquid hold-up, mean residence time, and liquid residence time distribution are all important in determining the conversion and selectivity of RD. This is in sharp contrast with conventional distillation where liquid hold-up and RTD are often irrelevant as the vapor–liquid mass transfer is usually "controlled" by the vapor side resistance. For trayed RD columns the preferred regime of operation would be the froth regime whereas for conventional distillation we usually adopt the spray regime.

### 1.4.6. *Designing for catalyst deactivation*

Even though, as discussed in Section 1.4.1, it is desirable to allow on-line catalyst removal and regeneration, such devices have not been commercialised as yet. Catalyst deactivation is therefore accounted for in the design stage by use of excess catalyst. Besides adding excess catalyst, the reaction severity can be increased by (a) increasing reflux, leading to increased residence time and (b) increasing reaction temperature (by increase of column pressure)

## 1.5. *Hardware aspects*

Before modelling aspects can be considered, careful attention needs to be paid to hardware design aspects. Towler and Frey (2000) have presented an excellent summary of hardware design aspects of RD columns. Some of the important issues are discussed below.

For homogeneous RD processes, counter-current vapor–liquid contacting, with sufficient degree of staging in the vapor and liquid-phases, can be achieved in a multi-tray column (cf. Fig. 7) or a column with random or structured packings (cf. Fig. 8). The hardware design information can be found in the standard sources for conventional distillation design (Lockett, 1986; Stichlmair & Fair, 1998). The Hatta number for most RD applications is expected to be smaller than about unity (Sundmacher, Rihko & Hoffmann, 1994) and the froth regime is usually to be preferred on the trays (cf. Fig. 9) because of the desire to maintain high liquid hold-up on the trays. High liquid hold-ups could be realised by use of bubble caps, reverse flow trays with additional sumps to provide ample tray residence time. In the Eastman process for methyl acetate manufacture specially designed high liquid hold-up trays are used (Agreda, Partin & Heise, 1990).

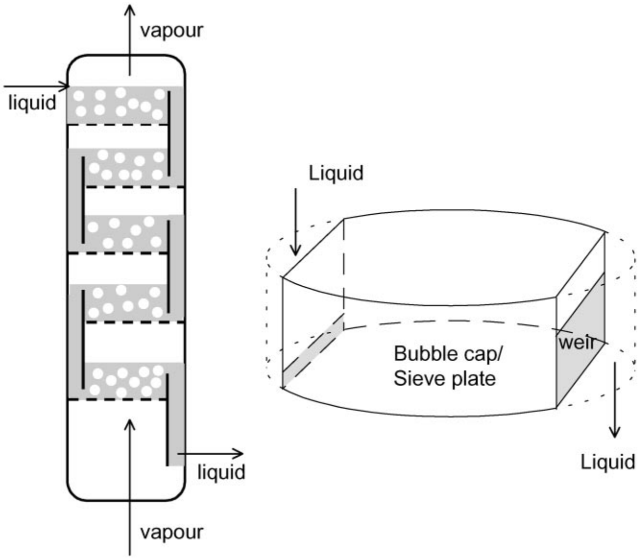


Fig. 7. Counter-current vapor–liquid contacting in trayed columns. Animations of CFD simulations of flows on the tray can be viewed on our web site: http://ct-cr4.chem.uva.nl/sievetrayCFD.

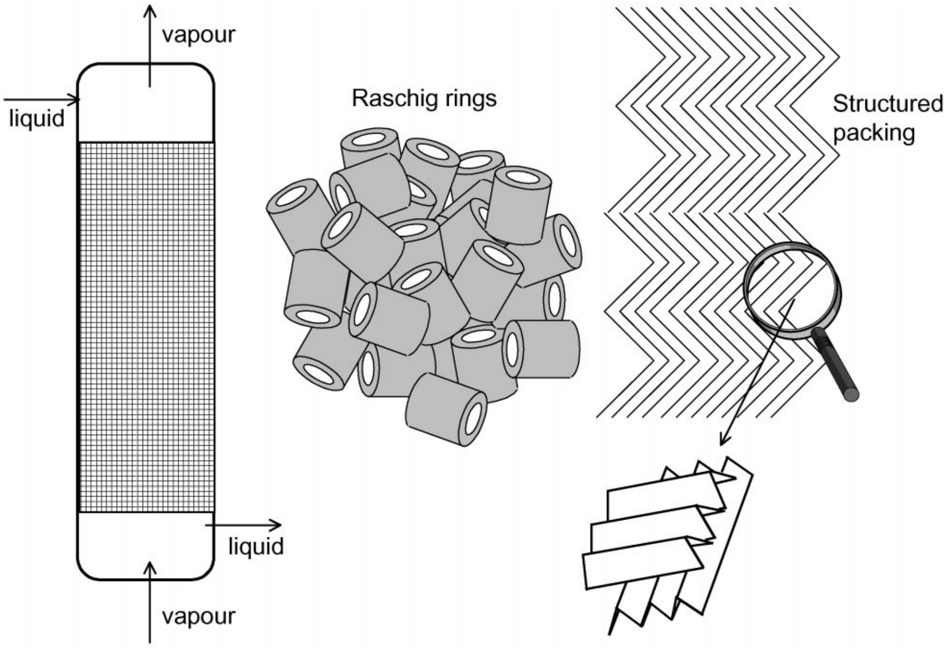


Fig. 8. Counter-current vapor–liquid contacting in packed columns.

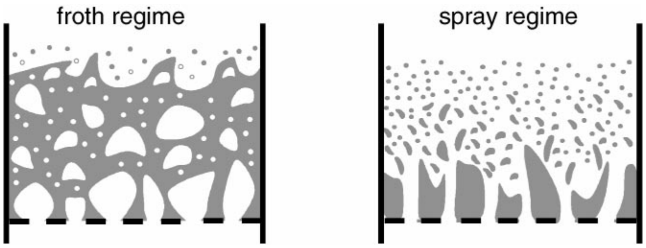


Fig. 9. Flow regimes on trays.

### 1.5.1. *Catalytically packed RD columns*

For heterogeneously catalysed processes, hardware design poses considerable challenges. The catalyst particle sizes used in such operations are usually in the 1–3 mm range. Larger particle sizes lead to intra-particle diffusion limitations. To overcome the limitations of flooding the catalyst particles have to be enveloped within wire gauze envelopes. Most commonly the catalyst envelopes are packed inside the column. Almost every conceivable shape of these catalyst envelopes has been patented; some basic shapes are shown in Figs. 10–14. These structures are:

1. Porous spheres filled with catalyst inside them (Buchholz, Pinaire & Ulowetz, 1995; Johnson, 1993); see Fig. 10(a).
2. Cylindrical shaped envelopes with catalyst inside them (Johnson, 1993); see Fig. 10(b).
3. Wire gauze envelopes with various shapes: spheres, tablets, doughnuts, etc. (Smith, 1984); see Fig. 10(c).
4. Horizontally disposed wire-mesh “gutters”, filled with catalyst (Van Hasselt, 1999); see Fig. 11(a).
5. Horizontally disposed wire-mesh tubes containing catalyst (Buchholz et al., 1995; Groten, Booker & Crossland, 1998; Hearn, 1993); see Fig. 11(b).
6. Catalyst particles enclosed in cloth wrapped in the form of bales (Johnson & Dallas, 1994; Smith, 1985). This is the configuration used by Chemical Research and Licensing in their RD technology for etherification, hydrogenation and alkylation of aromatic compounds (Shoemaker & Jones, 1987). The catalyst is held together by fibreglass cloth. Pockets are sewn into a folded cloth and then solid catalyst is loaded into the pockets. The pockets are sewn shut after loading the catalyst and the resulting belt or “catalyst quilt” is rolled with alternating layers of steel mesh to form a cylinder of “catalyst bales” as shown in Fig. 12. The steel mesh creates void volume to allow for vapor traffic and vapor/liquid contacting. Scores of these bales are installed in the reactive zone of a typical commercial RD column. Bales are piled on top of each other to give the required height necessary to achieve the desired extent of reaction. When the catalyst is spent the column is shut down and the bales are manually removed and replaced with bales containing fresh catalyst. Improvements to the catalyst bale concept have been made over the years (Johnson, 1993; Crossland, Gildert & Hearn, 1995). The hydrodynamics, kinetics, and mass transfer characteristics of bale-type packings have recently been published in the open literature (Subawalla, Gonzalez, Seibert & Fair, 1997; Xu, Zhao & Tian, 1997, 1999).

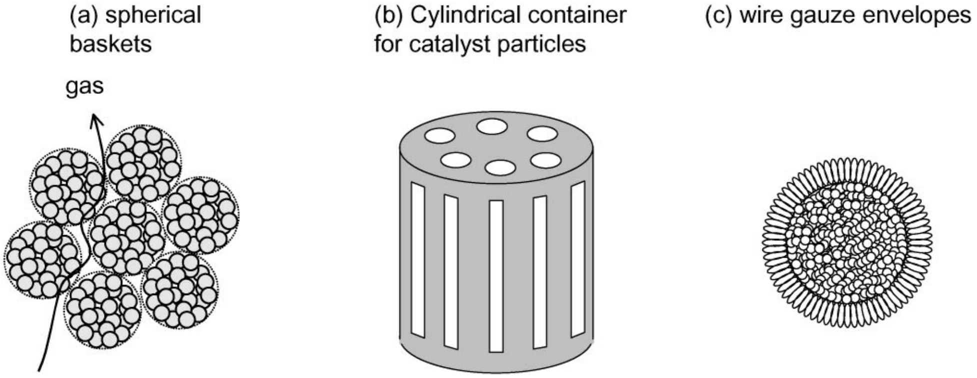


Fig. 10. Various "tea-bag" configurations. Catalyst particles need to be enveloped in wire gauze packings and placed inside RD columns.

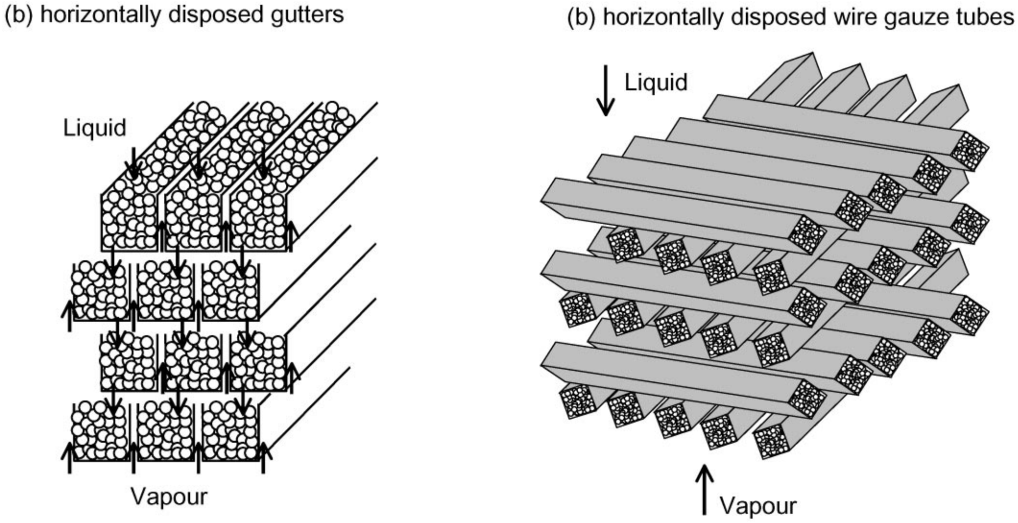


Fig. 11. Horizontally disposed (a) wire gauze gutters and (b) wire gauze tubes containing catalyst.

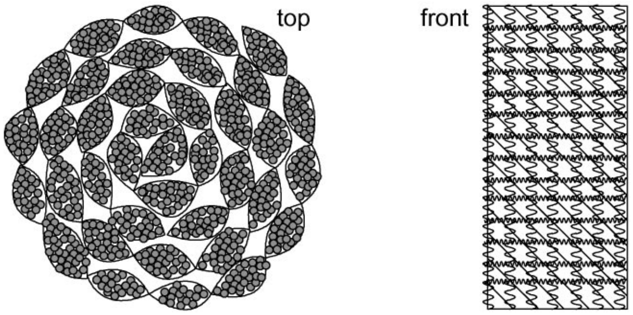


Fig. 12. Catalyst bales licensed by Chemical Research and Licensing.

7. Catalyst particles sandwiched between corrugated sheets of wire gauze (Stringaro, 1991, 1995; Gelbein & Buchholz, 1991; Johnson & Dallas, 1994); see Fig. 13. Such structures are being licensed by Sulzer (called KATAPAK-S) and Koch-Glitsch (called KATAMAX). They consist of two pieces of rectangular crimped wire gauze sealed around the edge, thereby forming a pocket of the order of 1–5 cm wide between the two screens. These catalyst "sandwiches" or "wafers" are bound together in cubes. The resulting cubes are transported to the distillation column and installed as a monolith inside the column to the required height. When the catalyst is spent, the column is shut down and the packing is manually removed and replaced with packing containing fresh catalyst. Information on the fluid dynamics, mixing and mass transfer in such structures is available in the open literature (Bart & Landschützer, 1996; Ellenberger & Krishna, 1999; DeGarmo, Parulekar and Pinjala, 1992; Higler, Krishna, Ellenberger & Taylor, 1999a; Moritz & Hasse, 1999). The important advantage of the structured catalyst sandwich structures over the catalyst bales is with respect to radial distribution of liquid. Within the catalyst sandwiches, the liquid follows a criss-crossing flow path. The radial dispersion is about an order of magnitude higher than in conventional packed beds (Van Gulijk, 1998).

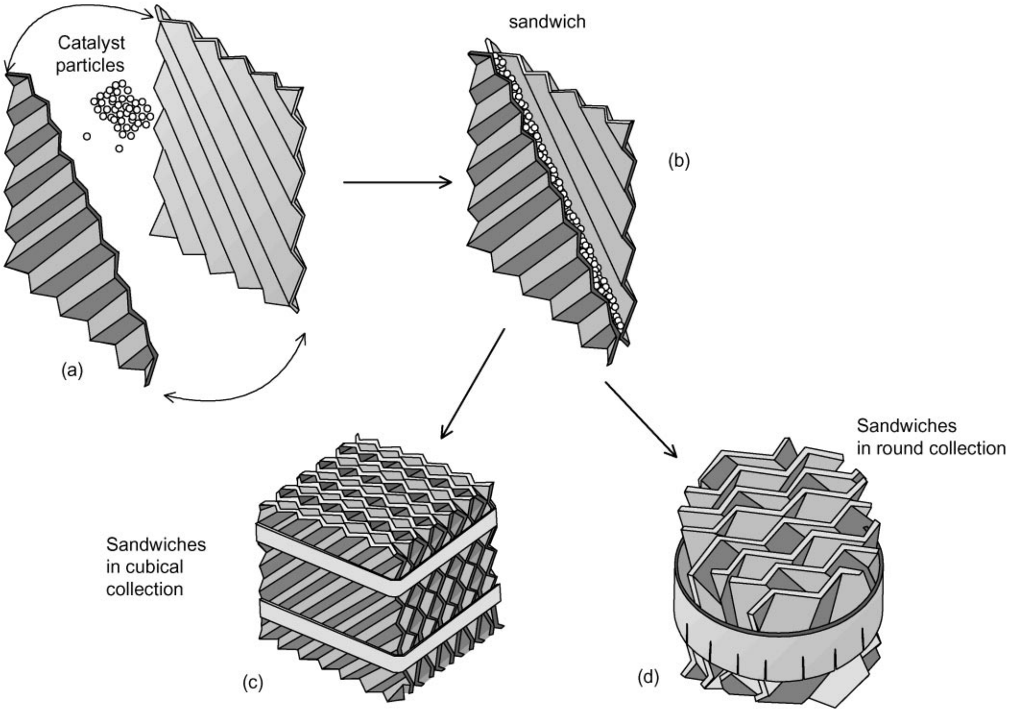


Fig. 13. Structured catalyst-sandwiches. (a) Catalyst sandwiched between two corrugated wire gauze sheets. (b) The wire gauze sheets are joined together and sewn on all four sides. (c) The sandwich elements arranged into a cubical collection. (d) The sandwich elements arranged in a round collection. Photographs of the structure, along with CFD simulations of the liquid flow within the sandwiches can be viewed at: http://ct-cr4.chem.uva.nl/strucsim.

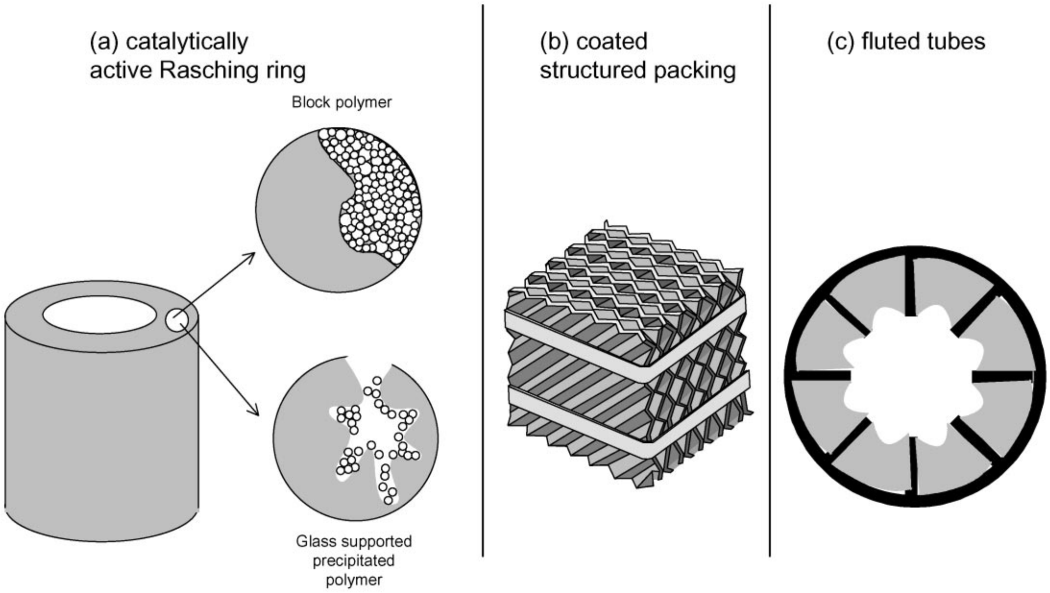


Fig. 14. (a) Catalytically active Raschig ring. Adapted from Sundmacher (1995). (b) Structured packings coated with catalyst. (c) Fluted catalyst monolith tubes.

> Furthermore, frequent criss-crossing leads to a significant improvement in mass transfer within the sandwich structures (Higler et al., 1999a).

Another alternative is to make the packing itself catalytically active. This is the strategy adopted by Flato and Hoffmann (1992) and Sundmacher and Hoffmann (1994a,b) wherein the Raschig ring-shaped packings are made catalytically active; see Fig. 14(a). The catalyst rings can be prepared by block polymerisation in the annular space. Their activity is quite high, however, osmotic swelling processes can cause breakage by producing large mechanical stresses inside the resin. An alternative configuration is the glass-supported precipitated polymer prepared by precipitation of styrene-divinylbenzene copolymer, which is subsequently activated by chlorsulphonic acid. Another possibility is to coat structured packing with zeolite catalysts (Oudshoorn, 1999); see Fig. 14(b). This concept has not been put into practice for the following reasons (Towler & Frey, 2000):

1. The amount of catalyst that can be loaded in a column in this manner is small compared to addition of catalyst pills or homogenous catalyst.
2. Coating or impregnation of catalyst materials on metal surfaces is expensive.
3. Production of catalyst materials in the shape of distillation packings is also expensive.
4. There is currently no generic manufacturing method that can economically produce different catalyst materials as coatings or structured packings.

The catalyst can also be "cast" into a monolith form and used for counter-current vapor–liquid contacting, Lebens (1999) has developed a monolith construction consisting of fluted tubes; see Fig. 14(c).

### *1.5.2. Trays or downcomers to hold catalyst particles*

The catalyst envelopes can be placed in a trayed RD column and many configurations have been proposed.

1. Vertically disposed catalyst containing envelopes can be placed along the direction of the liquid flow path across a tray (Jones, 1985); see Fig. 15. These envelopes are almost completely immersed in the froth on the tray, ensuring good contact between liquid and catalyst. Furthermore, since the vapor and liquid-phase pass along the packed catalyst in the envelopes, and not through them, the pressure drop is not excessive.
2. Catalyst envelopes can be placed within the downcomers (Carland, 1994); see Fig. 16(a). The primary drawback with installing the catalyst within downcomers is the limited volume available for catalyst inventory. Each "stage" can be regarded as a reaction device (downcomer) followed by a separation section (froth on the tray).
3. Catalyst envelopes can be placed near the exit of the downcomer (Asselineau, Mikitenko, Viltard & Zuliani, 1994); see Fig. 16(b). Catalyst inventory is necessarily limited. The vapor does not pass through the catalyst envelopes.
4. Trays and packed catalyst sections can also be used on alternate stages (Nocca, Leonard, Gaillard & Amigues, 1989, 1991; Quang, Amigues, Gaillard, Leonard & Nocca, 1989); see Fig. 16 (c). The vapor flows through the packed section through a central chimney without contacting the catalyst. The liquid from the separation trays is distributed evenly into the packed reactive section below by a distribution device.
5. Other designs have been proposed for tray columns with catalyst containing pockets or regions that are fluidised by the upflowing liquid (Quang et al., 1989; Marion, Viltard, Travers, Harter and Forestiere, 1998; Jones, 1992a,b). Catalyst attrition is a concern in a fluidised environment, but this can be taken care of by filtration of the liquid and by make-up of the catalyst.

In the tray configurations discussed above, the packed (or fluidised) catalyst containing envelopes are essentially vapor free. Furthermore, the vapor–liquid contacting efficiency can be considered practically unimpaired by

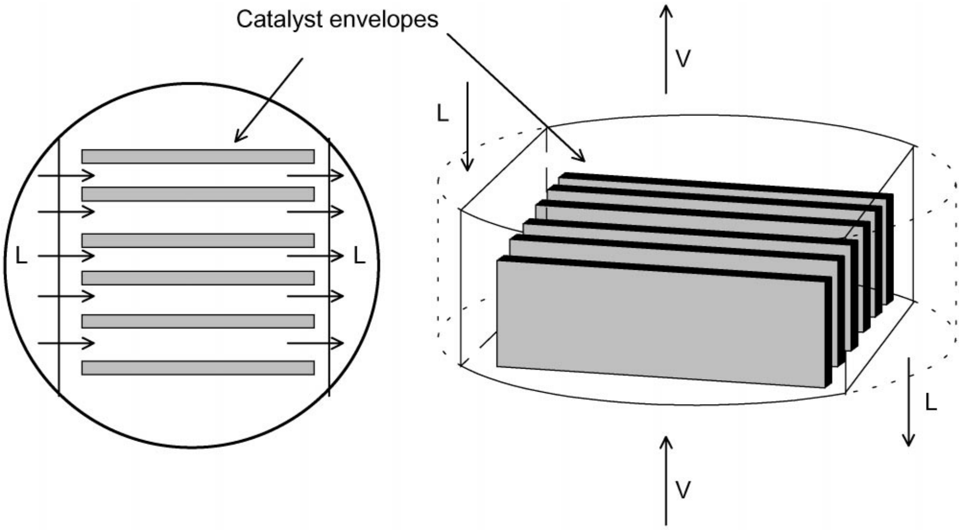


Fig. 15. Catalyst envelopes placed along the liquid flow path. For photographs of this configuration, along with CFD animations of the flow visit the web site: http://ct-cr4.chem.uva.nl/kattray.

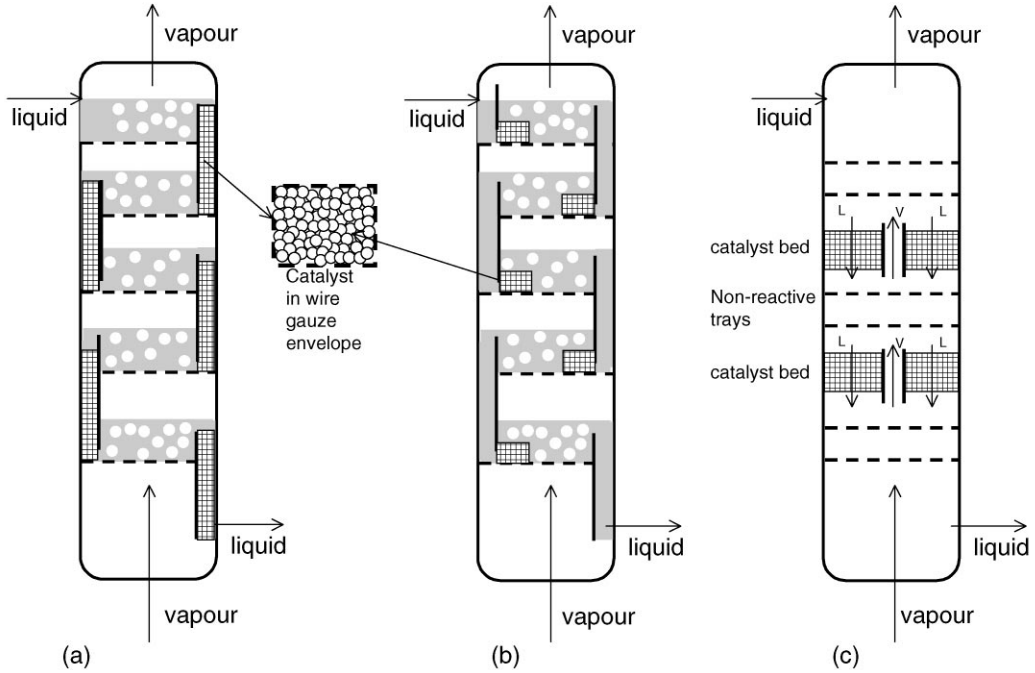


Fig. 16. Counter-current vapor–liquid–catalyst contacting in trayed columns. (a) catalyst in envelopes inside downcomers, (b) tray contacting with catalyst placed in wire gauze envelopes near the liquid exit from the downcomers and (C) alternating packed layers of catalyst and trays.

the presence of the catalyst envelopes. Therefore, standard tray design procedures (Lockett, 1986; Stichlmair & Fair, 1998) can be applied without major modification. Care must be exercised, however, in making a proper estimation of the liquid–catalyst contact time, which determines the extent of reaction on the stages.

## 2. Thermodynamics of reactive distillation

An introductory review of RD thermodynamics was provided by Frey and Stichlmair (1999a) (see, alternatively, Stichlmair & Fair, 1998).

The classical thermodynamic problem of determining the equilibrium conditions of multiple phases in equilibrium with each other is addressed in standard texts (see, e.g., Walas, 1985; Sandler, 1999) and not considered here. The equally important, and computationally more difficult, problem of finding the composition of a mixture in chemical equilibrium has also been well studied. Readers are referred to the text of Smith and Missen (1982). The combined problem of determining the equilibrium points in a multiphase mixture in the presence of *equilibrium* chemical reactions has been the subject of a recent literature review by Seider and Widagdo (1996). Two more recent developments are noted below.

Perez-Cisneros, Gani & Michelsen (1997a) discuss an interesting approach to the phase and chemical equilibrium problem. Their method uses chemical 'elements' rather than the actual components. The chemical elements are the molecule parts that remain invariant during the reaction. The actual molecules are formed from different combinations of elements. A benefit of this approach is that the chemical and physical equilibrium problem in the reactive mixture is identical to a strictly physical equilibrium model.

McDonald and Floudas (1997) present an algorithm that is theoretically guaranteed to find the global equilibrium solution, and illustrate GLOPEQ, a computer code that implements their algorithm for cases where the liquid-phase can be described by a Gibbs excess energy model.

The effect that equilibrium chemical reactions have on two-phase systems has been considered at length by Doherty and coworkers (Barbosa & Doherty, 1987a, b, 1988a–d, 1990; Doherty, 1990; Ung & Doherty, 1995a–e).

The first paper by Barbosa and Doherty (1987a) considers the influence of a single reversible chemical reaction on vapor–liquid equilibria. The second paper (Barbosa & Doherty, 1987b) introduces a set of transformed composition variables that are particularly useful in the construction of thermodynamic diagrams for reacting mixtures. For a system in which the components take part in either of the following reactions

$$A + B \rightleftharpoons C, \tag{1}$$

$$A + B \rightleftharpoons C + D \tag{2}$$

the following transformation is defined:

$$Z_i \leftarrow \frac{z_i/v_i - z_k/v_k}{v_k - v_T z_k}\,. \tag{3}$$

$z_i$ is the mole fraction of species $i$ in either the vapor or liquid-phase as appropriate and the subscript $k$ refers to the index of the reference component (one whose stoichiometric coefficient is non-zero).

In terms of the transformed composition variables the material balance equations that describe a simple open evaporation in a reacting mixture are given by

$$\frac{dX_i}{d\tau} = X_i - Y_i, \tag{4}$$

where $X_i$ is the transformed composition of species $i$ in the liquid-phase and $Y_i$ is the transformed composition for the vapor phase. $\tau$ is a dimensionless time. Numerical solution of these equations yields the *residue curves* for the system.

Barbosa and Doherty (1987a) consider two different definitions of an azeotrope and adopt the definition given by Rowlinson (1969): "A system is azeotropic when it can be distilled (or condensed) without change of composition". The conditions for the existence of a reactive azeotrope (and all other stationary points in the reactive mixture) are most easily expressed in terms of the transformed composition variables:

$$X_i = Y_i\,. \tag{5}$$

It is interesting to observe that reactive azeotropes can occur even for ideal mixtures (Barbosa & Doherty, 1987a, 1988a). Further, non-reactive azeotropes can disappear when chemical reactions occur. A reactive azeotrope has been found for the system isopropanol–isopropyl acetate–water–acetic acid (Song, Huss, Doherty & Malone, 1997). The influence the reaction equilibrium constant has on the existence and location of reactive azeotropes was investigated for single reaction systems by Okasinski and Doherty (1997a,b).

Barbosa and Doherty (1988a) provide a method for the construction of phase diagrams for reactive mixtures. Doherty (1990) develops the topological constraints for such diagrams. Ung & Doherty (1995a–e) have extended the methods of Barbosa and Doherty to deal with mixtures with arbitrary numbers of components and reactions.

The influence of homogeneous reaction kinetics on chemical phase equilibria and reactive azeotropy was discussed by Venimadhavan, Buzad, Doherty and Malone (1994) and Rev (1994). The residue curves are obtained from

$$\frac{dx_i}{dt} = \frac{V}{U}(x_i - y_i) + \sum_{j=1}^{r} r_j\Big(\nu_{i,j} - x_i \sum_{k=1}^{c} \nu_{k,j}\Big), \tag{6}$$

where $V$ is the molar flow rate in the vapor and $U$ is the molar liquid hold-up. These equations are more conveniently expressed in terms of actual mole fractions, rather than the transformed composition variables defined above. It will be apparent that the heating policy greatly influences the rate of vapor removal and the value of the equilibrium and reaction rate constants and, through this, the trajectories of the residue curves. Although it is not obvious from Eq. (6), it is the Damkohler number that emerges as the important parameter in the location of the residue curves for such systems. The Damkohler number is defined by

$$Da = \frac{Uk_1}{V}\,, \tag{7}$$

where $k_1$is a pseudo-first-order reaction rate constant. The Damkohler number is a measure for the rate of reaction relative to the rate of product removal. Low Damkohler numbers are indicative of systems that are controlled by the phase equilibrium; a high *Da* indicates a system that is approaching chemical equilibrium (see Towler & Frey, 2000).

Venimadhavan, Malone & Doherty (1999a) employed a bifurcation analysis to investigate in a systematic way the feasibility of RD for systems with multiple chemical reactions. Feasible separations are classified as a function of the Damkohler number. For the MTBE system they show that there is a critical value of the Damkohler number that leads to the disappearance of a distillation boundary. For the synthesis of isopropyl acetate there exists a critical value of the Damkohler number for the occurrence of a reactive azeotrope.

Frey and Stichlmair (1999b) describe a graphical method for the determination of reactive azeotropes in systems that do not reach equilibrium. Lee, Hauan & Westerberg (2000e) discussed circumventing reactive azeotropes.

Rev (1994) looks at the general patterns of the trajectories of residue curves of equilibrium distillation with nonequilibrium reversible reaction in the liquid-phase. Rev shows that there can be a continuous line of stationary points belonging to different ratios of the evaporation rate and reaction rate. Points on this line are called kinetic azeotropes. A reactive azeotrope exists when this line intersects with the surface determining chemical equilibrium.

Thiel, Sundmacher & Hoffmann (1997a,b) compute the residue curves for the heterogeneously catalysed RD of MTBE, TAME and ETBE and find them to have significantly different shapes to the homogeneously catalysed residue curves (Venimadhavan et al., 1994). They also note the importance of the Damkohler number and the operating pressure. These parameters influence the existence and location of fixed points in the residue curve map as seen in Fig. 17 adapted from Thiel et al. (1997a). An analysis was carried out to forecast the number of stable nodes as a function of Damkohler number and pressure.

Residue curve maps and heterogeneous kinetics in methyl acetate synthesis were measured by Song,

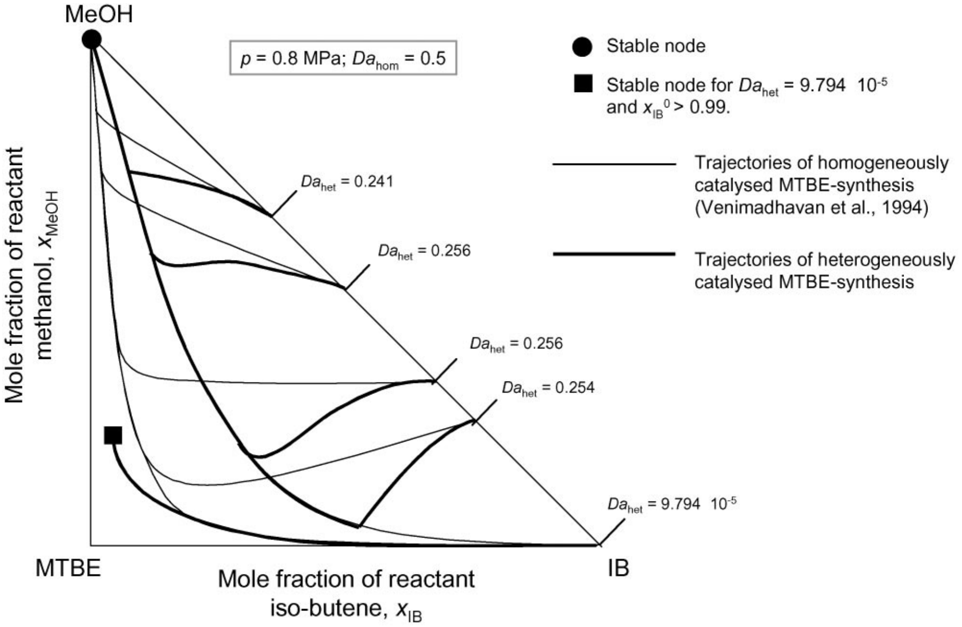


Fig. 17. Residue curves for the homogeneously and heterogeneously catalysed MTBE synthesis. After Thiel et al. (1997a).

Venimadhavan, Manning, Malone and Doherty (1998). They found that the residue curves for the kinetically controlled cases are qualitatively similar to the curves for the equilibrium case. Thus, the production of methyl acetate by RD can be carried out in either regime.

Open evaporation accompanied by liquid-phase chemical reactions has also been studied by Pisarenko, Epifanova & Serafimov (1988b) and Solokhin, Blagov, Serafimov & Timofeev (1990a,b).

## 3. Equilibrium (EQ) stage models

The development and application of the EQ stage model for conventional (i.e. non-reactive) distillation has been described in several textbooks (see, for example, Holland, 1963, 1981; Henley & Seader, 1981; Seader & Henley, 1998) and reviews (Wang & Wang, 1980; Seader, 1985; Taylor & Lucia, 1994). Here we are concerned with the extension of this standard model to distillation accompanied by chemical reaction(s).

### 3.1. The EQ stage model

A schematic diagram of an equilibrium stage is shown in Fig. 18(a). Vapor from the stage below and liquid from the stage above are brought into contact on the stage together with any fresh or recycle feeds. The vapor and liquid streams *leaving* the stage are *assumed* to be in equilibrium with each other. A complete separation process is modelled as a sequence of $s$ of these equilibrium stages (Fig. 18(b)).

The equations that model equilibrium stages are known as the MESH equations, MESH being an acronym referring to the different types of equation. The M equations are the material balance equations; the total material balance takes the form

$$\frac{\mathrm{d}U_j}{\mathrm{d}t} = V_{j+1} + L_{j-1} + F_j - (1 + r_j^V)V_j - (1 + r_j^L)L_j + \sum_{m=1}^{r} \sum_{i=1}^{c} \nu_{i,m} R_{m,j} \varepsilon_j. \tag{8}$$

$U_j$ is the hold-up on stage $j$. With very few exceptions, $U_j$ is considered to be the hold-up only of the liquid-phase. It is more important to include the hold-up of the vapor phase at higher pressures. The component material balance (neglecting the vapor hold-up) is

$$\frac{\mathrm{d}U_j x_{i,j}}{\mathrm{d}t} = V_{j+1} y_{i,j+1} + L_{j-1} x_{i,j-1} + F_j z_{i,j} - (1 + r_j^V)V_j y_{i,j} - (1 + r_j^L)L_j x_{i,j} + \sum_{m=1}^{r} \nu_{i,m} R_{m,j} \varepsilon_j \,. \tag{9}$$

In the material balance equations given above $r_j$ is the ratio of sidestream flow to interstage flow:

$$r_j^V = S_j^V / V_j, \quad r_j^L = S_j^L / L_j \,, \tag{10}$$

$\nu_{i,m}$ represents the stoichiometric coefficient of component $i$ in reaction $m$ and $\varepsilon_j$ represents the reaction volume.

The E equations are the *phase* equilibrium relations

$$y_{i,j} = K_{i,j} x_{i,j}. \tag{11}$$

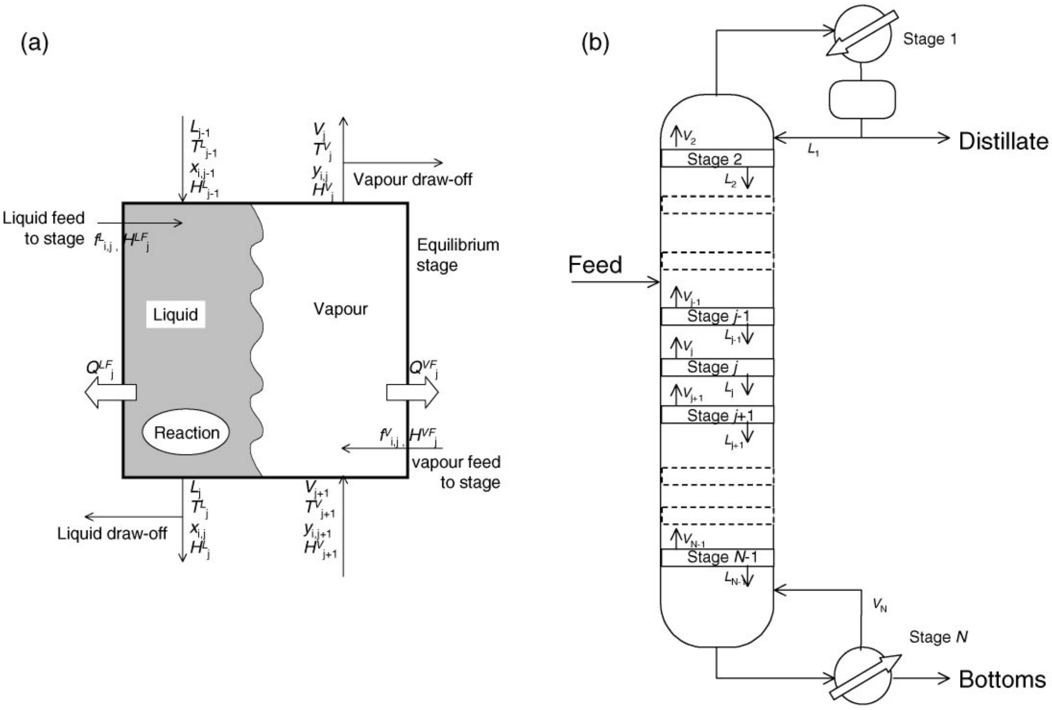


Fig. 18. (a) The equilibrium stage. (b) Multi-stage distillation column.

Chemical reaction equilibrium is not considered in many of the early papers because it is more difficult to model. There are, however, some exceptions to this statement and such works are noted below.

The S equations are the summation equations

$$\sum_{i=1}^{c} x_{i,j} = 1, \quad \sum_{i=1}^{c} y_{i,j} = 1. \tag{12}$$

The enthalpy balance is given by

$$\frac{\mathrm{d}U_j H_j}{\mathrm{d}t} = V_{j+1}H_{j+1}^V + L_{j-1}H_{j-1}^L + F_j H_j^F - (1 + r_j^V)V_j H_j^V - (1 + r_j^L)L_j H_j^L - Q_j . \tag{13}$$

The superscripted $H$'s are the enthalpies of the appropriate phase. The enthalpy in the time derivative on the left-hand side represents the total enthalpy of the stage but, for the reasons given above, this will normally be the liquid-phase enthalpy. Some authors include an additional term in the energy balance for the heat of reaction. However, if the enthalpies are referred to their elemental state then the heat of reaction is accounted for automatically and no separate term is needed.

Under steady-state conditions all of the time derivatives in the above equations are equal to zero.

Some authors include additional equations in their (mostly unsteady-state) models. For example, pressure drop, controller equations and so on.

### *3.2. Steady-state algorithms and applications*

Much of the early literature on RD modelling is concerned primarily with the development of methods for solving the steady-state EQ stage model. For the most part such methods are more or less straightforward extensions of methods that had been developed for solving conventional distillation problems. The number of examples that illustrate most of the early papers usually is rather limited, both in number as well as in the type of RD process considered (most often it is an esterification reaction). Only rarely is there any attempt to compare the results of simulations to experimental data (some exceptions are noted below). More and more of the more recent modelling studies are carried out using one or other commercial simulation package: Aspen Plus, Pro/II, HYSYS, and SpeedUp are the packages mentioned most often in the papers discussed in what follows.

Tray-to-tray calculations were carried out *by hand* by Berman et al. (1948a); Marek (1954), and Belck (1955). Marek also presents an elaborate graphical method related to the McCabe–Thiele method for conventional binary distillation. Berman et al. (1948a) considered the production of dibutyl phthalate, extensive data for which system had been reported by Berman et al. (1948b).

We may identify several classes of computer-based methods that have been developed for solving the EQ stage model equations; these methods are discussed briefly in what follows. Readers are referred to the review of Seader (1985) for background and original literature citations. Brief reviews of early RD algorithms are by Holland (1981) and by Hunek, Foldes and Sawinsky (1979).

Short-cut methods involve a number of simplifying assumptions that are made in order to derive simple approximate equations that can be used for rapid computations. It is quite difficult to derive generic short-cut procedures for RD because of the many ways in which chemical reactions influence the process (see, however, Ciric & Spencer, 1995). Bock and Wozny (1997) show that the assumption of chemical equilibrium, often made in developing short cut methods, is inappropriate for many RD processes.

Tearing methods involve dividing the model equations into groups to be solved separately. A brief description of computer based tray-to-tray calculations for the RD of ethylene oxide and water was given by Corrigan and Miller (1968). Tray-to-tray calculations and parametric studies for the simulation and optimisation of an RD column for trioxane synthesis are described by Hu, Zhou & Yuan (1999). The bubble-point method of Wang and Henke (1966) was extended by Suzuki, Yagi, Komatsu and Hirata (1971) to be able to deal with chemical reactions. Suzuki's method was used by Babcock and Clump (1978). The so-called $\theta$ method developed for conventional distillation columns by Holland and his many collaborators (see, Holland, 1963, 1981) was extended to RD operations by Komatsu and Holland (1977) and named the multi-$\theta$–$\eta$ method. The method is applied to the esterification of acetic acid. Other papers from this group are Izarraz, Bentzen, Anthony and Holland (1980) and Mommessin, Bentzen, Anthony and Holland (1980). Mommessin and Holland (1983) discuss the computational problems associated with multiple columns. Savkovic-Stevanovic, Mišic-Vukovic, Boncic-Caricic, Trišovic and Jezdic (1992) used the $\theta$ method to model an esterification of acetic acid and ethanol carried out in a glass column that was 33 mm in diameter and 1000 mm tall. The calculated temperature profile and product compositions are in good agreement with the measured quantities.

Solving all of the independent equations simultaneously using Newton's method (or a variant thereof) nowadays is an approach used very widely by authors of many of the more recent papers in this field (see, for example, Pilavachi, Schenk, Perez-Cisneros and Gani, 1997; Lee & Dudukovic, 1998). Holland (1981) provides a cursory description of this approach to RD simulation. More details and illustrative examples are to be found in the works of Block (1977); Block and Hegner (1977); Kaibel, Mayer and Seid (1979) and Simandl and Svrcek (1991).

Relaxation methods involve writing the MESH equations in unsteady-state form and integrating numerically until the steady-state solution has been found (Komatsu, 1977; Jelinek & Hlavacek, 1976). Komatsu compares his EQ stage model calculations to his own experimental data for one experiment showing that the EQ model composition profiles are qualitatively correct. The authors from Prague provide three numerical examples involving esterification processes. Relaxation methods are not often used because they are considered to be too demanding of computer time. They are, of course, closely related to dynamic models. Bogacki, Alejski & Szymanowski (1989) used the Adams–Moulton numerical integration method to integrate a simplified dynamic model that neglects the enthalpy balance to a steady-state solution. Numerical results for a single example are compared to numerical results obtained by Komatsu (1977).

There also exists a class of algorithm that really is a combination of equation tearing and simultaneous solution in that Newton's method is used to solve a subset of the MESH equations, but in which other methods are used to solve the remaining equations. Papers by Nelson (1971), Kinoshita, Hashimoto and Takamatsu (1983), and by Tierney and Riquelme (1982) fall into this category. Very few RD examples accompany these papers. Takamatsu, Hashimoto and Kinoshita (1984) and Kinoshita (1985) used a similar approach to model columns for an unusual application: heavy water enrichment using hydrophobic catalysts.

Isla and Irazoqui (1996) use Newton's method to solve the equations that model what they refer to as a "partial equilibrium" stage. However, despite the new name, theirs is essentially the same EQ model employed by almost everyone else in that the exiting streams are in phase equilibrium, but not in chemical equilibrium with each other. Parametric studies involving the effects of catalyst load and distribution, operating pressure and reflux ratio are reported.

Homotopy-continuation methods are employed most often for solving problems that are considered very difficult to solve with other methods (e.g. Newton's). For more details about this method, the reader is referred to Wayburn and Seader (1987). Homotopy-continuation was first applied to RD operations by Chang and Seader (1988). Their paper is illustrated by a number of case studies involving the esterification of acetic acid and ethanol to ethyl acetate and water. Bondy (1991) describes physical continuation approaches to solving RD problems. Lee and Dudukovic (1998) have also used homotopy continuation to solve both EQ and NEQ models of RD operations. Continuation methods are also useful for studying parametric sensitivity (see, for example, Sneesby, Tadé and Smith, 1997c) and for locating multiple steady-states (Pisarenko, Anokhina & Serafimov, 1993).

Alejski, Szymanowski and Bogacki (1988) used a minimisation method due to Powell (1965) to solve the MESH equations. This approach is, however, rather slow to converge. Numerical results for the esterification of acetic acid with ethanol were compared with data from Komatsu (1977). Komatsu carried out experiments on the esterification system of acetic acid and ethanol. The experiments were carried out in a column of 7 trays each with a single bubble cap. The trays had an inside diameter and spacing of 140 mm. Liquid-phase composition profiles are provided for five experiments. There are also 3 sets of data for a flash RD. Alejski et al. (1988), as well as Simandl and Svrcek (1991), show that the shape of the profiles obtained by the EQ model is largely in agreement with the shape of the profiles measured by Komatsu, although there are some significant quantitative differences. Alejski and Szymanowski (1988, 1989) provide a brief (in Polish) review of RD algorithms.

In a later paper Alejski (1991a) models the liquid flow across a tray by a sequence of mixing cells, each of which is considered to be a non-equilibrium cell. Departures from equilibrium were handled through the calculation (in the usual way) of the point efficiency. The model equations were solved using a relaxation method combined with Newton's method for computing the variables at each time step. A comparison between the numerical results of Alejski (1991a) obtained with an equilibrium-cells-in-series model and the experimental data of Marek (1956) shows that the assumption of complete mixing on the tray is much less successful than the multi-cell model at predicting the actual composition profiles. Marek (1956) had described a plant for the production of acetic anhydride. Experimental composition profiles are provided for a single set of operating conditions.

Alejski (1991b) investigated the steady-state properties of an RD column in which parallel reactions take place. It was assumed that reactions occur in the liquid-phase and the reactions are rate controlling. Each stage was assumed to be perfectly mixed, and the interstage flows were equimolar. The vapor leaving any stage was in physical equilibrium with the liquid in this stage. Alejksi looked at the influence of reactants' volatilities, reaction equilibrium constants, reaction rates, reflux ratio, location of feed inlets, number of theoretical stages and distillate rate upon the yield, selectivity and product distribution. As has been reported elsewhere, the column pressure is an important factor that strongly affects reaction rates by changing the column temperature profile.

Venkataraman, Chan and Boston (1990) describe the inside-out algorithm known as RADFRAC that is part of the commercial program Aspen Plus. Inside-out methods involve the introduction of new parameters into the model equations to be used as primary iteration variables. Four examples demonstrate that RADFRAC can be applied to a wide variety of reactive separation processes. RADFRAC is able to handle both equilibrium reactions as well as kinetically limited reactions. Simandl and Svrcek (1991) provide more details of their own implementation of an inside-out method for RD simulation.

RADFRAC has been used by many other authors. Quitain, Itoh & Goto (1999a) modelled a small-scale column used to produce ETBE from bioethanol. Simulation results are compared to experimental data. A second paper (Quitain, Itoh & Goto, 1999b) used RADRAC to model an industrial-scale version of the same process. Bezzo et al. (1999) used RADFRAC to study the steady-state behaviour of an actual industrial RD column producing propylene oxide from propylene chlorohydrin and calcium hydroxide. The thermodynamic properties of this system are complicated by the presence of electrolytes in the liquid-phase and by salting out effects. Reaction kinetics were modelled using the expressions reported by Carra, Santacesaria, Morbidelli and Cavalli (1979b). By adjusting the Murphree efficiency the authors were able to obtain the best possible agreement between the plant data and the simulations.

Davies, Jenkins and Dilfanian (1979) describe a variation on the standard EQ stage model that is depicted in Fig. 19. The vapor/liquid contacting section is modelled as a conventional vapor–liquid equilibrium stage (without reaction). The outgoing liquid stream passes to a reactor where chemical equilibrium is established. The stream leaving this reactor passes on to the next equilibrium stage. The disadvantage of this approach is that it fails to properly account for the influence that chemical equilibrium has on vapor–liquid equilibrium (and vice versa). The model is used to predict the temperature and composition profiles in a 76 mm diameter column in which formaldehyde is reacting with water and methanol. Good agreement between predicted and measured values

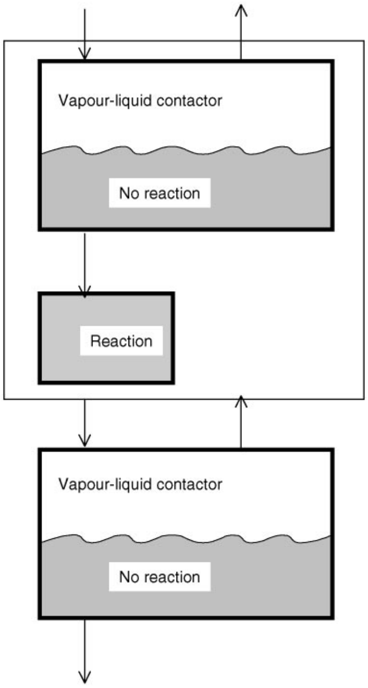


Fig. 19. Equilibrium stage model used by Davies et al. (1979).

is claimed, but the figures provided in their paper are small and hard to read.

Barbosa and Doherty (1988d) point out that the EQ stage model equations (including those that account for simultaneous phase and chemical equilibrium) can be rewritten so that they are identical in form to the EQ model equations in the absence of chemical reactions. The actual flows and compositions are replaced by the transformed flows and compositions, the latter being defined by Eq. (3). The advantage of this approach is that existing algorithms and programs can be used to solve the equations. All that is required is to replace that part of the program that carries out the phase equilibrium calculations with a new procedure that computes the phase and chemical equilibrium computation and evaluates the transformed variables.

### *3.3. Multiple steady-states with the EQ model*

Multiple steady-states (MSS) in conventional distillation have been known from simulation and theoretical studies dating back to the 1970s and have been a topic of considerable interest in the distillation community. However, it is only recently that experimental verification of their existence has been forthcoming. It is beyond the scope of this article to review this body of literature; readers are referred to Güttinger (1998) for citations of the original literature and discussions of the different kinds of multiplicity that have been found.

The first report of MSS in RD appeared in the Russian literature. Pisarenko, Epifanova and Serafimov (1988a) found three steady-states for an RD column with just one product stream, two of which were stable. Timofeev, Solokhin and Kalerin (1988) provided a simple analysis of their RD column configuration. Karpilovsky, Pisarenko and Serafimov (1997) developed an analysis of single-product columns at infinite reflux. Pisarenko et al. (1993) used homotopy methods to locate MSS in RD with more conventional configurations.

RADFRAC has been used by, among others, Jacobs and Krishna (1993); Nijhuis, Kerkhof and Mak (1993), Hauan, Hertzberg and Lien (1995, 1997), Perez-Cisneros, Schenk and Gani (1997b) and Eldarsi and Douglas (1998a) for investigation of multiplicity of steady-states in RD columns. For MTBE synthesis using the Jacobs–Krishna column configuration, shown in Fig. 20(a), varying the location of the stage to which methanol is fed results in either a high or low conversion. When the methanol is fed to stages 10 or 11, steady-state multiplicity is observed (Baur, Higler, Taylor & Krishna, 1999). Explanation for the occurrence of MSS in the MTBE process was provided by Hauan et al. (1995, 1997).

The ethylene glycol RD process also appears to be particularly interesting for the investigation of MSS. Ciric and Miao (1994) found as many as nine steady-states, but Kumar and Daoutidis (1999) found "only" five!

Güttinger and Morari (1997, 1999a,b) develop the so-called $\infty/\infty$ analysis for RD columns. The two

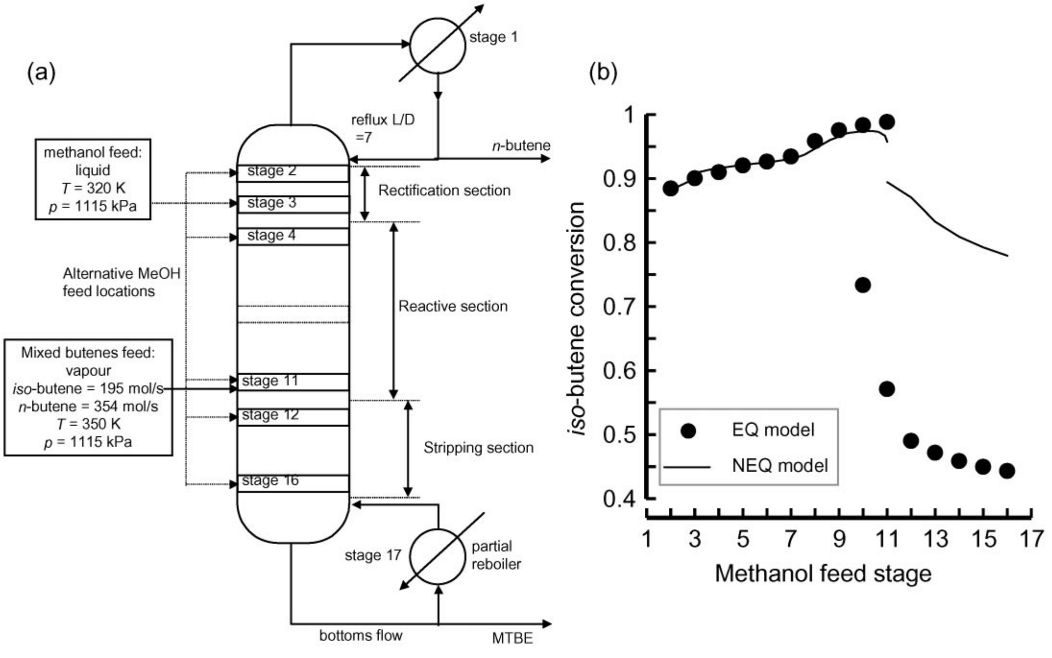


Fig. 20. (a) Configuration of the MTBE synthesis column, following Jacobs and Krishna (1993). The column consists of 17 stages. (a) High- and low-conversion branches obtained by EQ and NEQ simulations. The bottoms flow in these simulations was fixed at 203 mol/s. The details of the calculations are given in Baur et al. (1999).

infinities refer to infinite internal flow rates and an infinite number of stages and the method is for the prediction of MSS in distillation. Güttinger and Morari (1997) extended prior work of Morari and co-workers that was restricted to conventional distillation operations to develop a unified approach to the prediction of MSS in systems involving equilibrium chemical reactions. The method is applied to the MTBE process studied by others; they conclude that the MSS are easily avoided by selecting appropriate control strategies. The methodology is further refined and developed by Güttinger and Morari (1999a,b). The first of these two papers deals with what the authors call non-hybrid columns, in which the reaction is assumed to take place on every stage of the column. The second paper relaxes this restriction and considers MSS in columns with a reactive section, and non-reactive stripping and rectification sections.

Gehrke and Marquardt (1997) developed a method based on singularity theory for elucidating the possible causes of MSS in a single equilibrium stage RD process. Their method requires no analytical solution of the equations and uses homotopy methods as well as interval computing techniques to identify the highest order singularity.

Mohl et al. (1997) and Mohl, Kienle & Gilles (1998) implemented a dynamic EQ model (with Murphree-type efficiencies) in the DIVA simulator and carried out a numerical bifurcation and stability analysis on the MTBE and TAME processes. They also show that the window of opportunity for MSS to actually occur in the MTBE process is quite small. For the TAME process MSS occur in the kinetic regime and vanish when chemical equilibrium prevails. The window of opportunity for MSS in the TAME process is larger than for the MTBE process.

Experimental confirmation of MSS in RD has been provided by Thiel et al. (1997) and Rapmund et al. (1998). Mohl et al. (1999) used a pilot-scale column used to produce MTBE and TAME. Multiple steady-states were found experimentally when the column was used to produce TAME, but not in the MTBE process. The measured steady-state temperature profiles for the low and high steady-states for the TAME process are shown in Fig. 21(a). For a column operating at the low steady-state, a pulse injection of pure TAME for a short period results in a shift from the low to the higher steady-state; see Fig. 21(b).

We will have more to say on the subject of MSS in RD in a later section on NEQ modelling.

### 3.4. Primarily dynamic models and applications

Savkovic-Stevanovic (1982) put forth an unsteady-state EQ stage model of a distillation process in which one component takes part in an association reaction in both phases. Euler's method was used to integrate the differential equations. A comparison with data for the acetic acid–benzene system shows good agreement with the model, but no actual data are provided.

One of the first papers to discuss dynamic simulation of RD processes is the work of Roat et al. (1986). Their model integrates the control system equations with the column model equations. Using the Eastman methyl acetate process, they show that control schemes with good steady-state characteristics may fail under unsteady-state conditions.

Ruiz, Basualdo and Scenna (1995) describe a software package called READYS (REActive Distillation dYnamic Simulator) for which an EQ stage model is used

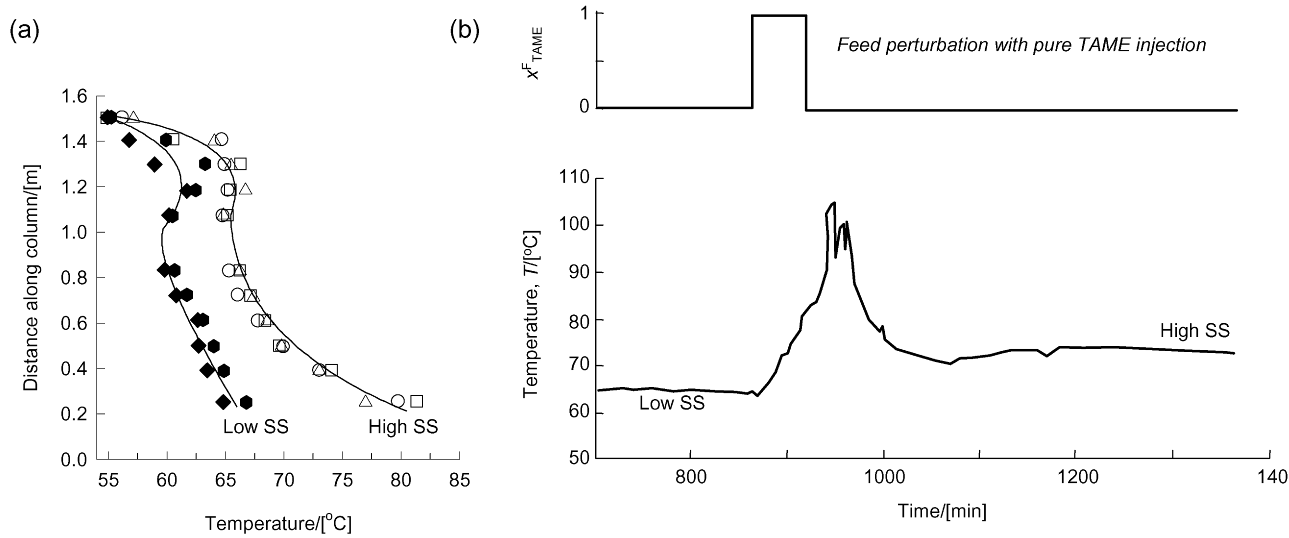


Fig. 21. (a) Multiple steady-states in TAME synthesis. Experimental data on low- and high-conversion steady-states. (b) Response of TAME column to injection of pure TAME in the feed during the period 860–920 min. The column shifts from a low steady-state to the higher one. Measurements of Mohl et al. (1999).

which adopts the assumption of physical equilibrium, ideal mixing, thermal equilibrium with a chemical reaction confined to the liquid-phase. Column hydraulics is accounted for through a pressure drop equation and departures from equilibrium can be modelled using a Murphree-type efficiency factor. Extensive numerical results are provided. The authors state that their program can be used to study unsteady and unstable column operations such as start-up, shutdown and abnormal hydraulic column behaviour. The package allows for a number of standard thermodynamic property packs as well as user-supplied models. Scenna, Ruiz and Benz (1998) employ READYS to study the start-up of RD columns. They show that the start-up policy can have a strong influence on the ultimate steady-state behaviour by sending the column to an undesirable operating point.

READYS and Aspen Plus were used by Perez-Cisneros, Schenk, Gani and Pilavachi (1996) and Perez-Cisneros et al. (1997b) who also discussed their own somewhat different approach to the EQ model. Their model uses chemical 'elements' rather than the actual components. The chemical elements are the molecule parts that remain invariant during the reaction. The actual molecules are formed from different combinations of elements. A benefit of this approach is that the chemical and physical equilibrium problem in the reactive mixture is identical to a strictly physical equilibrium model. A comparison with the RD data of Suzuki et al. (1971) is provided and it is noted that these data are difficult to match unless the "fitted" activity coefficient model is used.

Gani, Jepsen and Perez-Cisneros (1998) described a generalised reactive separation unit model. Theirs is an unsteady-state EQ stage model that can handle systems both with and without reactions and with more than two fluid phases. The methodology is quite unique in that it is based on the element approach of Perez-Cisneros et al. (1997b). Several numerical examples cover a range of simulation problems. Pilavachi et al. (1997) use the same approach, but their paper does not dwell on the computational methods; rather its focus is on some of the parameters that are important in RD modelling. For example, they discuss the effect of thermodynamic models and their parameters on RD simulation.

Abufares and Douglas (1995) use an EQ stage model for steady-state and dynamic modelling of an RD column for production of MTBE. The steady-state model is RADFRAC from Aspen Plus. The unsteady-state model equations are solved using SpeedUp, a commercial dynamic process simulation program. The focus of this paper is the transient response of the system.

Alejski and Duprat (1996) described a dynamic model for modelling kinetically controlled RD processes. The model is based on the conventional assumptions of negligible vapor-phase hold-up and perfect mixing of the two phases. Departures from phase equilibrium could be handled by specification of a vaporisation efficiency, and corrections of the conversion due to imperfect mixing are accounted for using a "conversion efficiency", the latter being calculated from an eddy diffusion model in terms of the Peclet number. The model is compared to data obtained in a pilot-scale column for the esterification of ethanol with acetic acid and sulphuric acid as homogeneous catalyst. Column start-up and disturbances of continuous operation were investigated. The dynamic temperature profiles are in reasonable agreement with the data, but the predicted dynamic concentration profiles are very different from the observed profiles. Alejski and Duprat (1996) also recommend that tray hydraulics be accounted for in any dynamic model of RD.

Schrans, de Wolf & Baur (1996) carried out dynamic simulations, using SPEEDUP, of the MTBE synthesis process using essentially the Jacobs–Krishna column configuration shown in Fig. 20(a). Their simulations showed that increase in the *iso*-butene feed by 4% leads to oscillatory behaviour. A further increase of *iso*-butene feed by 5% causes a jump from the high-conversion steady-state to the lower one. Hauan, Schrans and Lien (1997) also showed oscillatory behaviour and suggested that it is due to an internal recycle of MTBE in the reactive zone.

Sneesby, Tadé, Datta & Smith (1997a) model the synthesis of ETBE using an EQ stage model that they solve with SpeedUp. Simulation results are compared to results obtained with the commercial simulation program Pro/II. Homotopy methods are used to investigate the effects of important design variables (feed composition, ethanol excess, pressure, number of equilibrium stages — reactive or non-reactive, reboiler duty and so on). A process design methodology is suggested. In a companion paper Sneesby, Tadé, Datta and Smith (1997b) develop a dynamic model of the same process using SpeedUp. Their dynamic model assumes that reaction equilibrium is attained on all stages, neglecting reaction kinetics. The authors recommend including control issues early in the design process. Subsequent papers from this group look at multiple steady-states in RD (Sneesby, Tadé & Smith, 1998c–e). Sneesby et al. (1998d) (as well as Bartlett and Wahnschafft (1998) using RADFRAC) report that the transition from one steady-state to another can be prevented using appropriate control strategies. Sneesby et al. (1998a) show that an increase in fractionation (by increasing reflux ratios, or numbers of equilibrium stages) does not always lead to improved performance of RD columns. This is exactly opposite to the situation in conventional distillation.

Espinosa, Martinez and Perez (1994) presented a simplified dynamic model for an RD column. Vapor hold-ups, heat losses to the environment and the heat of reaction were neglected. In addition, equimolar overflow and physical and chemical equilibrium were assumed. The resulting equations were rewritten in terms of the transformed variables presented by Barbosa and Doherty (1987b). In order to save calculation time, the order of the model was reduced using an orthogonal collocation method. Some calculations were done for an ideal quaternary system. The reduced order model was verified against a "rigorous" model and a reasonably good match was found. No extensive numerical dynamic data are presented.

Grosser, Doherty and Malone (1987) use a dynamic model based on the following assumptions:

- the mixture reaches reaction and phase equilibrium instantaneously on each tray;
- the solutions are dilute (thus the temperature change can be ignored);
- the liquid hold-up is constant on each tray (the vapor hold-up is ignored);
- constant molar overflow (modified somewhat) relates the flows from stage to stage.

They study the separation by RD of close-boiling mixtures such as mixtures of xylenes, C4 hydrocarbons, and chlorobenzenes. They report that RD is an attractive alternative to conventional distillation when the relative volatility is less than 1.06. RD of close-boiling mixtures has also been studied by Terrill, Sylvestre and Doherty (1985) who suggest that it is possible to separate *m*- and *p*-xylene using sodium in a column with very few equilibrium stages. Cleary and Doherty (1985) provided experimental support for this conclusion.

Kumar and Daoutidis (1999) presented a comprehensive dynamic EQ stage model of an ethylene glycol RD column. They compare a model that includes vapor-phase balances to a more conventional model that ignores the vapor hold-up and suggest that it is important to include the vapor phase in order to more accurately model the process dynamics. The major thrust of this work is the design of a control system that performs well with stability in the high-purity region.

Moe, Hauan, Lien and Hertzberg (1995) discuss possible numerical problems when developing dynamic models of RD based on phase and chemical equilibrium principles.

### 3.5. *Batch reactive distillation*

Batch reactive distillation, an inherently unsteady-state process has been studied by Corrigan and Ferris (1969), Egly, Ruby and Seid (1979), Cuille and Reklaitis (1986), Reuter, Wozny and Jeromin (1989), Albet, Le Lann, Joulia and Koehret (1991); Machietto and Mujtaba (1992); Mujtaba and Machietto (1992); Sørensen and Skogestad (1992, 1994); Sørensen, Machietto, Stuart and Skogestad (1996); Patlasov (1996); Bollyn and Wright (1998); Xu and Dudukovic (1999) and Wajge and Reklaitis (1999), and Venimadhavan, Malone and Doherty (1999b).

Corrigan and Ferris (1969) provided a limited quantity of data for the methanol acetic acid esterification reaction in an Oldershaw column. The paper does not include any attempt at modelling the process. The models of Albet et al. (1991) and of Mujtaba and Machietto (1992) allow for changes in the component hold-ups but assume constant liquid molar hold-ups. These models also use steady-state energy balances. Reuter, Wozny and Jeromin (1989) develop the most complete EQ stage model of batch RD that includes the hold-up of both phases and process controller equations. A relaxation method is used to solve the unsteady-state model equations while Newton's method is used to solve the steady-state equations at each time step. A comparison with some dynamic product composition data for a transesterification plant shows good agreement with the calculated product composition. Cuille and Reklaitis (1986) neglect the vapor-phase hold-up, assume that the volumetric hold-up on each stage is constant, and assume pressure drops and stage efficiencies to be constant. The DAE system was solved using the LSODI numerical integration routine. Egly et al. (1979), Machietto and Mujtaba (1992), and Mujtaba and Machietto (1992) look at the optimal design and operation of batch RD.

Sørensen and Skogestad (1992, 1994) and Sørensen et al. (1996) consider the controllability of batch RD. Bollyn and Wright (1998) develop a model of a batch RD process for the synthesis of the ethyl ester of pentenoic acid. In this process the reaction occurs only in the reboiler and not at all in the column itself. Thus, the model is somewhat simpler than other dynamic models that are discussed here. Xu and Dudukovic (1999) developed a dynamic model for semi-batch photo RD. The DAE equations that formed their model were solved using the LSODI routine. Wajge and Reklaitis (1999) describe in detail a package called RDBOPT for the design of operation policies for reactive batch distillation. The model is essentially the same as that used by Cuille and Reklaitis (1986), but the DAE system of model equations is solved using the DASPK solver.

Venimadhavan et al. (1999b) examined a novel distillate policy and propose a new reflux policy for equimolar reactions. For the special case of butyl acetate production the new policies lead to complete conversion of the reactants and high-purity products that are unobtainable by conventional methods.

### 3.6. *Primarily experimental papers*

In addition to the papers cited above, there are some others whose main thrust is on providing experimental data, and in which the modelling activity provides only a supporting role.

Carra et al. (1979b) and Carra, Morbidelli, Santacesaria & Buzzi (1979a) studied the synthesis of propylene oxide from propylene chlorohydrins in an RD column. Reaction kinetics of this reaction were derived and presented in the first paper; A limited quantity of column data is reported in their second paper. Few details of the column design are given other than to say the column was a continuous multistage micropilot column. The authors used Newton's method to solve the equations that model the synthesis of propylene oxide from propylene chlorohydrins in an RD column. A good match was found between simulation results and top and bottom stream composition data obtained in the two experiments for which they provide data. However, it must be remembered that matching only top and bottom compositions is not a particularly good test of a complete column model. A much more demanding test is to be able to predict observed composition profiles along the length of a column.

Neumann and Sasson (1984) used the method of Suzuki et al. (1971) to model the production of methyl acetate by methanol esterification in a small-scale column packed with an acidic organic acid polymer catalyst. A limited quantity of experimental data is included in the paper.

Duprat and Gau (1991b) study the separation of close-boiling mixtures using RD. The process studied is the separation of 3-picoline and 4-picoline through complexation with trifluroacetic acid. Newton's method was used to solve the EQ stage model equations. A companion paper (Duprat & Gau, 1991a) provides equilibrium data for this system. RD of close-boiling mixtures (*m*- and *p*-xylene) has also been studied by Saito, Michishita & Maeda (1971).

Fuchigami (1990) reported top and bottom column temperature and composition data for 13 experiments for the methyl acetate process carried out in a laboratory-scale column. No attempt to model the column is provided.

Flato and Hoffmann (1992) discuss the development and start-up of a small-scale packed distillation column for the production of MTBE. The manufacture of the Raschig ring-shaped packing elements is described in some detail, as is the control system installed around their column. Experimental results are provided for the mole percent of MTBE as a function of time, the *iso*-butene conversion and MTBE selectivity as a function of methanol/*iso*-butene ratio in the feed, and data showing the effect of pressure on *iso*-butene conversion.

Krafczyk and Ghmeling (1994) used RADFRAC to model an experimental column with 2 m of KATAPAK-S with bubble cap trays above and below. The main goal of this study was to test the feasibility of heterogeneous RD for methyl acetate production. No data are provided that could be useful to other investigators.

Bravo et al. (1993) provide some preliminary results obtained from a catalytic distillation pilot plant used to produce TAME. The pilot-scale column was 11 m in height and 15 cm in diameter. The catalyst was Amberlite XAD ion-exchange resin. Composition profiles are provided for a few experimental runs. Some of the experiments show composition profiles that appear almost flat, indicating little composition change from stage to stage. Pekkanen (1995a) refers to such regions as "reactive pinches". The experiments were simulated with the proprietary simulation program FLOWBAT, but comparisons with the data are provided for only one experiment. Insufficient data are available for others to attempt a simulation using anything other than an EQ model.

Bart and Reidetschlager (1995) used RADFRAC to model experiments involving the esterification of succinic anhydride with methanol to produce dimethyl succinate and water in laboratory-scale column. When tray efficiencies were specified, the simulations could be made to agree with the experimental composition profiles. Simulations are used to compare the performance of several different plant designs. They suggest that a standard RD column is preferable to a reactor/column for fast reactions and high relative volatilities.

Acetalisation of formaldehyde with methanol in batch and continuous RD columns was studied by Kolah, Mahajani & Sharma (1996). Their paper provides more data than usually is the case in experimental papers. The column was modelled using the transformed composition approach of Ung & Doherty (1995), with the calculation of the minimum reflux and of the number of stages.

Gonzalez and Fair (1997) present data for the production of *tert*-amyl-alcohol from water and iso-amylenes. Their paper provides an unusually comprehensive description of the experimental work carried out. The RD column has an internal diameter of 5.1 cm and a total length of 2.25 m. The column was loaded with bales of catalytic packing similar to that shown in Fig. 12. In some of their experiments the column was loaded with 6 bales, in others just 2, the rest of the column being filled with Sulzer BX gauze packing. An important conclusion from their experimental work is that over design of an RD column can lead to unacceptably low yields of the desired products, with correspondingly high yields of undesired products. Gonzalez, Subawalla and Fair (1997) used the RADFRAC model in Aspen Plus to simulate the process. The simulation results were in reasonable agreement with the data. A parametric study showed the effect of varying the feed composition and other important operational parameters.

Gaspillo, Abella and Goto (1999) studied experimentally the dehydrogenation of 2-propanol to acetone and hydrogen in a small-scale RD column. The separation of acetone from 2-propanol is strongly influenced by the feed flow rate, the reflux ratio, and the temperature of the heat source. The motivation for the study was to investigate the possibility of using the system in chemical heat pump.

### 3.7. Use of efficiencies in RD models

Some authors (e.g. Reuter et al., 1989; Ruiz et al., 1995; Isla & Irazoqui, 1996; Lee & Dudukovic, 1998) use a modified EQ stage model in which the phase equilibrium equations incorporate a stage efficiency factor. There are many different definitions of the stage efficiency; that of Murphree is most often used in EQ stage simulation:

$$E_i^{MV} = \frac{\overline{y_{iL}} - y_{iE}}{y_i^* - y_{iE}}; \; i = 1,2,\ldots,n, \tag{14}$$

where $\overline{y_{iL}}$ is the average composition of the vapor leaving the tray, $y_{iE}$ is the composition of the vapor entering the tray and $y_i^*$ is the composition of the vapor in equilibrium with the liquid leaving the tray. Since the mole fractions add to unity, only $(n-1)$ of the Murphree component efficiencies are independent. For distillation of systems with three or more species, the component efficiencies are almost always unequal to one another and these can routinely assume values greater than unity or less than zero (Taylor & Krishna, 1993). Ilme, Keskinen, Markkanen & Aittamaa (1997) simulated an industrial MTBE (non-reactive) distillation column using an EQ stage model using a more rigorous multicomponent (matrix) efficiency prediction method; this paper illustrates the complex nature of component efficiencies. For packed columns it is common to use the height equivalent to a theoretical plate (HETP). The behaviour of HETPs in multicomponent mixtures is closely related to the behaviour of stage efficiencies.

To the best of our knowledge there are no fundamentally sound methods for estimating either efficiencies or HETPs in RD operations. Davies et al. (1979) employed a conventional binary efficiency prediction method in the absence of anything better. In general, the presence of chemical reactions will have an influence on the component efficiencies. This is illustrated by calculations of the component efficiencies for an RD column for hydration of ethylene oxide (EO) with water to mono-ethylene glycol (EG). In situ distillation is used to suppress the unwanted side reaction to diethylene glycol (DEG) produced from the reaction EO + EG → DEG. Using a rigorous non-equilibrium (NEQ) model (discussed below), the component efficiencies were calculated for an RD column (using the configuration described by Baur et al., 1999) and also for a column in which the reactions were deliberately suppressed. The component efficiencies for EO, Water, EG and DEG, calculated from the NEQ model are shown in Fig. 22 with filled symbols for the RD case and with open symbols for the non-reactive case. For the non-reactive column the component efficiencies are close to one another and in the range 0.5–0.65. The smallest molecule, water, has the highest component efficiency. The component efficiencies of EO and EG lie in between those of water and DEG. For RD operation, the component efficiencies show great variation between the different components. Clearly, chemical reactions influence the values of the component efficiencies in a complex and unpredictable way. This aspect has also been highlighted in the simulations presented by Higler, Taylor and Krishna (1998).

For a more complete understanding of RD processes it is necessary to consider in detail the interaction between mass transfer and chemical reaction. We take up this subject next.

## 4. Mass transfer

For the purposes of this discussion it suffices to adopt a film model description of the transport processes in RD. Representative film profiles for homogeneous systems are shown in Fig. 5(a), and for heterogeneous systems in Fig. 5(b).

In homogeneous RD processes the reaction takes place only in the liquid-phase. If it is sufficiently rapid, the reaction will also take place in the liquid film adjacent to the phase interface. Very fast reactions may occur only in the film. A slow reaction also takes place in the film but its influence on the mass transfer process can safely be ignored.

The most fundamentally sound way to model mass transfer in multicomponent systems is to use the Maxwell–Stefan theory (see Krishna & Wesselingh, 1997; Taylor & Krishna, 1993). The Maxwell–Stefan equations for mass transfer in the vapor and liquid-phases respectively are given by

$$\frac{y_i}{\mathbb{R}T^V}\frac{\partial \mu_i^V}{\partial z} = \sum_{k=1}^{c} \frac{y_i N_k^V - y_k N_i^V}{c_t^V Đ_{i,k}^V} \tag{15}$$

and

$$\frac{x_i}{\mathbb{R}T^L}\frac{\partial \mu_i^L}{\partial z} = \sum_{k=1}^{c} \frac{x_i N_k^L - x_k N_i^L}{c_t^L Đ_{i,k}^L}, \tag{16}$$

where $x_i$ and $y_i$ are the mole fractions of species $i$ in the liquid and vapor phases, respectively. The $Đ_{i,k}$ represents the corresponding Maxwell–Stefan diffusivity of the $i-k$ pair in the appropriate phase. Only $c-1$ of Eqs. (15) and (16) are independent; the mole fraction of the last component is obtained by the summation equations for both phases. At the vapor–liquid interface we have the continuity equations

$$\mathbb{N}_i^V|_I = \mathbb{N}_i^L|_I\,. \tag{17}$$

For a homogeneous system, the molar fluxes in the liquid film may change due to any chemical reaction that takes place there

$$\frac{\partial N_i}{\partial z} = \sum_{m=1}^{r} v_{i,m} R_m\,. \tag{18}$$

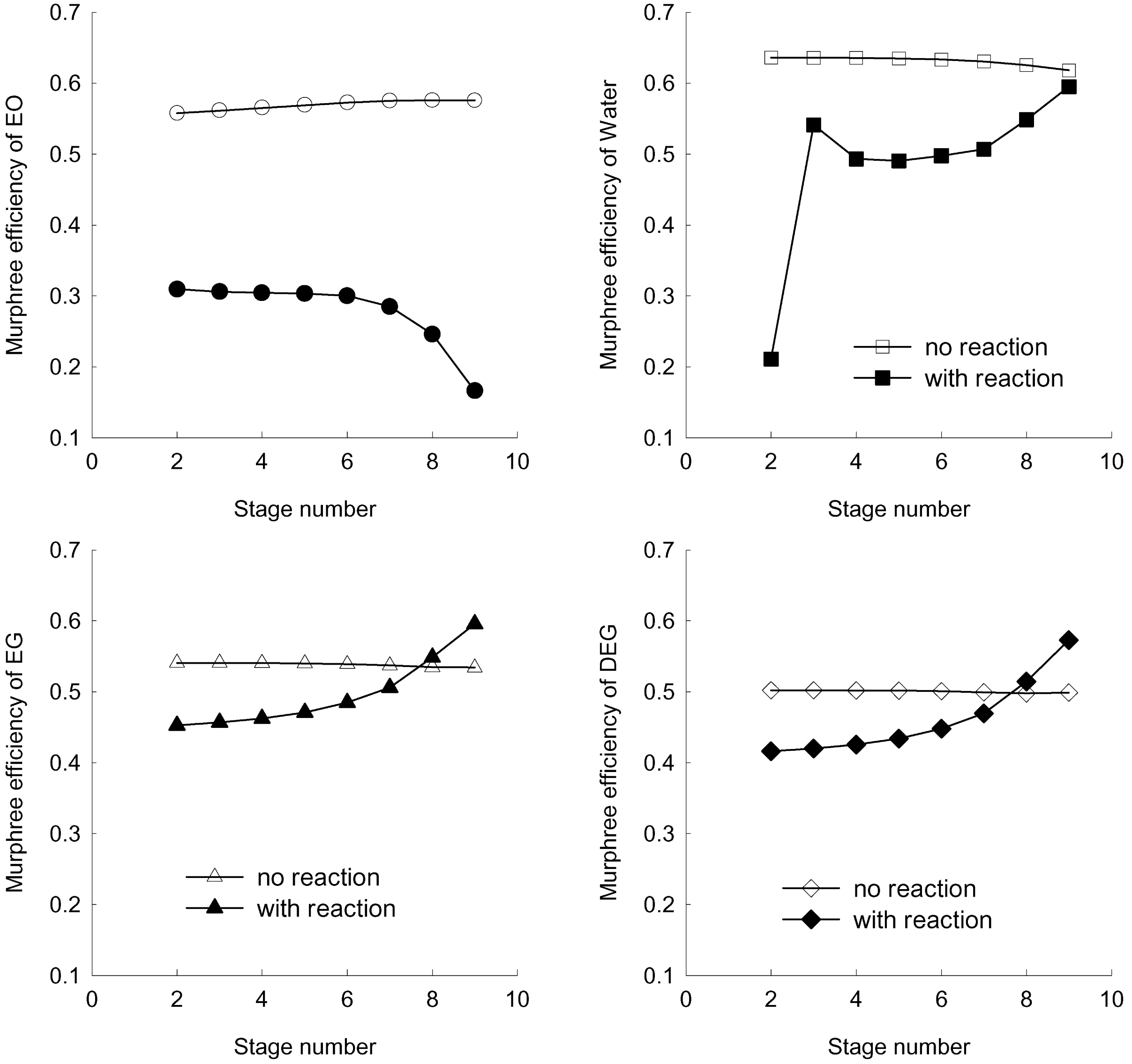


Fig. 22. Component efficiencies for EO, water, EG and DEG for reactive and non-reactive operation. The RD column configuration is shown in Fig. 24(a). Unpublished results of Baur, Taylor and Krishna (2000).

For most reactive distillations the change in the fluxes through the film will not be significant because the Hatta numbers are smaller than unity (Sundmacher et al., 1994). The composition profile with the "diffusion" film will be nearly linear. For other reactive separation processes (e.g. reactive absorption) the composition change in the film will be very important. It will not always be clear in advance in which regime a particular process will be operating, and the regime may even vary from stage to stage. Thus, the most general approach is to solve the MS and continuity equations simultaneously for all cases involving homogeneous reactions.

Eqs. (16) and (18) form a system of non-linear coupled differential equations that must be solved numerically in most cases. Frank, Kuipers, Versteeg and van Swaaij (1995b) and Frank, Kuipers, Krishna and van Swaaij (1995a) provide perhaps the most comprehensive study of simultaneous mass (and heat) transfer with chemical reaction modelled using the MS equations. They report that thermal effects can affect mass transfer rates by as much as a factor of 30!

In view of their complexity, the MS equations sometimes are written in greatly simplified form

$$N_i = -\, c_t D_{i,\mathrm{eff}} \frac{\partial x_i}{\partial z}\,. \tag{19}$$

This expression ignores the coupling between the species gradients as well as mass transfer by convection. $D_{i,\mathrm{eff}}$ is an effective diffusivity and it should be regarded as a function of the binary MS diffusion coefficients, the mixture composition, and the mass transfer rates themselves. However, if, as is usually done, we assume the effective diffusivity to be constant, then analytical solutions to Eqs. (18) and (19) may be derived. Indeed, the literature on mass transfer with chemical reaction based on these two equations is vast and such equations often are used. Results usually are expressed in the form

$$N_i^L = k_i E_i (x_i^I - x_i^L), \tag{20}$$

where $k_i$ is the mass transfer coefficient and $E_i$ is an enhancement factor that accounts for the influence of chemical reaction on the molar fluxes. Among other things, enhancement factors depend quite strongly on the reaction kinetics; thus, there is no universal expression for $E_i$ that can be used in all situations. Indeed, in many cases it is not even possible to obtain analytical expressions for the enhancement factor, even for the much-simplified constitutive relation given by Eq. (19). Danckwerts (1970) and Van Swaaij and Versteeg (1992) review the field of mass transfer with chemical reaction. Frank, Kuipers, Krishna and van Swaaij (1995a) cite other studies of non-isothermal mass transfer with simultaneous chemical reaction modelled using the simpler constitutive relation given by Eq. (19). Effective diffusivity models of this sort have been used with some success in the modelling of amine-based gas treating processes (see, for example, Cornelisse, Beenackers, van Beckum & van Swaaij, 1980; Carey, Hermes & Rochelle, 1991; Altiqi, Sabri, Bouhamra & Alper, 1994 and the extensive lists of references in these papers).

A more rigorous approach to modelling mass transfer in multicomponent systems is afforded by the generalized Fick's law:

$$J_i = -c_t \sum_{k=1}^{c-1} D_{i,k} \frac{\partial x_i}{\partial z}, \tag{21}$$

where $J_i$ is the molar diffusion flux of species $i\,(N_i = J_i + x_i N_t)$ and the $D_{i,k}$ are the Fick diffusion coefficients for the multicomponent mixture. The Fick diffusion coefficients can be related to the binary MS diffusion coefficients; see Taylor and Krishna (1993) for details of this. Solutions of Eq. (21) and the continuity equation (18) are known for a few cases involving simultaneous diffusion and reaction (see, for example, Toor, 1965; Kenig & Gorak, 1995, 1997). In most cases of practical significance Eq. (21) is just as difficult to solve as the full MS equations and it is necessary to employ numerical methods here as well.

A rigorous approach to modelling heterogeneous systems (Fig. 5(b)) would involve a complete description of mass transport to the catalyst and diffusion and reaction inside the catalyst particles, if the catalyst is porous, or reaction at the surface if it is not. In either case it is unnecessary to allow for reaction in the vapor or liquid films as described above.

For all cases involving a heterogeneous reaction we may model transport through the vapor–liquid interface using the MS equations given above (assuming no reaction in the liquid film). We also need to model diffusion of reactants to and products away from the solid catalyst surface using a separate set of diffusion equations. For those cases where the reaction takes place at the catalyst surface the boundary conditions at the liquid–solid interface will be determined by the reaction kinetics. However, if the reaction takes place inside a porous catalyst then we need to model diffusion and reaction inside the catalyst as well as transport from the bulk liquid to/from the catalyst surface.

Modelling multicomponent mass transfer in porous media is complicated when the mean free path length of the molecules is of the order of magnitude of the pore diameter. The difficulties posed by this case may be circumvented by a method originally introduced by Maxwell (1866) and developed further by Mason and co-workers (see Mason & Malinauskas, 1983). Maxwell suggested that the porous material itself be described as a supplementary "dust" species, consisting of very large molecules that are kept motionless by some unspecified external force. The Chapman–Enskog kinetic theory is then applied to the new pseudo-gas mixture, in which the interaction between the dust and gas molecules simulates the interaction between the solid matrix and the gas species. In addition, one is no longer faced with the problem of flux and composition variations across a pore and problems related to catalyst geometry.

The dusty fluid model as developed by Krishna and Wesselingh (1997) is a modification of the dusty gas model so as to be able to model liquid-phase diffusion in porous media. For a non-ideal mixture we have:

$$\frac{x_i}{\mathbb{R}T}\frac{\partial \mu_i}{\partial z} + \frac{x_i}{\mathbb{R}T}\overline{V}_i\frac{\partial p}{\partial z} + \frac{x_i}{\eta}\frac{B_0}{D_{i,e}} = \sum_{k=1}^{c} \frac{x_i N_k - x_k N_i}{c_t Đ_{i,k}^e} - \frac{N_i}{c_t Đ_i^e}, \tag{22}$$

where $Đ_i^e$ is the effective Knudsen diffusion coefficient for species $i$ in the porous catalyst.

The mass transfer rates are obtained by multiplying the fluxes by the interfacial area of the catalyst particles. This is not as straightforward, as it looks, since, depending on the geometry of the catalyst, the cross-sectional area can change along the diffusion path. It is necessary to take catalyst geometry into account in the solution of these equations.

The dusty gas model is often used as the basis for the calculation of a catalyst effectiveness factor (Jackson, 1977). The extension to non-ideal fluids noted above has not been used as often, partly because of the greater uncertainty in the parameters that appear in the equations. Berg and Harris (1993) have developed a detailed model of diffusion and reaction in MTBE synthesis. However, their model focuses only on the transport and reaction issues and they have not developed a complete column/process model. Sundmacher, Hoffmann and their co-workers (Sundmacher & Hoffmann, 1992, 1993, 1994a,b, 1995; Sundmacher et al., 1994; Sundmacher, Zhang & Hoffmann, 1995) have carried out an extensive study of mass transfer and activity in and around RD catalysts. Sundmacher and Hoffmann (1992) recommend the MS equations over Fick's law for modelling mass transfer in the liquid-phase surrounding an ion-exchange catalyst particle. The reaction is modelled by an activity-based Langmuir–Hinshelwood expression derived from an extensive experimental study by Rehfinger and Hoffmann (1990a,b). The model is used to determine the catalyst effectiveness factor, and the model is in good agreement with extensive experimental data. Sundmacher and Hoffmann (1994a) developed a detailed model to investigate the interaction between mass and energy transport and reaction in an ion-exchange resin. Catalyst effectiveness factors and selectivities computed from the model are in good agreement with experimental data for MTBE formation obtained in a CSTR. In other papers Sundmacher & Hoffmann (1994, 1995) use the Maxwell–Stefan equations as a basis for a films-in-series mass transfer model for a vapor–liquid–porous catalyst system. However, diffusion in the catalyst is described using an effective diffusivity model that is equivalent to a rearrangement of the dusty fluid model while ignoring the Knudsen diffusion terms. The effect of the reaction is lumped into a component consumption term, corrected by the catalyst efficiency. The reaction term is evaluated at bulk liquid conditions. Non-idealities in the liquid-phase were described with the UNIQUAC equation. The SRK equation of state was used for the gas phase. Sundmacher and Hoffmann introduce "artificial inertia terms" into the interface mass balances in order to create a system of differential and algebraic equations (DAEs). The DAE system was solved with the LIMEX solver (Deuflhard, Hairer & Zugck, 1987). Important conclusions from their theoretical work are that the mass transfer resistance inside the catalyst can vary significantly along the packing and that the main resistance to mass transfer is on the liquid side.

## 5. Non-equilibrium (NEQ) stage modelling

The NEQ stage model for RD follows the philosophy of rate-based models for conventional distillation (Krishnamurthy & Taylor, 1985; Taylor & Krishna, 1993; Taylor, Kooijman & Hung, 1994; Seader & Henley, 1998).

### 5.1. The conventional NEQ model

It will be helpful to begin with a brief review of the NEQ model for conventional distillation operations. A schematic representation of the NEQ stage is shown in Fig. 23. This NEQ stage may represent a tray or a cross-section of a packed column. The component molar balances for the vapor and liquid-phases are

$$V_j y_{i,j} - V_{j+1} y_{i,j+1} - f^V_{i,j} + \mathbb{N}^V_{i,j} = 0, \tag{23}$$

$$L_j x_{i,j} - L_{j-1} x_{i,j-1} - f^L_{i,j} - \mathbb{N}^L_{i,j} = 0, \tag{24}$$

where $\mathbb{N}_{i,j}$ is the interfacial mass transfer rate and is the product of the molar flux and the net interfacial area. The overall molar balances are obtained by summing Eqs. (23) and (24) over the total number ($c$) of components in the mixture. The $\mathbb{N}_{i,j}$ are obtained from the Maxwell–Stefan (16) modified as follows:

$$\frac{x_{i,j}}{\mathbb{R}T_j}\frac{\partial \mu^L_{i,j}}{\partial \eta} = \sum_{k=1}^{c} \frac{x_{i,j}\mathbb{N}^L_{k,j} - x_{k,j}\mathbb{N}^L_{i,j}}{c^L_{t,j}(\kappa^L_{i,k}a)_j} \tag{25}$$

with a similar relation for the vapor phase. The $\kappa^L_{i,k}$ represents the mass transfer coefficient of the $i-k$ pair in the liquid-phase; this coefficient is estimated from information on the corresponding Maxwell–Stefan diffusivity $Đ^L_{i,k}$ using the standard procedures discussed in Taylor and Krishna (1993). $a$ is the interfacial area. Only $c-1$ of Eq. (25) are independent. The mole fraction of the last component is obtained by the summation equations for both phases. The enthalpy balances for both vapor and liquid-phases are

$$V_j H^V_j - V_{j+1} H^V_{j+1} - F^V_j H^{VF}_j + \mathbb{E}^V_j + Q^V_j = 0, \tag{26}$$

$$L_j H^L_j - L_{j-1} H^L_{j-1} - F^L_j H^{LF}_j - \mathbb{E}^L_j + Q^L_j = 0. \tag{27}$$

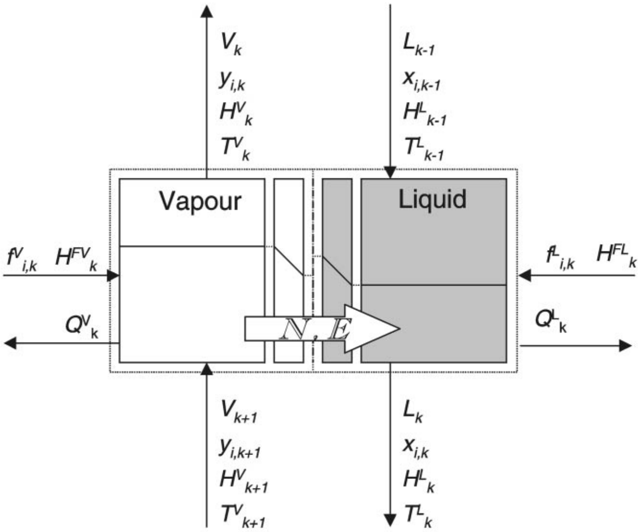


Fig. 23. The non-equilibrium stage (cell) for homogeneous liquid-phase reaction.

The interphase energy transfer rates $\mathbb{E}_j$ (equal in both phases) have conductive and convective contributions

$$\mathbb{E}_j^L = -h_j^L a \frac{\partial T^L}{\partial \eta} + \sum_{i=1}^{c} \mathbb{N}_{i,j}^L H_{i,j}^L \tag{28}$$

with a similar relation for the vapor phase. $h_j^L$ is the heat transfer coefficient in the liquid-phase. The conductive contributions are ignored in some modelling studies. This omission results in liquid-phases being (predicted to be) slightly superheated and vapor phases that are subcooled (Taylor et al., 1994).

At the vapor–liquid interface we assume phase equilibrium

$$y_{i,j}|_I = K_{i,j}\, x_{i,j}|_I, \tag{29}$$

where the subscript $I$ denotes the equilibrium compositions and $K_{i,j}$ is the vapor–liquid equilibrium ratio for component $i$ on stage $j$. The $K$-values are evaluated at the temperature, pressure and composition of the interface from appropriate thermodynamic models (the same models used in conventional equilibrium stage models).

In addition to Eqs. (23)–(29), we have the summation equations for the mole fractions in the vapor and liquid-phase and equations expressing the continuity of fluxes of mass and energy across the interface. Furthermore, in the NEQ model we take account of the pressure drop across a stage

$$p_j - p_{j-1} - (\Delta p_{j-1}) = 0, \tag{30}$$

where $p_j$ and $p_{j-1}$ are the stage pressures and $\Delta p_{j-1}$ is the pressure drop per tray from stage $(j-1)$ to stage $j$. The pressure drop over the stage is considered to be a function of the stage flows, the physical properties and the hardware design. In the NEQ model, hardware design information must be specified so that mass transfer coefficients, interfacial areas, liquid hold-ups, etc. can be calculated. The NEQ model requires thermodynamic properties, not only for calculation of phase equilibrium but also for calculation of driving forces for mass transfer and, in RD, for taking into account the effect of non-ideal component behaviour in the calculation of reaction rates and chemical equilibrium constants. In addition, physical properties such as surface tension, diffusion coefficients, viscosities, etc. for calculation of mass (and heat) transfer coefficients and interfacial areas are required. The steady-state model equations most often are solved using Newton's method or by homotopy-continuation. A review of early applications of NEQ models is available in Taylor & Krishna (1993, Chapter 14).

### 5.2. NEQ modelling of RD

Building an NEQ model of a reactive separation process is not as straightforward as it is for the EQ stage model in which we simply (or not so simply) add a term to account for reaction to the liquid-phase material balances. For a reactive separation process, we first need to know whether the reaction is heterogeneous or homogeneous.

For homogeneous systems the component molar balance for the liquid-phase becomes

$$L_j x_{i,j} - L_{j-1} x_{i,j-1} - f_{i,j}^L - \mathbb{N}_{i,j}^L - \sum_{m=1}^{r} \nu_{i,m} R_{m,j} \varepsilon_j = 0, \tag{31}$$

where $R_{m,j}$ is the rate of reaction $m$ on stage $j$. $\nu_{i,m}$ represents the stoichiometric coefficient of component $i$ in reaction $m$ and $\varepsilon_j$ represents the reaction volume on stage $j$. For homogeneous reactions this is given by the total liquid hold-up on stage $j$ and, in an NEQ model, is obtained directly from the column internals specifications and appropriate hydrodynamic correlations.

If it is sufficiently rapid, the reaction will also take place in the liquid film adjacent to the phase interface, and very fast reactions may occur only in the film. In either case the continuity equations for the film are required for taking into account the effect of the reaction on the interphase mass transfer rates. The combined set of MS and continuity equations usually must be solved numerically.

The phase equilibrium equations for the interface may need to be modified for the influence of additional species on the thermodynamic properties at the interface. Amine-based gas treating again provides a case in point where reactions in the liquid-phase create additional species (including ions) that affect the interfacial equilibrium (Glasscock & Rochelle, 1989).

For a heterogeneous reaction, there are two options for the description of the reaction term. The simplest approach is to treat the reaction pseudo-homogeneously, whereby catalyst diffusion and reaction is lumped into an overall reaction term. For heterogeneous reactions that are modelled in this way the liquid-phase material balance is as given above and $\varepsilon_j$ is given by the total amount of catalyst present on the stage under consideration. In this case, one only needs to specify catalyst mass and activity. A more rigorous approach would involve the use of the dusty fluid model discussed above if the catalyst is porous, or reaction at the surface if not. In this case one also needs information about the catalyst geometry (surface area, mean pore diameter, etc). In either case it is unnecessary to allow for reaction in the vapor–liquid film and the vapor–liquid transport equations are exactly as given above.

### 5.3. NEQ models

Sawistowski and Pilavakis (1979, 1988) modelled a packed RD column for the esterification of methanol and acetic acid to methyl acetate. They used an effective diffusivity method for their mass transfer model. Unless the equilibrium constant has some unconventional definition, the reaction equation given in their first paper represents an irreversible reaction. The system of differential equations that constitute their model was solved numerically. Their second paper includes parametric studies that show how conversion changes as a function of catalyst flow rate, pressure, feed composition, reflux ratio, reboil ratio, feed flow rates, and feed position.

In 1990 ASPEN Technology Inc. introduced the RATEFRAC model for rate-based multicomponent separation modelling (Sivasubramanian & Boston, 1990). RATEFRAC appears to be based on the NEQ model of Krishnamurthy and Taylor (1985) with the addition of equations to account for the effect of reaction on mass transfer, and chemical equilibrium constraints (if needed).

Zheng and Xu (1992b) have used an NEQ model to simulate catalytic distillation operations in a packed column with bag-type porous catalyst. Theirs is a pseudo-homogeneous model very similar to that described above. Vapor–liquid mass transfer is modelled using the MS equations. However, it is not completely clear how the reaction is modelled. Elsewhere in the paper it is stated that liquid–solid mass transfer coefficients in the catalyst bed are computed from a correlation derived in their first paper (Zheng & Xu, 1992a). Yet no equations or terms for mass transfer from the liquid to the catalyst appear anywhere else in the paper. It is possible that the reaction is treated pseudo-homogeneously where effects of reaction on mass transfer (and the effects of mass transfer on reaction) in the catalyst are lumped into the bulk liquid reaction term. Thermodynamic properties for the liquid-phase are described with the UNIFAC model and the virial equation is used for the vapor phase. The resulting set of algebraic equations was solved using Newton's method. They model production of MTBE and provide numerically calculated concentration, temperature and flux profiles. Only for the temperature profile is there any comparison with experimental data.

Zhu and Shen (1995) discussed the modification of the NEQ model of Krishnamurthy and Taylor (1985) to handle RD. Few precise details are provided, however, and it is impossible to be sure how the presence of reaction(s) modifies any of the NEQ model equations. Simulation results appear to show reasonable agreement with temperature and liquid composition profiles measured for the esterification of ethanol and acetic acid carried out in an Oldershaw column.

Kreul, Gorak and Barton (1999a) used an NEQ model of homogeneous RD and, via a series of case studies, studied the importance of various model simplifications. They found little difference between the full MS description of multicomponent mass transfer and the simpler effective diffusivity models. However, they also conclude that there can be significant differences between EQ and NEQ models, and that the additional effort of the more complicated NEQ approach is justified.

Baur et al. (1999) have compared the EQ and the NEQ models for the MTBE process. They underlined some counter-intuitive features of RD processes. For example, for a methanol feed location yielding a low-conversion steady-state, the introduction of mass transfer resistance (i.e. use of the NEQ model), leads to a conversion higher than that predicted by the EQ model; see Fig. 20 (b). The introduction of a mass transfer resistance alleviates a "bad situation" and has the effect of improving conversion.

Lee and Dudukovic (1998) described an NEQ model for homogeneous RD in tray columns. The Maxwell–Stefan equations are used to describe interphase transport, with the AIChE correlations used for the binary (Maxwell–Stefan) mass transfer coefficients. Newton's method and homotopy continuation are used to solve the model equations. A close agreement between the predictions of EQ and NEQ models was found only when the tray efficiency could be correctly predicted for the EQ model. In a subsequent paper Lee and Dudukovic (1999) extend the dynamic NEQ model of Kooijman and Taylor (1995) to cover the dynamic operation of RD in tray columns. The DAE equations were solved by use of an implicit Euler method combined with homotopy-continuation. Murphree efficiencies calculated from the results of a simulation of the production of ethyl acetate were not constant with time.

Kenig et al. (1999) described a software package for the synthesis and design of RD operations. The package is one of the results of a major research program on RD supported by the European Union under the BRITE-EURAM program. The designer part of the package is based on an NEQ model that accounts for possible reaction in the mass transfer film and includes a catalyst efficiency calculation to account for diffusion and reaction in the catalyst. A large number of correlations for the mass transfer coefficients in different types of column internal are available in the program. Stage hydrodynamic models included in the package are:

- completely mixed vapor and liquid;
- completely mixed liquid, plug-flow vapor;
- mixed pool model for the liquid-phase;
- eddy diffusion model for the liquid-phase.

No mathematical details of the model are provided in the paper. The model equations are solved using Newton's method. The program is illustrated by modelling the MTBE process and a comparison with some experimental data (numerical values not given) shows excellent agreement with the calculated profiles.

Schenk, Gani, Bogle and Pistikopolous (1999) describe in considerable detail a hybrid-modelling environment in which distillation-type processes can be simulated using a combination of steady-state, dynamic, EQ stage, and/or rate-based models. Two of the three examples that illustrate their paper concern RD (ethyl acetate production and an MTBE column). The models are compared to experimental data of Suzuki et al. (1971). The agreement between the profiles obtained with the rate-based model and the data is very encouraging. The authors do, however, demonstrate a sensitivity of the computed profiles to the activity coefficient model used. A particularly novel feature of their paper is the introduction of Gibbs energy profiles in the column.

In an interesting experimental study Sundmacher and Hoffmann (1995) obtained oscillatory behaviour of a packed laboratory-scale distillation column. The oscillations were encountered in the MTBE process as well as in the distillation of non-reactive binary mixtures. It appears likely that these oscillations originate from the hydrodynamics in their packed RD column. The authors use an NEQ model for non-reactive distillation that completely neglects mass transfer in the liquid-phase and, by extension, any effects due to reaction. The model equations were solved by a relaxation method, the results used to demonstrate multiple steady-states. The NEQ model does not provide an explanation for the observed oscillations.

Sundmacher and Hoffmann (1996) presented a detailed NEQ stage model for vapor–liquid–porous catalyst systems. The model differs from that described above only in that the phases are assumed to be in thermal equilibrium with each other. This means that sensible heat transfer between phases is ignored and that the overall energy balance replaces the individual phase balances. Mass transfer in the vapor and liquid-phases is modelled using an explicit approximate solution of the Maxwell–Stefan equations (see Chapter 8 of Taylor and Krishna (1993) for details). The system of equations is solved via a pseudo-relaxation method using the DAE solver LIMEX cited earlier. The model is used to simulate some data obtained on a laboratory-scale MTBE column. One of the conclusions from this study is that it is absolutely necessary to account for diffusion and reaction in the porous catalyst (modelled in this paper using the catalyst effectiveness factor approach developed in other papers from these authors and discussed above).

The influence of side reactions on RD processes has been investigated by Schoenmakers (1982), Sundmacher, Hoffmann and co-workers (Sundmacher, Uhde & Hoffmann, 1999; Oost, Sundmacher & Hoffmann, 1995; Oost & Hoffmann, 1996). Sundmacher, Uhde and Hoffmann (1999) used both EQ stage (with Murphree efficiency) and NEQ models to simulate the MTBE and TAME processes. The reactions were handled using both quasi-homogeneous and heterogeneous methods. Simulation results were compared to experimental data obtained in two laboratory-scale columns. A detailed NEQ model was needed to describe the TAME process, but both NEQ and the EQ stage (with an efficiency of 0.8) model could adequately represent the MTBE process. In the latter case it was necessary to account for the catalyst effectiveness along the packing. The authors conclude that it is necessary to account for the side reactions in RD process design.

Bart and Landschützer (1996) studied the esterification reaction of acetic acid and propanol to propyl acetate, catalysed by an exchange resin in a packed column. Mass transfer across the vapor–liquid interface and between liquid bulk and catalyst surface is described with the Maxwell–Stefan equations. The reaction is assumed to take place only at the catalyst surface and is modelled with an Eley–Rideal kinetic expression. Their model accounts for axial dispersion along the column, the dispersion coefficient being obtained from a Bodenstein relation that was determined experimentally for their model column.

Yu, Zhou and Tan (1997) developed a steady-state NEQ model that takes into account mass transfer from the bulk liquid to the catalyst. Separate rate equations are written for the vapor–liquid and liquid–solid interfaces. Empirical methods are used for estimating the liquid–solid (and other) phase mass transfer coefficients. Diffusion within the catalyst phase is ignored. The system of non-linear equations is solved by a Newton homotopy method. The solitary numerical example that accompanies the paper concerns the reactive stripping process for the production of Bisphenol-A.

Ng, Rempel and their co-workers at the University of Waterloo (Huang, Podrebarac, Ng & Rempel, 1998a; Huang, Yang, Ng & Rempel, 1998b; Podrebarac et al., 1998a,b) have carried out an in-depth study of the aldol condensation of acetone to diacetone alcohol (DAA) and mesityl oxide. Experiments were carried out in a pilot-scale column with 6 mm Intalox saddles and a reactive section containing bale-type packing. It was found that the DAA production rate was controlled by mass transfer. DAA selectivity was influenced by the liquid distribution. Correlations for the solid–liquid mass transfer coefficients and for the overall mass transfer coefficients for the vapor–liquid transport were developed by Huang et al. (1998a). Their papers also include the development of an NEQ model. The model appears to be derived from the Krishnamurthy–Taylor model for conventional distillation, although it is interesting to note that the material balances are expressed in terms of the mass flows and mass fractions and include a separate term for the rate of vaporisation caused by the heat of reaction. Mass transfer between vapor and liquid-phases is described by a single overall mass transfer coefficient for each species, a correlation for which was derived for their column. They assume that the rate of reaction is equal to the rate of mass transfer to the catalyst surface and correlations for the liquid–solid mass transfer coefficients were also developed. Mass transfer in the non-reactive sections was modelled using a film model for each phase; mass transfer coefficients being estimated using the correlations of Onda, Takeuchi and Okumoto (1968). The model equations were solved simultaneously. A predicted temperature profile appears to be in good agreement with one determined experimentally. However, it must be remembered that the all important mass transfer coefficients were fitted to data obtained in their own column. Thus, the true predictive abilities of their model are untested. It is reported that the amount of catalyst and the condensation rate are important design variables for this RD process, and that the DAA selectivity would have improved if the liquid–catalyst mass transfer improved.

Podrebarac et al. (1998b) modelled the reactive section as a plug-flow reactor with radial dispersion. The set of differential and algebraic equations was solved using the gPROMS system. The authors were able to fit their own experimental data quite well. However, the model could not be used for predictive purposes due, it was claimed, to the random nature of the flow in a packed column.

The recent study of Baur et al. (1999) comparing the EQ and NEQ models for hydration of ethylene oxide to ethylene glycol throws a new light on the phenomena on MSS and the importance of using the NEQ model. For the Ciric and Gu (1994) configuration for the ethylene glycol column (see Fig. 24(a)), multiple steady-states are found with both EQ and NEQ models. Three steady-states SS-1 (high conversion), SS-2 (intermediate conversion) and SS-3 (low conversion) were found. The desired high-conversion steady-state solution (SS-1) corresponds to high column temperatures and lowest molar flow rate of the vapor up the column. Let us now consider the NEQ model simulations for the 1.7 m diameter column configuration. For this chosen column diameter, only one solution, SS-1, can be realised in the column. The other solutions SS-2 and SS-3 could not be realised in the NEQ because for the higher vapor flows, the column floods in some (SS-2) or all (SS-3) of the stages; the flooding boundaries are drawn in Fig. 24(c). Baur et al. (1999) also show that if the column diameter was chosen to be 3 m, only the lowest conversion steady-state can be realised!

## 5.4. NEQ cell model

An issue that is not adequately addressed by most NEQ models is that of vapor and liquid flow patterns on distillation trays or maldistribution in packed columns. Since reaction rates and chemical equilibrium constants are dependent on the local concentrations and temperature, they may vary along the flow path of liquid on a tray, or from side to side of a packed column. For such systems the residence time distribution could be very important, as well as a proper description of mass transfer. On distillation trays, vapor will rise in plug-flow through a layer of froth. The froth will pass through the liquid more or less in plug-flow, with some axial dispersion due to the vapor jets and bubbles. In packed sections, maldistribution of internal vapor and liquid flows

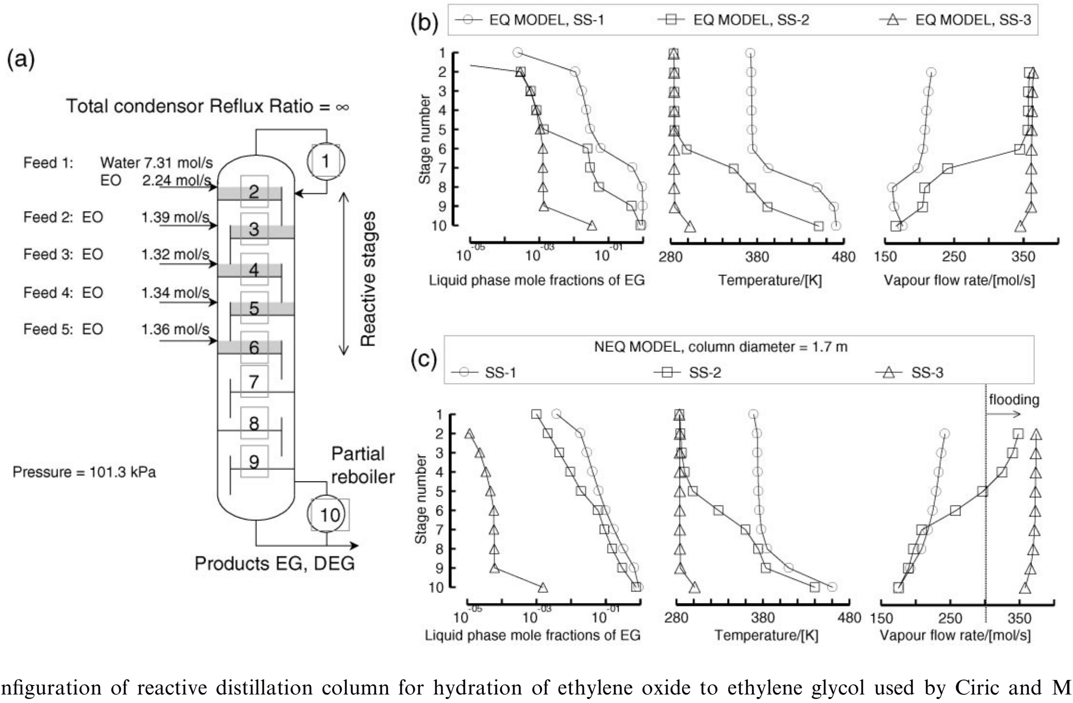


Fig. 24. (a) Configuration of reactive distillation column for hydration of ethylene oxide to ethylene glycol used by Ciric and Miao (1994). (b) Equilibrium model calculations for the ethylene glycol process showing column profiles for liquid-phase mole fraction, temperature and vapor-phase molar flow. (c) Non-equilibrium model calculations for the ethylene glycol process for a column of diameter 1.7 m showing the corresponding column profiles. Details of the simulations are available in Baur, Higler, Taylor and Krishna (1999).

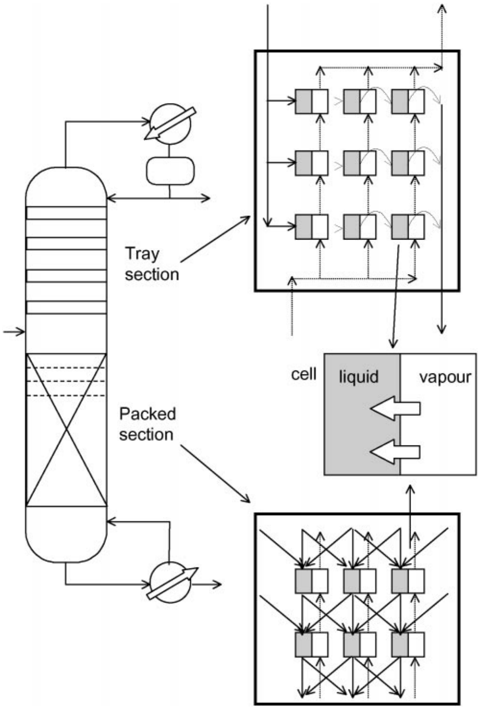


Fig. 25. The non-equilibrium cell model of Higler, Krishna and Taylor (1999a).

over the cross-sectional area of the column can lead to loss of interfacial area. This is known to be one of the main reasons for inadequate performance of packed columns.

To deal with this shortcoming of earlier models, Higler, Taylor and Krishna (1999c) and Higler, Krishna and Taylor (1999a,b) developed an NEQ cell model. The distinguishing feature of this model is that stages are divided into a number of *contacting cells*, as shown in Fig. 25. These cells describe just a small section of the tray or packing, and by choosing an appropriate connection pattern, one can very easily study the influence of flow patterns and maldistribution on the distillation process.

Flow patterns on distillation trays are modelled by choosing an appropriate number of cells in each flow direction. A column of cells can model plug-flow in the vapor phase, and multiple columns of cells can model plug-flow in the liquid-phase as depicted in Fig. 26. Backmixing may also be taken into account by using an appropriate number of cells. This may be derived from calculating an equivalent number of cells from eddy diffusion models. Flow patterns in packed columns are evaluated by means of a natural flow model. The flows are split up according to the ratio of the cell surface areas between the cells. Various flow patterns may be approximated using different flow splitting policies.

A schematic diagram of the unit cell for a vapor–liquid–porous catalyst system is shown in Fig. 27. Each cell is modelled essentially using the NEQ model for heterogeneous systems described above. The bulk of both vapor and liquid-phases is assumed to be completely mixed. Mass transfer resistances are located in films near the vapor/liquid and liquid/solid interfaces, and the Maxwell–Stefan equations are used for calculation of the mass transfer rates through each film. Thermodynamic equilibrium is assumed only at the vapor–liquid interface. Mass transfer inside the porous catalyst may be described with the dusty fluid model described above.

The unit cell for homogeneous systems (and for heterogeneous systems modelled as though they were homogeneous) is as depicted in Fig. 23. The equations for each cell are essentially as given above.

For RD, the staging in the liquid-phase could have a significant influence on the reaction selectivity. This is emphasised in the study by Baur et al. (1999) of the influence of hardware design on the formation of the by-product DEG in the hydration column (sieve tray) shown in Fig. 24(a). Their simulation results are presented in Fig. 28. For five mixing cells in both vapor and liquid-phases (which corresponds closely to plug-flow conditions for either phase), the formation of by-product DEG is reduced while the conversion to EG is increased. Removing the mass transfer resistances, i.e. assuming the EQ model, gives the best performance with respect to conversion and selectivity; see the point towards the bottom right of Fig. 28. Reaction selectivity can be influenced by tray hardware design. Decreasing the weir height from 80 mm (base case) to 50 mm decreases formation of EG and increases by-product DEG formation. This reduction is due to a lowering in the interfacial area with decreasing weir height. Increasing the weir height from 80 to 100 mm leads to improved conversion and improved selectivity. High weir heights, and operation in the froth regime, are generally to be preferred in RD operations. Increasing the number of passes from 1 to 2 increases by-product formation; see the top point in Fig. 28. This is because the liquid load per weir length is reduced by 50%. This reduction in the liquid load leads to a reduction in the clear liquid height and lowering in the total interfacial area, which has a detrimental influence on both the conversion and selectivity. It appears that the usual design rules for conventional distillation column design cannot be carried over to RD columns because, for a column of 1.7 m diameter the conventional design philosophy would be to use two passes for the liquid flow.

### 5.5. *Pseudo-homogeneous vs. heterogeneous NEQ modelling*

Higler, Krishna and Taylor (2000) used the dusty fluid equations to model diffusion and reaction in porous catalysts in RD. The MTBE process (following the configuration of Jacobs and Krishna (1993) shown in

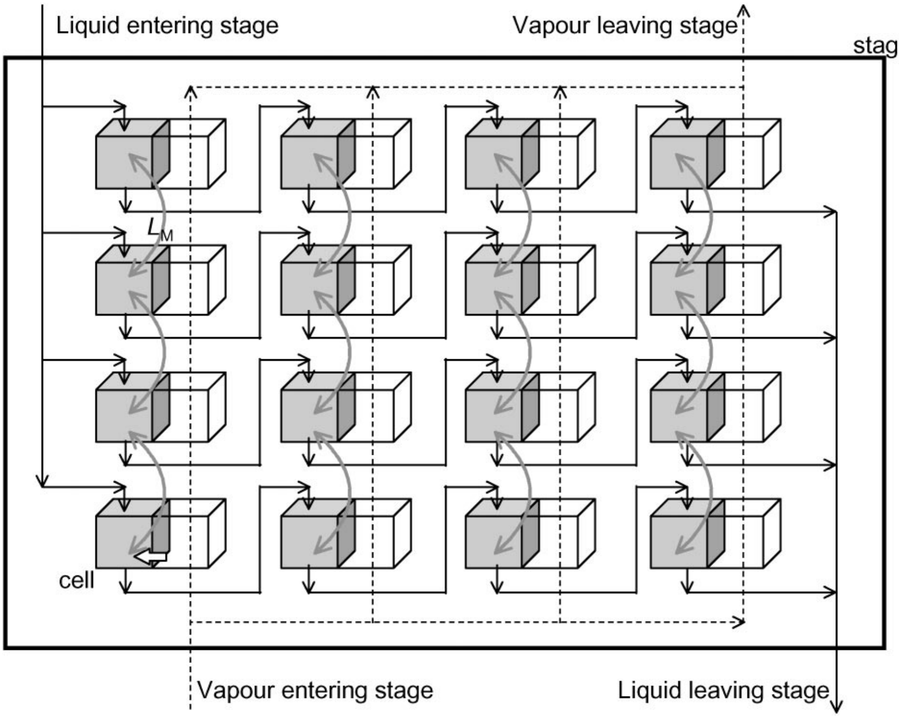


Fig. 26. Details of flows in and out of multiple cells used to model the hydrodynamics of trayed columns.

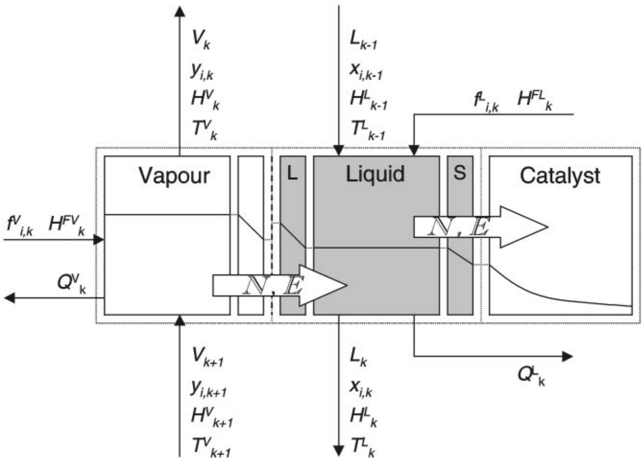


Fig. 27. The non-equilibrium stage (cell) for heterogeneous catalysed reaction.

Fig. 20(a)) was simulated under three different sets of assumptions:

A A pseudo-homogeneous approach, in which the catalyst is neglected and the reaction rate is evaluated at liquid bulk conditions.

B A case in which the Knudsen diffusion coefficient is large, in which case the mass transfer interaction with the catalyst is ignored

C A case one in which the Knudsen diffusion coefficient is a factor five times smaller than the smallest of the Maxwell–Stefan diffusion coefficients. The value of the Knudsen diffusion coefficient is assumed to be the same for all components.

Shown in Fig. 29 is the steady-state conversion of *iso*-butene as a function of the bottom product flowrate. The multiple steady-state region has disappeared for the dusty fluid model, and the Knudsen diffusion term has a substantial influence on the results of the dusty fluid model simulations. This may be explained by the fact that, in the lower branch of the multiple steady-state region, MTBE is consumed in *part* of the column. The rate of consumption of MTBE is very much influenced by additional mass transfer resistances. Additional mass transfer resistances, therefore result in a higher conversion. This is not the case for the TAME process where the reaction rate is very much lower than it is for MTBE and mass transfer influences are not significant. Multiple steady-states have been found experimentally for an RD column used to produce TAME, but not in the MTBE process (Rapmund et al., 1998), appearing to confirm the results shown in Fig. 29.

### 5.6. Dynamic NEQ models

Kreul, Gorak, Dittrich and Barton (1998) described an NEQ model for RD in packed columns. Theirs is a dynamic model that, as is usual in such models, neglects the hold-up in the vapor-phase. Their paper addresses the problems of modelling mass transfer and reaction in a vapor–liquid–porous catalyst system. In addition, they

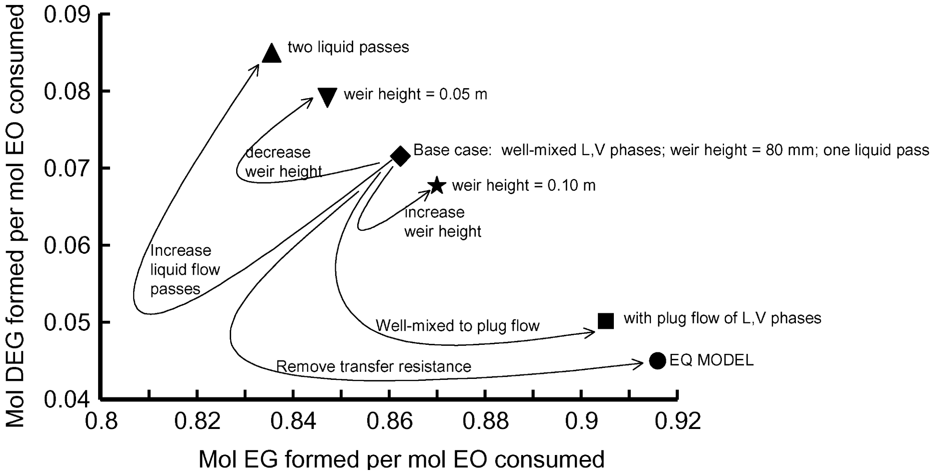


Fig. 28. Influence of tray hardware and number of mixing cells on the formation of by-product DEG in the hydration of ethylene oxide to ethylene glycol (EG). The column configuration (diameter = 1.7 m) is that shown in Fig. 24(a). Details of the simulations are available in Baur, Higler, Taylor and Krishna (1999).

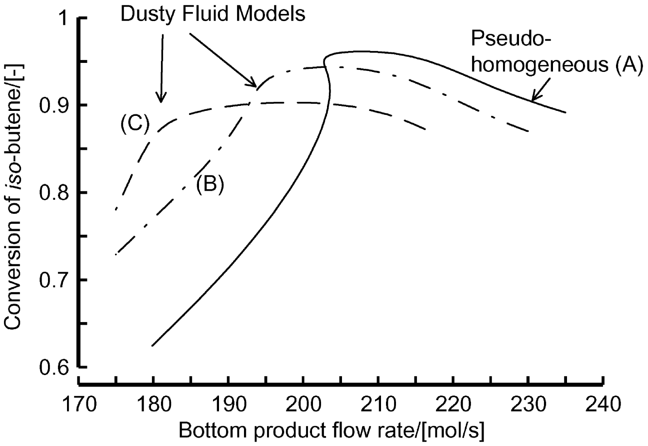


Fig. 29. Comparison of the results for conversion of iso-butene obtained by three different model formulations for taking account of chemical reactions: (A) pseudo-homogeneous, (B) dusty fluid model without Knudsen contribution, and (C) dusty fluid model with Knudsen contribution. Adapted from Higler, Krishna and Taylor (2000).

describe a two-phase model in which diffusion and reaction to and within the solid catalyst is not accounted for by additional equations (and parameters), but their effects are lumped into a kinetic term that appears in the liquid-phase material balances. The choice of which of these two approaches was adopted for their simulations is not completely clear. The material balances (partial differential equations) are discretised in the spatial dimension (the column height) using the method of lines. The model equations were solved using the equation-based modelling environment ABACUS (Allgor, Berrera, Barton & Evans, 1996). The paper by Kreul et al. includes a limited comparison with some unsteady-state data for a methyl acetate column. The results shown in the paper suggest that their dynamic model is well able to describe the product composition transients. The actual experimental data are not provided in the paper.

Kreul, Gorak and Barton (1999b) described an NEQ model to study batch distillation. In essence, the model is an extension and generalisation of the dynamic NEQ models of Kooijman and Taylor (1995) for tray columns and Pelkonen, Gorak, Kooijman and Taylor (1997) for packed columns. The MS equations were used to model vapor and liquid-phase mass transfer. The model system was implemented and solved using the ABACUS system. The paper includes extensive comparisons of true model *predictions* of experiments performed in a pilot plant column involving the system methanol–acetic acid–methyl acetate–water. Under the conditions in the experiments there was essentially no liquid-phase chemical reaction; vapor-phase dimerisation was, however, taken into account. The agreement between the predicted and measured compositions is exceptionally good.

Strictly speaking, reactive absorption falls outside the scope of this review. However, NEQ models as outlined above apply more or less unchanged in principle to reactive absorption and RD alike. The only differences between the models are the inclusion of different submodels for the reaction kinetics and thermodynamic properties. A nitric acid recovery plant modelled by Wiesner, Wittig and Gorak (1996) and by Kenig and Gorak (1997) involves nine different reactions and simultaneous transport and reaction of 10 different species. Schneider, Kenig and Gorak (1999) used the Maxwell–Stefan approach to model the dynamics of reactive absorption processes. Of particular interest in their model is the inclusion of the gradient of the electrical potential in the Maxwell–Stefan equations and the electro-neutrality equation that must be satisfied at all points in the liquid due to the presence of ions in the processes they model. Rascol, Meyer, Le Lann and

Prevost (1998) briefly addressed some numerical problems that can be encountered in the simulation of reactive absorption using NEQ models. We have already noted the success (using effective diffusivities and enhancement factor approaches to mass transfer with reaction) of NEQ models of amine-based gas treating processes (Carey et al., 1991; Altiqi et al., 1994).

## 6. Reactive distillation design

Design and simulation of RD operations are very different types of calculation, calling for very different approaches. Most conceptual design models are based on the EQ stage model described above. However, as discussed below, some recent developments have opened up the possibility of using NEQ models for RD design, and a limited number of papers suggest that NEQ models already have a place in industrial RD design practice.

### *6.1. Conceptual design*

Barbosa and Doherty (1988c) developed the fixed-point method for the design of single-feed RD columns. The method is based on the following assumptions:

- the column is adiabatic;
- the molar heat of vaporisation is constant;
- the heat of mixing is negligible;
- sensible heat effects can be ignored;
- the heat of reaction is negligible compared to the enthalpy of the vapor;
- the feed is a saturated liquid;
- phase equilibrium is achieved on each stage;
- the column operates with a partial condenser.

These assumptions ensure that the vapor and liquid flows inside the column are constant, thereby permitting the energy balances to be solved essentially independent of the remaining stage equations.

The fixed-point method uses material balance equations written around a stage in each section of the column (above and below the feed stage) and the corresponding end of the column. With reference to Fig. 18(a), for example, we have, for the rectifying section

$$X_{i,j} = \frac{r_j^* + 1}{r_j^*} Y_{i,j} - \frac{1}{r_j^*} Y_{i,D} \tag{32}$$

and for the stripping section the material balance reads

$$X_{i,j+1} = \frac{s_j^*}{s_j^* + 1} Y_{i,j} - \frac{1}{s_j^* + 1} X_{i,B} \, . \tag{33}$$

Note that these equations have been written in terms of the transformed composition variables defined by Eq. (3). The transformed reflux and stripping ratios are defined as follows:

$$r_j^* = \frac{L_j(v_k - v_T x_{k,j})}{D(v_k - v_T y_{k,D})}, \quad s_j^* = \frac{V(v_k - v_T y_{k,j})}{B(v_k - v_T x_{k,B})}. \tag{34}$$

Barbosa and Doherty convert these equations to differential form. To determine a feasible design the equations are integrated numerically starting with the desired product composition. They illustrate their design procedure for a quaternary system shown in Fig. 30(a). If the trajectories intersect, as shown in Fig. 30(b), then the resulting column is feasible, if the trajectories fail to intersect, then no column will produce the desired products (Fig. 30(c)). The minimum reflux can be found from the special case of two trajectories that just touch each other (Fig. 30(d)).

A number of extensions of the approach of Barbosa and Doherty (1988c) have appeared in the literature. Barbosa and Doherty (1988d) extend their own methodology to double-feed columns. Buzad and Doherty (1994, 1995) and Doherty and Buzad (1994) provide a further extension in order to handle kinetically controlled reactions in three-component systems. Ung and Doherty (1995e) consider RD processes involving multiple reactions. Okasinski and Doherty (1998) relax some of the assumptions underlying the methods of Barbosa, Buzad, and Doherty. They develop a systematic method for the design of kinetically controlled staged RD columns while taking into account a single liquid-phase reaction, heat effects, non-ideal phase equilibrium, and a range of liquid-phase hold-ups on the different stages. The Damkohler number defined for the entire column is a key parameter in their approach. Melles, Grievink and Schrans (2000) also relaxed the uniform hold-up assumption by allowing different hold-ups per section of the column (not on each tray), taking into account heat effects, and non-zero stoichiometric sum reactions.

The design of RD columns in which the feed stream contains species that do not react at all was addressed by Espinosa, Aguirre and Perez (1995a,b). Most of the methods cited above are based on an assumption that the reaction takes place on all stages in the column. Espinosa, Aguirre and Perez (1996) described a method of dealing with columns in which the reaction takes place only in a central portion of the column. The latter issue was revisited by Espinosa, Aguirre, Frey and Stichlmair (1999) who proposed a design method for a column with a reactive section, a stripping section, and *two* rectifying sections.

Mahajani and Kolah (1996) extended the methods of Doherty and co-workers for packed RD columns. An assumption in their method is that liquid-phase backmixing is totally absent. It is pertinent to note that the overall methodology and some important results (e.g. minimum reflux) are unchanged from the methods for tray columns. Mahajani (1999b) also addresses the design of RD processes for multicomponent kinetically controlled reactive systems.

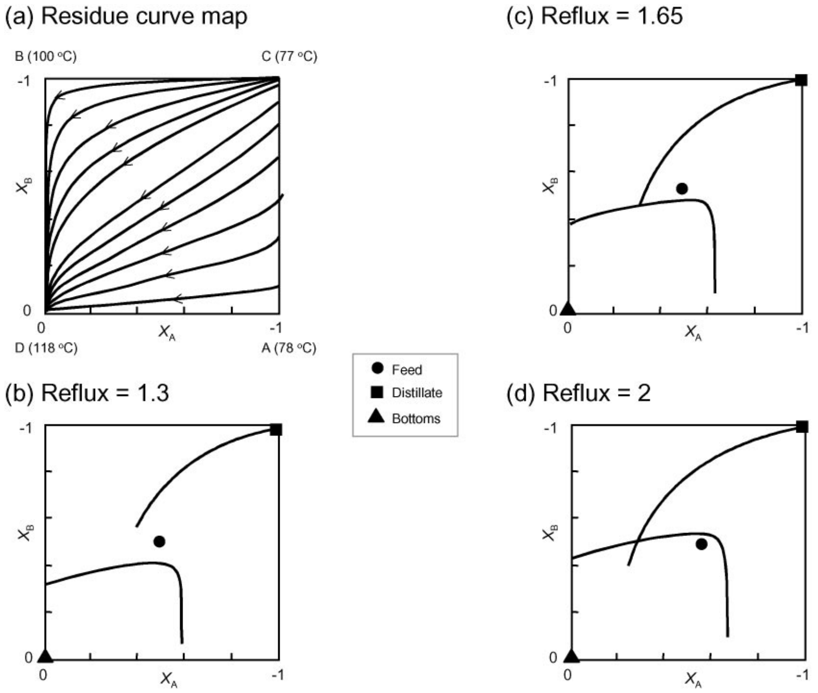


Fig. 30. Column profiles in RD design (Doherty method).

The attainable region approach to reactor network feasibility is based on geometric properties and has been studied in depth mainly by Glasser, Hildebrandt, and their co-workers (see, for example, Glasser & Hildebrandt, 1997; Feinberg & Hildebrandt, 1997; Feinberg, 1999). McGregor, Glasser & Hildebrandt (1997) and Nisoli, Malone and Doherty (1997) apply the attainable region approach in order to develop a systematic approach to identifying the feasible compositions that can be obtained in RD processes. Once again, the Damkohler number emerges as the important parameter.

Hauan and co-workers (see Hauan, 1998; Hauan & Lien, 1996, 1998; Hauan, Westerberg & Lien, 2000b) have developed what they call a phenomena-based method for the analysis and design of reactive separation processes. Within this framework the change in the composition of any particular phase is given by the vector equation

$$\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} = \mathbf{mix} + \mathbf{sep} + \mathbf{rx} \tag{35}$$

where $\mathbf{x}$ is the composition of the phase in question, and **mix**, **sep**, and **rx** are vectors that represent the composition changes due to mixing, separation, and reaction, respectively. For these vectors Hauan et al. (2000b) write

$$\mathbf{mix} = M(\mathbf{x}^F - \mathbf{x}^0), \tag{36}$$

$$\mathbf{rx} = R(\mathbf{v} - \mathbf{x}^0 \textstyle\sum v), \tag{37}$$

$$\mathbf{sep} = [S](\mathbf{x} - \mathbf{y}), \tag{38}$$

where $M$ is a scalar equal to the relative amounts of material being mixed, $\mathbf{x}^0$ is the current composition and $\mathbf{x}^F$ is the feed composition, and $R$ is a scalar that depends on such things as catalyst activity, hold-up, and temperature. $[S]$ is matrix of component specific mass transfer rates. If the phases are assumed to be in equilibrium then $[S]$ reduces to a simple scalar. The direction of these combined vectors indicates the feasibility of a particular process; their length is a measure of the process efficiency. Hauan and Lien (1998) illustrated their methodology with an analysis of the MTBE process.

More interestingly, this formulation admits the possibility, so far unexplored, of using a properly formulated model of mass transfer in multicomponent systems as discussed above.

A fixed point exists when the **mix**, **sep**, and **rx** vectors nullify each other.

$$0 = \mathbf{mix} + \mathbf{sep} + \mathbf{rx}. \tag{39}$$

When the reaction and separation vectors have zero magnitude then the fixed point is an equilibrium point. A kinetic fixed point (azeotrope) arises when all three vectors have non-zero magnitudes, but still nullify each other. The location of these kinetic fixed points has a direct influence on the product compositions that can be realised in an RD column (see, also, Mahajani, 1999a). Hauan et al. (2000b) have provided a comprehensive analysis of the kinds of fixed point that can arise from cancellation of different combinations of these vectors. They also introduce the reaction difference point as the difference between an arbitrary composition and a singular point. The use of these difference points in RD process design is the subject of two recent papers by Hauan, Ciric, Westerberg and Lien (2000a) and by Lee, Hauan, Lien and Westerberg (2000c).

Pistikopolous and co-workers (see Papalexandri & Pistikopolous, 1996; Ismail, Pistikopolous & Papalexandri, 1999) have developed a phenomena-based modelling framework that is able to capture hybrid reactive/separation processes. In their approach an RD process (here meaning more than just a single RD column) is synthesised from a collection of modules that involve reaction, reaction and separation, or only separation. In this context a module does not necessarily represent a single model stage, but a collection of such stages. Either EQ or NEQ stage models could be used in this approach. Papalexandri and Pistikopolous (1996) illustrate their methodology with the design of an ethylene glycol column, while Ismail et al. (1999) considered the production of ethyl acetate from acetic acid and ethanol.

Bessling, Schembecker and Simmrock (1997a,b) combine heuristic rules, numerical computation, and RD line diagrams to study the feasibility of RD processes. They devise a method for identifying RD processes in which the RD column needs to be divided into reactive and non-reactive sections. Bessling, Loning, Ohligschlager, Schembecker and Sundmacher (1998) use these RD line diagrams to identify the main process parameters and to provide a basis for an experimental study in the methyl acetate process. The significant influence of the reflux ratio on conversion is shown by simulation using an EQ stage model and by experiments in a small-scale column that employed packing in the form of Raschig rings.

Serafimov and co-workers (Balashov & Serafimov, 1980; Balashov, Patlasov & Serafimov, 1981; Pisarenko & Serafimov, 1988, 1992; Pisarenko et al., 1988a, b; Pisarenko, Danilov & Serafimov, 1995, 1996, 1997; Giessler et al., 1998, 1999; Serafimov, Pisarenko & Kulov, 1999b; Serafimov et al., 1999a) have developed a method they call static analysis. It is the result of an extensive investigation of the thermodynamic and topological structure of distillation diagrams. The method requires very little fundamental data on the system and is based on an assumption that the vapor and liquid flow rates in the column are very large. As a result of this assumption the composition change caused by the reaction is small on each stage and can be neglected. The desired product compositions, extent of reaction, and number of stages need not be fixed a priori. The most accessible work from this group is the paper by Giessler et al. (1998) who outline the steps of the method and illustrate it with a case study of the MTBE process. Giessler et al. (1999) applied the method to five other RD processes: the production of acetic acid, cumene, ethylene glycol, ethyl or methyl acetate, and butyl acetate. The influence of inerts can also be considered with this approach.

### 6.2. Graphical design methods

A graphical (Ponchon–Savarit type) design procedure for RD columns based on the transformed composition variables of Barbosa & Doherty (1988) is described by Espinosa, Scenna and Perez (1993). The MTBE process is used to illustrate their method.

Lee, Hauan, Lien and Westerberg (2000a,b) and Lee et al. (2000d) have recently presented an in-depth analysis of the classical Ponchon-Savarit and McCabe–Thiele graphical methods for RD systems.

### 6.3. Design via optimisation methods

RD design via optimisation methods has been the subject of a few studies. Ciric and Gu (1994) formulated a *mixed integer nonlinear programming model*, solution of which yields the optimal number of EQ stages, feed rates and reflux ratios at a minimal annual cost. To the best of our knowledge this was the first paper that combines RD column design and cost estimation, thereby emphasizing the fact that the usual optimisation techniques for ordinary distillation processes may be inappropriate for RD. Gumus and Ciric (1997) used a bilevel optimisation procedure to explore the design of RD columns that could have more than one liquid-phase. The number of phases and the phase equilibria were determined by minimising the Gibbs free energy. Their paper was illustrated by considering the liquid-phase hydrogenation of nitrobenzene to aniline, in which the resulting aniline–nitrobenzene–water system can split into two liquid-phases.

Eldarsi and Douglas (1998b) used the optimisation capability in Aspen Plus to optimise an MTBE column. Their study indicated that the market price of the MTBE product, the cost of the butylenes, the isobutylene composition and utility costs all influence the MTBE column profit. Pekkanen (1995b) described a local optimisation method for the design of RD. Duprat, Gassend & Gau (1988) constructed a set of empirical formulae that was used to optimise an RD process for the separation of the close-boiling mixture of 3-picoline and 4-picoline. The latter method leads to the most rapid optimisation calculations once the empirical formulae have been constructed (by fitting the results of rigorous model simulations). However, the differences between RD processes means that the formulae developed for one process have no value for modelling others.

### 6.4. From conceptual design to column design

Until recently, a procedure to go from a viable EQ stage design to an actual column design was not available in the literature. An important paper by Subawalla and Fair (1999) addresses this issue with a lengthy discussion of the importance of several key design parameters: pressure, reactive zone location, reactant feed ratio, feed

Table 1
Procedure to estimate the reactive zone height, reflux ratio, and column diameter (from: Subawalla and Fair, 1999)

1. Assume that the column feed stream consists of a prereacted mixture of products and reactants at a desired conversion.
2. Specify the distillate and bottom product compositions and determine minimum reflux requirements using the Underwood method. Use a reflux ratio 20% greater than the minimum reflux ratio as an initial estimate to determine column vapor and liquid velocities.
3. Estimate the diameter form the maximum allowable vapor velocity (80% of flood velocity).
4. Estimate the catalyst volume from the catalyst mass and maximum packing catalyst density:

$$V_{\text{cat}} = \frac{m_{\text{cat}}}{\rho_{\text{cat}}}$$

5. Determine the reactive zone height from the calculated catalyst volume and estimated diameter.

$$h_{\text{cat}} = \frac{V_{\text{cat}}}{(\frac{\pi}{4})d_{\text{col}}^2}$$

6. Determine the number of reactive stages by dividing the total reactive zone height by the catalytic packing HETP.

$$N_{\text{cat}} = \frac{h_{\text{cat}}}{\text{HETP}_{\text{cat}}}$$

7. Simulate a reactive column with the calculated number of rectification, reaction, and stripping stages.
8. Increase the reflux ratio by 10%. If the conversion decreases, go to step 9. If the conversion increases, calculate the new maximum vapor velocity and column diameter and repeat steps 4–7. Keep increasing the reflux ratio in 10% increments and repeating steps 4–7 (if necessary) until there is no charge in conversion. Go to step 10.
9. If the conversion decreases with increasing reflux, decrease the reflux ratio by 10%, calculate a new maximum vapor velocity and column diameter, and repeat steps 4–7. Keep decreasing the reflux ratio in 10% increments and repeating steps 4–7 (if necessary) until there is no change in conversion. Go to step 10.
10. If the desired conversion is attained, then we have reliable estimates for the reactive zone height, reflux ratio and column diameter. If the desired conversion is not attained, increase the catalyst mass and repeat the procedure starting with step 3.

location, catalyst mass, number of equilibrium stages, reactive zone height, column diameter, reflux ratio, and HETP. Their detailed step-by-step procedure for designing an RD column is summarised in Table 1. Their paper includes a case study in which their design procedure is applied to the production of TAME. The authors make the important point that their procedure is not applicable to all RD processes: “each system has certain characteristics that make the use of one or more of these guidelines difficult”.

Step 7 in Table 1 should be singled out for particular attention as the one that relies on the models discussed in this article. At the end of their paper the authors recommend using NEQ or rate-based models for this purpose.

### *6.5. RD design in industrial practice*

At the time the Eastman methyl acetate process was developed there were no commercially available simulation programs capable of modelling RD operations. Agreda et al. (1990) reported that stage-to-stage hand calculations were done using flash and reaction programs to calculate the vapor and liquid compositions in the reactive section. The conventional distillation column sections were modelled using an existing EQ model simulation program. Computer programs to model a complete RD column had to be developed in-house at the same time as pilot plant work was being carried out.

Pinjala, DeGarmo, Ulowetz, Marker and Luebke (1992) used the NEQ model RATEFRAC to model MTBE and TAME processes in columns filled with Koch KataMax packing. Very little information on the form of the model is provided (i.e. how the reaction is brought into the model, the actual kinetic expressions are left to the imagination. Limited comparisons with pilot-plant data look quite good. However, the data are provided in such a way as to render them unusable in independent modelling studies.

Frey, Ozmen, Hamm, Pinjala and DeGarmo (1993) have reported that RATEFRAC has been used to accurately predict the performance of commercial RD processes in Germany and Texas, and that the model has been validated for the design of TAME, ETBE, and TAEE units with data from semi-commercial operations.

## 7. Concluding remarks

Belck (1955) concludes his paper describing a hand calculation method for RD columns with the following words:

> …as the complexity of the system increases, the calculation becomes increasingly difficult … the uncertainty inherent in the experimental determination of reaction rate constants and liquid–vapor diagrams

> also tends to make the value of such calculations questionable. Whether or not the experimental work and calculation time — for a detailed computation of such a process in a system with four or more components — can be justified or not will then ultimately depend upon the economic importance of the products.

There remains more than a grain of truth to these remarks even today, when the computer, which would make its mark in chemical engineering soon after these words were written, has largely rendered moot the issue of computational cost.

There are a variety of models now available in the literature for screening, analysis, design and optimisation of RD columns. Each model has its place in the process development cycle. Residue curve maps are invaluable for initial screening and flowsheet development. EQ models have their place for preliminary designs. However, recent NEQ modelling works have exposed the limitations of EQ models for final design and for the development of control strategies. NEQ models have been used for commercial RD plant design and simulation.

Column hardware choice can have a significant influence on the conversion and selectivity; such aspects can be properly described only by the NEQ cell model. It is insufficiently realised in the literature that say for tray RD columns, the tray design can be deliberately chosen to improve conversion and selectivity. Even less appreciated is the fact that the design methodology for RD tray columns is fundamentally different from that of conventional trays. Liquid residence time and residence time distributions are more important in RD. The froth regime is to be preferred to the spray regime for RD applications; this is opposite to the design wisdom normally adopted for conventional distillation. Though the phenomena of MSS has received considerable attention in the literature, it is possible that not all of the steady-states can be realised in practice due to hydraulic aspects, which are taken into account in the NEQ model. For relatively fast reactions, it is essential to properly model intra-particle diffusion effects. Pseudo-homogeneous reaction models may be inadequate for fast reactions. RD columns using dumped (random) packings are susceptible to maldistribution and there is a case to be made for choosing regular structured packings such as that shown in Fig. 13. For proper description of the column dynamics, it is essential to adopt the NEQ model.

Though sophisticated NEQ design models are available already, detailed information on the hydrodynamics and mass transfer parameters for the various hardware configurations sketched in Figs. 10–16, is woefully lacking in the open literature. Paradoxically, such information has vital consequences for the conversion and selectivity of RD columns. There is a crying need for research in this area. It is perhaps worth noting here that modern tools of computational fluid dynamics could be invaluable in developing better insights into hydrodynamics and mass transfer in RD columns (Van Baten & Krishna, 2000; Higler, A.P., et al., 1999a; Krishna, Van Baten, Ellenberger, Higler & Taylor, 1999).

Besides more research on hydrodynamics and mass transfer, there is need for more experimental work with the express purpose of model validation. In such process studies, parameters need to be measured along the height of RD columns. Too often measurements are confined to feed and product stream conditions. Such data cannot serve as a reliable discriminant of computer-based process models.

## Notation

| | |
|---|---|
| $a$ | interfacial area, m$^2$ |
| $B$ | bottoms flow, mol s$^{-1}$ |
| $B_0$ | permeability, m$^2$ |
| $c$ | number of components, dimensionless |
| $c_t$ | total concentration, mol m$^{-3}$ |
| $D$ | distillate flow, mol s$^{-1}$ |
| $Da$ | Damkohler number, dimensionless |
| $D_{i,\mathrm{eff}}$ | effective Fick diffusivity, m$^2$ s$^{-1}$ |
| $Đ_i^e$ | effective Knudsen diffusivity in porous catalyst, m$^2$ s$^{-1}$ |
| $Đ_{i,k}$ | Maxwell–Stefan diffusivity, m$^2$ s$^{-1}$ |
| $E_i$ | enhancement factor, dimensionless |
| $E$ | energy flux, W m$^{-2}$ |
| $\mathbb{E}$ | energy transfer rate, J s$^{-1}$ |
| $E_i^{MV}$ | overall Murphree tray efficiency, dimensionless |
| $h_{\mathrm{cl}}$ | clear liquid height, m |
| $F^V$ | vapor feedstream, mol s$^{-1}$ |
| $F^L$ | liquid feedstream, mol s$^{-1}$ |
| $f$ | component feed stream, mol s$^{-1}$ |
| $h_w$ | weir height, m |
| $h$ | heat transfer coefficient, W m$^{-2}$ K$^{-1}$ |
| $H$ | molar enthalpy, J mol$^{-1}$ |
| $k_1$ | pseudo-first-order reaction rate constant, s$^{-1}$ |
| $K$ | vapor–liquid equilibrium constant, dimensionless |
| $L$ | liquid flow rate, mol s$^{-1}$ |
| $L_M$ | interchange liquid flow rate between horizontal rows of cells, mol s$^{-1}$ |
| $N_i$ | molar flux of species $i$, mol m$^{-2}$ s$^{-1}$ |
| $\mathbb{N}$ | Mass transfer rate, mol s$^{-1}$ |
| $p_j$ | stage pressure, Pa |
| $Q$ | heat duty, J s$^{-1}$ |
| $r$ | number of reactions, dimensionless |
| $r_j$ | ratio of side stream flow to interstage flow on stage $j$, dimensionless |
| $r_j^*$ | transformed reflux ratio, dimensionless |
| $R_{m,j}$ | reaction rate, mol m$^{-3}$ s$^{-1}$ |

| | |
|---|---|
| $R$ | gas constant, J mol$^{-1}$ K$^{-1}$ |
| $s_j^*$ | transformed stripping ratio, dimensionless |
| $S$ | side draw-off, mol s$^{-1}$ |
| $t$ | time, s |
| $T$ | temperature, K |
| $U$ | molar hold-up, mol |
| $V$ | vapor flowrate, mol s$^{-1}$ |
| $W$ | weir length, m |
| $x$ | mole fraction in the liquid–phase, dimensionless |
| $\mathbf{x}$ | mole fraction vector, dimensionless |
| $X$ | transformed liquid-phase mole fraction, dimensionless |
| $y$ | mole fraction in the vapor-phase, dimensionless |
| $Y$ | transformed vapor-phase mole fraction, dimensionless |
| $z$ | mole fraction in either vapor or liquid-phase, dimensionless |
| $Z$ | transformed mole fraction, dimensionless |

*Greek letters*

| | |
|---|---|
| $\varepsilon$ | reaction volume, m$^3$ |
| $\gamma_i$ | activity coefficient of species $i$, dimensionless |
| $\Gamma$ | thermodynamic correction factor for binary mixture, dimensionless |
| $[\Gamma]$ | matrix of thermodynamic factors, dimensionless |
| $\kappa$ | mass transfer coefficient, m s$^{-1}$ |
| $\mu$ | chemical potential, J mol$^{-1}$ |
| $\nu$ | stoichiometric coefficient, dimensionless |
| $\tau$ | dimensionless residence time, dimensionless |
| $\eta$ | viscosity of fluid mixture, Pa s |
| $\eta$ | distance along diffusion path, dimensionless |

*Subscripts*

| | |
|---|---|
| eff | effective |
| $i$ | component index |
| $I$ | referring to interface |
| $j$ | stage index |
| $k$ | alternative component index |
| $m$ | reaction index |
| $t$ | total |

*Superscripts*

| | |
|---|---|
| $F$ | referring to feed stream |
| $L$ | referring to liquid-phase |
| $V$ | referring to vapor-phase |

*List of abbreviations*

| | |
|---|---|
| DAE | differential-algebraic equations |
| DEG | diethylene glycol |
| EG | ethylene glycol |
| EQ | equilibrium |
| EO | ethylene oxide |
| MeOH | methanol |
| MeOAc | methyl acetate |
| AcOH | acetic acid |
| HETP | height of a theoretical plate |
| HTU | height of a transfer unit |
| MS | Maxwell–Stefan |
| MSS | multiple steady-states |
| MTBE | methyl *tert*-butyl ether |
| NEQ | non-equilibrium |
| RD | reactive distillation |
| SRK | Soave–Redlich–Kwong |
| TAME | tertiary amyl ether |

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