

## **(DI)STILL MODELING AFTER ALL THESE YEARS: A VIEW OF THE STATE OF THE ART**

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Modeling distillation is one of those activities that distinguish chemical engineers from their peers. Modeling distillation is something that chemical engineers have been doing continuously (or in batches) for 113 years. Despite predictions of an earlier demise, distillation modeling is not dead. And, while such forecasts have played a role in the lessening of financial support available for distillation research, it is premature to say that there has been any actual lessening of distillation modeling work. Of course, all the activity is merely a reflection of the immense importance of distillation processes in the chemical process industry, a position that has not weakened over time and which is not likely to diminish in the near future (and perhaps not in the intermediate future either in view of recent trends in the cost of energy). At a time when the chemical engineering profession is expanding rapidly into new fields (many of them with bio and/or nano as part of their names), the author finds it refreshing that conventional (=old fashioned) distillation still retains a position of singular importance to the CPI, and that distillation modeling remains a topic of interest. This paper takes a look at trends in distillation modeling, highlights the current state of the art, and takes a stab at predicting where models might be going and what will be needed to get there.

### **CATCHING UP WITH THE PAST**

For at least the last 10 years about 200 papers on distillation and absorption are published each year in the more important English language journals (and with ever increasing numbers in the non-English language journals). Since the majority of these papers do not describe experimental work, I was curious as to what exactly we have been doing all these years. To find out I searched the technical literature for papers on distillation and absorption dating back to 1997 (chosen because it was the year of the last but one I.Chem.E. conference on Distillation and Absorption).

These days, research papers are available electronically, and it should be simple, at least in principle, to search one of a number of computer data bases to find papers on distillation. Two computerized systems that can be useful for searching the technical literature are Chemical Abstracts (CA) and the Web of Science (WoS) from the Institute for Scientific Information (ISI). Unfortunately, asking CA or WoS for papers on distillation or absorption published in the last ten years will return many thousands of records. This is simply because the keywords distillation and absorption are so much a part of the lexicon of science and engineering and are very widely used by writers on topics

that lie entirely beyond the realm of interest to a reader of this article. The foregoing is not to imply that CA and the WoS are not useful to us, quite the contrary; it is necessary simply to ask better questions of these databases. For example: How many papers on reactive distillation were published in 2000. It is questions of this sort that were used to compile Table 1. CA was not used to fill out Table 1 because its search engine did not permit the kind of AND/OR queries that are possible with WoS (and that was found to be essential to performing meaningful searches). Also included in Table 1 is data compiled from a series of bibliographies by Ray<sup>1-10</sup> who simply (or not really so simply) listed papers on distillation, absorption, and extraction for each year from 1980 to 2004 (at the time of writing this article the bibliography for 2005 was not available). The figures for 2006 are incomplete because this table was compiled in April.

Table 1 shows that the WoS usually reports more papers than does Ray in part because it is often difficult to compose a query for WoS that returns only the truly relevant papers. In addition, Ray surveys just 50 of the journals most likely to publish papers related to equilibrium stage separation processes; WoS (and CA) search titles, abstracts, and keywords for many more journals, including non-English language journals. The numbers of papers in each category identified in the Ray reports were obtained by scanning (by computer program) only the titles, which is all the textual data Ray provides for any particular paper. Neither the WoS nor the Ray reports include conference papers (unless separately published in an archival journal; thus the papers from prior distillation and absorption conferences are not included here). Many of the queries of WoS include the phrase "AND (distillation OR absorption)" in order to ensure that appropriate papers are listed. In some case it is necessary to add still more qualifying phrases such as "AND (sieve tray OR structured packing)." Failure to include restrictive phrases such as this will result in thousands of responses most of which are entirely outside our field of interest.

The discrepancies between the ISI and Ray data in Table 1 are, in the end, not very important; both sources paint essentially the same picture of a fairly steady overall rate of publication of papers on distillation and absorption. Table 1 also allows us to identify a number of subplots. For example, interest in both distillation control and batch distillation appears to be more or less at steady state. Batch distillation is of interest because of its importance in the fine chemicals industry with an emphasis there on higher value products. Column operators are storing greater quantities of long term performance data that allows new approaches to control. Work on distillation sequences, whether thermally coupled or not, is very much alive. There are also many papers on azeotropic and extractive distillation. Reactive distillation, however, jumps out as the area receiving considerable (and apparently growing) attention. Of at least as much interest as what we are doing, is what we are not doing, or not doing as much as we were (e.g. developing algorithms) or as, perhaps, we should!

### **MODELS, MODELS EVERYWHERE!**

Chemical engineers have been modeling distillation and absorption processes using the *equilibrium (EQ) stage model* since 1883 when Sorel outlined the concept in order to

Table 1. Numbers of distillation and absorption papers since 1997

Topic	Source	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	All since	
												1997	2000
All	Ray	205	173	184	219	174	200	202	232			1589	1027
Distillation	Ray	96	88	80	98	76	98	88	127			751	487
Absorption	Ray	31	21	19	23	26	21	26	24			191	120
Batch distillation	ISI	20	25	29	25	27	12	19	25	20	6	208	134
	Ray	15	21	17	17	14	7	13	15			119	66
Distillation control	ISI	15	11	13	20	13	19	29	19	27	4		
	Ray	20	13	5	16	12	14	9	10			99	
Residue curves	ISI	7	10	6	9	4	17	11	19	16	6	105	82
Sequences and Coupled systems	ISI	14	16	23	19	26	12	26	18	21	4	179	126
	Ray	13	12	15	17	18	19	21	24			139	99
Minimum reflux or minimum energy	ISI	6	7	9	11	6	5	9	10	10	2	75	
	Ray	1		2	1	1		4					
Azeotropic and Extractive distillation	ISI	16	16	20	24	20	29	16	33	20	7	201	149
	Ray	13	12	11	16	15	24	15	27			133	97
Algorithms	Ray	1			1	1		2	1			6	5
Tray efficiency	ISI	3	2	2	5	3	6	2	3	4	2	32	25
	Ray	6		3	4	4	4	4	4			29	20
Tray column	ISI	13	16	15	30	27	35	23	33	33	9	234	190
	Ray	6	6	10	13	6	11	7	6			65	43
Packed column	ISI	7	3	14	15	15	15	16	15	13	3	116	92
	Ray	24	27	37	34	41	30	44	37			274	186
Nonequilibrium or Rate-based model	ISI		5	10	4	3	5	6	9	4	4	50	35
	Ray	1	4	6	6	4	3	5	10			39	28

(Continued)

**Table 1.** Continued

Topic	Source	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	All since	
												1997	2000
Reactive distillation	ISI	34	43	67	53	53	50	75	90	74	22	561	417
	Ray	22	18	28	26	21	29	25	47			216	148
Reactive absorption	ISI	3	7	7	3	4	5	10	8	11	3		
	Ray	1	4	2	1	1		4	2				
CFD	ISI			1		3	3	4	2	2	2	17	16
	Ray			2	2		2	6	3			15	13
Three-phase distillation	ISI	6	3	5	10	11	6	9	17	16	5	88	74
	Ray	7	2	4	5	7	5	6	15			51	38
Mass transfer	ISI	5	2	5	6	9	13	6	11	13	3	73	61
	Ray	10	10	15	15	13	12	21	23			119	84
Other papers on internals performance	Ray	7	10	18	14	13	20	14	17			113	78

Sources: ISI Web of Science and annual bibliographies compiled by M.S. Ray.

describe the distillation of alcohol (for a more recent paper on modeling the distillation of alcohol see Decloux & Coustel<sup>2</sup>). In more recent times it has become more common to model distillation and absorption processes using *nonequilibrium* (NEQ) or *rate-based* models. Of still more recent origin are detailed computational fluid dynamics (CFD) models.

The modeling of distillation and absorption processes, whether done using EQ, NEQ, or CFD models, requires us to address the following:

- How are the model equations formulated and solved?
- How are the thermodynamic and physical properties needed by the model to be estimated?
- How will we model mass (and energy) transfer between phases?
- How do we model the capacity and performance of actual distillation and absorption columns and how do we incorporate this information in our column models?

These are the questions that frame the discussion that follows.

The equilibrium stage model has been used as the basis for the **conceptual design** of a great many distillation processes and the actual design of thousands of columns despite the fact that the model is essentially divorced from either of the latter two questions posited above. In other words, questions concerning mass transfer and capacity (which, ultimately, determine the size of any column) are dealt with separately from the problem of solving the basic material and energy balances and equations of phase (and possibly chemical) equilibrium that comprise the basic column model. The nonequilibrium models (and to some extent CFD models as well) require us to address all of these issues simultaneously. In fact, it is, the essential separation of questions concerning actual equipment design that is both the strength and the weakness of the equilibrium stage models and their combination that allows the nonequilibrium models to better describe processes with which equilibrium stage models have difficulty (e.g. reactive absorption).

## CONCEPTUAL DESIGN

Modern conceptual design methods lean heavily on residue curve maps (RCMs). The literature on residue curve maps (and distillation lines) now is very extensive and readers are referred to the comprehensive review by Kiva et al.<sup>3</sup> Much of our current knowledge with regard to RCMs has evolved from the work of Doherty & Malone<sup>4</sup> and coworkers. Table 1 suggests that interest in RCMs, never low at any time in the last decade, actually has increased sharply in recent years.

For mixtures that have azeotropes separation boundaries may exist and these boundaries are important in separation process synthesis<sup>4</sup>. Recently Lucia & Taylor<sup>5</sup> showed that separation boundaries for ternary azeotropic liquid mixtures can be characterized as local maxima in the line integral from any unstable node to all reachable stable nodes. This property of separation boundaries permits the use of an optimization method to locate precisely these boundaries. Moreover, Lucia et al.<sup>6</sup> have shown that there is a connection

between the length of residue curves (or distillation lines) and the energy needed to perform a given separation. In particular, the longest residue curve is related to the highest energy costs associated with performing a given separation, and the shortest curve is related to the most energy efficient process.

Conceptual design has become part of mainstream chemical engineering; computer-based tools now are commercially available and the methodologies based on residue curves are described in standard undergraduate textbooks (see refs 7 and 8 to identify just two).

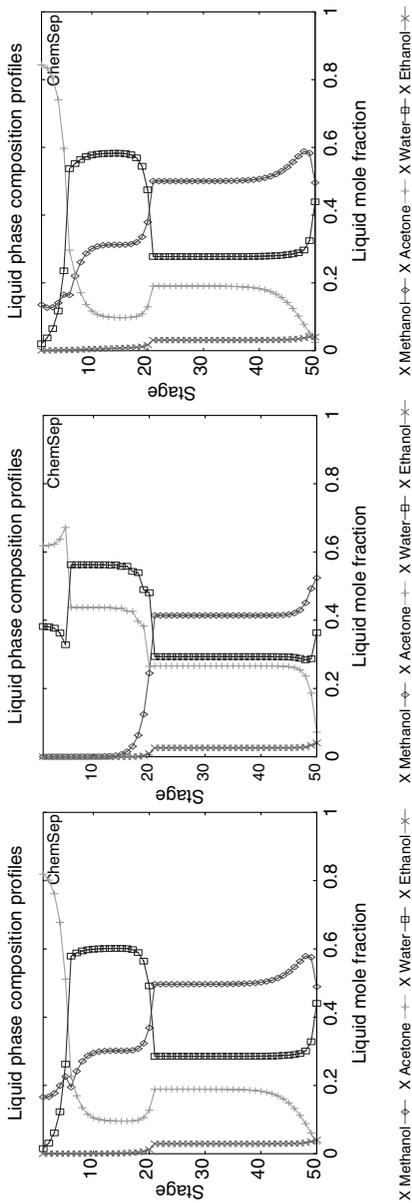
Table 1 also shows that there has been considerable activity devoted to the question of what sequence(s) of (sometimes coupled) columns allows us to separate mixtures in the best way. See, for example, refs 4 and 9. This work is of particular current interest in view of the current high cost of energy. One might also discern (or perhaps just imagine) in the data shown in Table 1 a possible increase in the number of papers devoted to finding minimum energy (reflux) designs.

### **NO ESCAPE: THERMODYNAMICS IS UNAVOIDABLE!**

It is no doubt unnecessary to mention that the essential assumption of the equilibrium stage model is that the vapor and liquid streams leaving a stage are assumed to be in equilibrium with each other. Residue curve maps and other conceptual design tools also require a detailed knowledge of the phase and chemical equilibria. Even nonequilibrium models, which assume equilibrium at a phase interface, do not eliminate or reduce in any way the need for phase equilibrium properties. Thus, our ability accurately to represent equilibria of multiphase systems is of paramount importance no matter what kind of column model we use.

Chen and Mathias<sup>10</sup> have written a short but timely perspective on applied thermodynamics for process modeling. In limited space they review the major achievements of thermodynamics as well as current practice in industry. There has been no lessening of work on applied thermodynamics; the number of papers in this area far exceeds the number of papers on distillation and absorption and this is, in fact, one area in which experimental studies are on a more equal footing with theoretical or modeling papers. WoS lists 170 papers on cubic equations of state between 1997 and 2006, about 1600 on activity coefficients and 395 were found with the simple query "VLE data".

The last two decades have seen the utility of the ubiquitous cubic equation of state increase dramatically with the development of mixing rules that allow their application to nonideal systems previously considered beyond the domain of such models<sup>11,12</sup>. Figure 1 shows composition profiles for an extractive distillation column model obtained with the UNIFAC activity coefficient model and with the Peng-Robinson EOS with both conventional mixing rules and with the so-called Universal Mixing Rule<sup>13</sup>. The agreement between the first and third of these models is very satisfying indeed. This is an application of the PR EOS that would not normally have been considered not too long ago. Note that no claim is made regarding the superiority of the UMR over any of nearly two dozen mixing rules that could have been used<sup>11,12</sup>, it simply happens to be the one chosen to illustrate the developments that have taken place in this field. These modern mixing



**Figure 1.** Extractive distillation modeled with: UNIFAC (left), the PR EOS with conventional mixing rules (centre) and, the PR EOS with Universal Mixing Rule (right)

rules when combined with the UNIFAC model allow use of cubic EOS for chemical systems at high pressures as well as for gas-liquid systems<sup>14</sup>, thereby reducing the need for methods based on Henry's law.

Among the new developments mentioned by Chen and Mathias are newer predictive models based on quantum chemistry. An example of such a model is the COSMO-RS model of Klamt<sup>15</sup>. It is certain that there will be further development of this class of model and their availability in distillation simulation software<sup>16</sup>.

In the words of Chen and Mathias applied thermodynamics is an enabling technology that rests on the foundations provided by experimental work, fundamental theory, and molecular simulation. In another timely perspective de Pablo and Escobedo<sup>17</sup> review the present status and future of molecular simulation in chemical engineering. This field has come a long way since the first direct simulations of phase equilibria were carried out in 1987, but the point has not yet been reached where molecular simulations can replace the assortment of thermodynamic models currently used commercially in distillation simulation. It seems likely that it will not be long before models based on molecular simulations are coupled directly to process simulation tools. Escobedo<sup>18</sup> appears to have been the first (and so far only) investigator to show a residue curve map as well as equilibrium stage column profiles obtained by combining molecular simulations with the appropriate material balance equations. Pfennig<sup>19</sup> has demonstrated a two dimensional molecular simulation that led to (simulated) molecules arranging themselves to give the appearance of the gas and liquid phases in a distillation column with trays and downcomers. Pfennig also was able to compute a McCabe–Thiele diagram from the simulation results.

## **COMPUTER METHODS FOR SOLVING THE EQUILIBRIUM STAGE MODEL EQUATIONS**

For many decades chemical engineers invested considerable effort into developing methods for solving the so-called MESH equations. The earliest practical methods were graphical in nature (and indeed the McCabe-Thiele method retains value for pedagogical reasons as well as being a useful tool for the interpretation of results obtained with modern computer-based simulation methods).

It wasn't until the 1960s that widely applicable thermodynamic models for nonideal chemical systems with more than 2 components became available. It was the development of the Wilson (1964), NRTL (1968), and UNIQUAC (1975) equations, and the UNIFAC group contribution method (1975) that allowed us to model a wide variety of nonideal distillation processes. Such applications demonstrated that the computer algorithms available at that time needed attention. This led to the development of simultaneous solution (SC) methods in the mid to late 1960s, the Inside-Out (IO) methods of the later 1960s and early 1970s (see Seader<sup>20</sup> for an historical review of equilibrium stage simulation). SC and IO methods have evolved to become the algorithms of choice and are included in all commercially successful process simulation programs. Almost inevitably, it was found that there were simulation problems with which these methods had difficulty and that was sufficient incentive to develop still more sophisticated homotopy and continuation methods<sup>20</sup>.

From 1957 to the early 1990s hardly a year passed without the publication of at least one (and usually more than one) new algorithm or improvement to an existing method. Since 2000 the number of publications with novel approaches to solving the MESH equations can, it seems, quite literally be counted on the fingers of one hand as can be seen from Table 1. It proved to be very difficult to craft a query for WoS that would correctly identify the few papers that describe algorithms for solving the equilibrium stage model equations. Indeed, one of the entries in Table 1 is, in fact, a short correction to a different paper separately counted when compiling the Table.

The reason for the dearth (and death might be a more appropriate word here) of purely algorithmic papers really is quite simple: the methods that have been developed and that are widely available in simulators now are capable of solving the great majority of simulation problems. In addition, computers are significantly faster than they were and devising methods to save tiny fractions of a second no longer should be an adequate reason for developing new computer-based solution methods: *reliability* (actually getting an answer) is far more important. To this end it is worth mentioning the tunneling method of Lucia and Yang<sup>21</sup> that represents perhaps the most original approach to solving the MESH equations that has been proposed for some time.

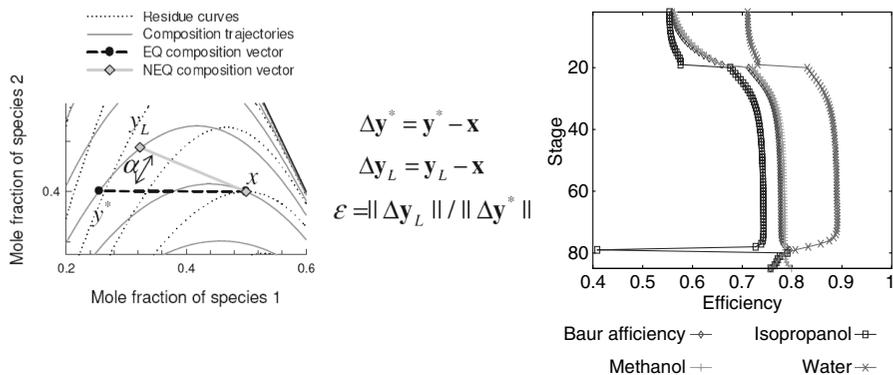
## EFFICIENCY OF DISTILLATION

There is another aspect to the word *reliability* that has nothing to do with the convergence properties of any particular computer method: does the model actually describe a real distillation (or absorption) process? For about as long as chemical engineers have been using the equilibrium stage model it has been known that real distillation processes nearly always operate away from equilibrium. The usual way of dealing with departures from equilibrium is through the use of stage and/or overall efficiencies.

There are many different definitions of stage (or tray) efficiency, that of Murphree<sup>22</sup> being by far the most widely used in separation process calculations. Other types of efficiency have been defined and their merits debated; possibly the most soundly based definition, the generalized Hausen efficiency of Standart<sup>23</sup> is too complicated to use in industrial practice. Seader<sup>24</sup> summarizes some of the shortcomings of efficiencies.

For multicomponent systems (i.e. those with more than two components) there are  $c - 1$  independent component efficiencies and there are sound theoretical reasons as well as experimental evidence for not assuming the individual component efficiencies to be alike; indeed, they may take values between plus and minus infinity. While models exist for estimating efficiencies in multicomponent systems (see chapter 13 in Taylor and Krishna<sup>25</sup> for a review), they are not widely used outside of academia and have not (yet) been included in any of the more widely used commercial simulation programs, although they are available in some proprietary programs<sup>26</sup>.

The fact that component efficiencies in multicomponent systems are unbounded means that the arithmetic average of the component Murphree efficiencies is useless as a measure of the performance of a multicomponent distillation process. Baur<sup>27</sup> has provided an alternative (and novel) definition of efficiency that is depicted in Figure 2. This



**Figure 2.** Geometric efficiency defined (left) as the ratio of the lengths of the actual composition change vector to that of the equilibrium composition change. Right, composition profiles in a column separating a mixture of methanol – isopropanol – water (adapted from an example in references 4 and 28)

“geometric efficiency” has a simple and appealing physical significance; it is the ratio of the length of the actual composition profile (in mole fraction space) to the length of the composition profile given by the equilibrium stage model. The geometric or Baur efficiency has just one value regardless of the number of components in the mixture and it can never be negative. For binary systems in tray columns the geometric efficiency simplifies to the Murphree efficiency, for packed columns it is related to the HETP.

The component Murphree efficiencies calculated for a distillation of methanol – isopropanol – water also is shown in Figure 2 along with the geometric average (Baur) efficiency. The efficiency of methanol in the stripping section is seen to be around 80%, that of isopropanol to be approximately 75%, while that of water is close to 90% in the bulk of the column before falling off on the bottom few trays. All component efficiencies are found to be lower in the rectifying section. The Baur efficiency is close to the Murphree efficiency of methanol and varies from 60% in the top of the column to 78%. The difference between these component efficiencies is important for the design of the column as explained in detail in reference 28. The angle between the composition vectors, shown in Figure 2 as  $\alpha$ , is a second parameter that characterises the separation. Composition angles usually are small for hydrocarbon systems, increasing for nonideal systems to likely maxima of around 20 degrees.

Murphree efficiencies are easily incorporated within some computer-based algorithms. (As an aside it should be noted that vaporization efficiencies are even easier to incorporate in any computer algorithm, a fact that has helped to prolong the life of these quantities despite the lack of any convenient way to relate them to the fundamental processes of heat and mass transfer.) Unfortunately, it is not as easy to include the more

fundamentally sound geometric efficiency in a computer method for equilibrium stage simulations (although it is possible), and this will likely hinder its adoption as a convenient and soundly defined measure of the separation performance of a distillation column. The accumulated inertia of 80 years of Murphree efficiencies has already proved too great a hurdle to overcome for other – mostly better – alternatives to Murphree's definition of efficiency that have been proposed over the years.

### MASS TRANSFER RATE-BASED OR NONEQUILIBRIUM MODELS

It is worth pointing out that E.V. Murphree understood perfectly well that it was a mass transfer model that was needed and presented equations for such in his paper. In fact, Murphree devised the efficiencies that bear his name simply because he did not know how to solve the mass transfer model in his paper. He wrote:

*The use of the general [mass transfer rate] equation in rectifying column problems would cause the calculations to become very much involved and is therefore not considered feasible for practical purposes.*

Murphree's paper appeared over 80 years ago and about 30 years before computers would be used by chemical engineers. Times have changed and it is now possible to model distillation and absorption operations using so-called *nonequilibrium* or *rate-based* models that avoid entirely the (*a priori*) use of potentially confusing concepts like component specific efficiencies and HETPs<sup>29,30</sup>.

In a nonequilibrium model, separate balance equations are written for each distinct phase, the individual phase balances including terms for the rates of mass (or energy) transfer across the interface that separates the vapor (or gas or liquid) phase from the (other) liquid phase. It is necessary, therefore, necessary to face up to the challenge of describing interfacial mass and energy transfer in the multiphase system that is encountered in real tray and packed columns. This is something that is not done in the conventional equilibrium stage model (although the same difficulties must be faced if efficiencies are to be estimated from a mathematical model (see, e.g. Lockett<sup>31</sup>).

Any standard chemical engineering text on mass transfer will tell us that the molar fluxes at a vapour-liquid interface may be expressed as:

$$N_i^V = c_i^V k_i^V (y_i^V - y_i^I) \quad N_i^L = c_i^L k_i^L (x_i^I - x_i^L)$$

where  $c_i^V$  and  $c_i^L$  are the molar densities of the superscripted phases,  $y_i^V$  is the mole fraction in the bulk vapor phase,  $x_i^L$  is the mole fraction in the bulk liquid phase, and  $x_i^I$  and  $y_i^I$  are the mole fractions at the interface.  $k_i^V$  and  $k_i^L$  are the mass transfer coefficients for the vapor and liquid phases.

These equations, so much a part of chemical engineering (and, in fact, the basis for the mass transfer equations in Murphree's paper) are not generally applicable to distillation, and even less to absorption with or without reaction. Thus, the more fundamental nonequilibrium models make use of the Maxwell-Stefan (MS) equations in order to

describe mass transfer in multicomponent systems more rigorously than is possible with the equations above<sup>25</sup>. It is interesting to note that the MS equations have been with us for more years than has the equilibrium stage model! Moreover, the application of the MS equations to describe the mechanism of rectification dates back to a remarkably prescient paper by Lewis and Chang<sup>32</sup> that appears largely to have been ignored. They wrote: “engineers generally are unfamiliar with [the MS equations]” – a situation that has persisted until relatively recent times. Perhaps it is indeed true after all that there is essentially nothing new in distillation modeling, and that all we are doing is revisiting concepts developed by others more than 80 years ago!

It is safe to say that nonequilibrium models have at last come of age, although many years after this author thought that would happen. Rate-based simulation models now are available from all of the major vendors of chemical process simulation software. The number of papers describing new applications of nonequilibrium models has shown significant growth in the last decade with applications to processes that simply cannot be simulated with sufficient accuracy with equilibrium stage models (see Table 1).

### **REACTIVE DISTILLATION (AND ABSORPTION)**

There is now an extensive literature on using both equilibrium and nonequilibrium models for reactive distillation; see, for example, references 33–38 for reviews. Gas absorption accompanied by chemical reaction has for a long time been modeled using mass transfer rate-based concepts.<sup>37</sup> Chemical reactions also influence efficiencies in ways that are essentially unknown and there are no widely accepted models for efficiencies in multicomponent reacting systems. Thus, the use of Murphree efficiencies in reactive distillation modeling almost never is done.

Building a NEQ model of a reactive separation process is not as straightforward as it is for the EQ stage model, in which we simply add a term to account for reaction to the liquid phase material balances. It must be recognized that no single NEQ model can deal with all possible situations; separate models are needed depending on whether the reaction takes place within only the liquid phase or if a solid phase is present to catalyze the reaction. Readers are referred to references 33–38 for much further discussion.

If the reaction rate is very slow then the reaction takes place essentially only in the bulk liquid then it is necessary only to modify the liquid phase material balances to account for the chemical reactions. No modification of the interface mass transfer or equilibrium equations is needed. In other words, the influence of reaction in the liquid film may safely be ignored. 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 region close to the phase interface (aka the “film”). In either case the continuity equations are required for taking into account the effect of the reaction on the interphase mass transfer rates. For most reactive distillations the change in the fluxes through the film will not be significant because the Hatta numbers often are smaller than unity. The composition profile within the film will be approximately 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. In this case the combined set of MS and continuity equations usually must be solved numerically<sup>38</sup>.

The phase equilibrium equations for the interface may also need to be modified for the influence of additional species on the thermodynamic properties at the interface. A case in point is acid gas treating where reactions in the liquid phase create additional species (including ions) that affect the interfacial equilibrium. Enhancement factors have been derived for many reactions but there is no single model that can be used in all cases. Indeed, each process must be considered on its merits.

If a solid catalyst influences the reaction then it is necessary to consider the nature of the catalyst as well. Two kinds of solid catalyst need be considered: Non-porous (e.g. coated sheet metal) and Porous (e.g. Raschig rings made of Amberlyst). In either case the mass transfer model is more complicated.

It is abundantly clear from Table 1 that there has been a great deal of effort devoted to reactive distillation in the last ten years. The great majority of the papers identified by the search of the ISI database and Ray's bibliographies deal with modeling of one or more aspect of reactive distillation; there are far too few papers that present experimental data of any kind. Taylor and Krishna<sup>33</sup> reviewed the literature on the modeling of reactive distillation that cited over 300 sources, about half of which had appeared since the publication of an earlier review by Doherty and Buzad<sup>38</sup> who identified areas for further research. One thing is very clear: the number of papers published in the last decade on reactive distillation alone far exceeds the number of papers on any other single aspect of distillation technology. One might be tempted into thinking that the number of reactive distillation processes in industry is much larger than the number of conventional (i.e. non-reactive) distillation processes; in fact, the reverse is true. An important factor behind the increased attention paid to reactive distillation was the spectacular success of the Eastman methyl acetate process (see references 33 or 38 for literature sources). As a result of the vast body of research carried out in recent years we now know that reactive distillation can be a very valuable technology for certain products, but it is far from a universal processing solution and yet it continues to generate research interest significantly in excess of its commercial importance.

## FLUID DYNAMICS

An issue that is not adequately addressed by most nonequilibrium column simulation models is that of vapour and liquid flow patterns on distillation trays or maldistribution in packed columns. Since phase and chemical equilibrium properties and reaction rates are dependent on the local concentrations and temperature, they will vary along the flow path of liquid on a tray, or from point to point inside a packed column. For such systems the residence time distribution could be very important, as well as for a proper description of mass transfer.

In most NEQ models, as well as in models for estimating the tray efficiency, a flow pattern for the vapor and liquid phases is assumed and this allows us to determine appropriate average mole fractions for use in the mass transfer rate equations. There are three flow models in general use: Mixed flow, plug flow, and dispersion flow<sup>31</sup>. A flow model needs to be identified for each phase. If both phases are assumed well mixed then the average mole fractions are indeed equal to the mole fractions in the exit streams. This is the simplest (and an often used) approach that leads to the most conservative simulation (lowest mass transfer rates, tallest column); at the opposite extreme is plug flow. A most realistic model is dispersion flow<sup>31</sup> but this model is not included in most computer implementations of NEQ models as it is quite complicated.<sup>39</sup>

To deal with this shortcoming of earlier models, NEQ cell models have been developed<sup>40</sup>. The distinguishing feature of these models is that stages are divided into a number of *contacting cells*. These cells describe just a small section of the tray or packing, and by choosing an appropriate set of cell connections one can study the influence of flow patterns on the distillation process. For example, a column of cells can model plug flow in the vapour phase, and a series of cells can model plug flow in the liquid phase<sup>41</sup>. Backmixing may also be taken into account by using an appropriate number of cells. Flow patterns in packed columns are evaluated by means of a cell flow model<sup>42</sup>.

Cell models can be thought of as a small step towards the considerably more challenging task of using computational fluid dynamics to model the two phase flows over trays and packings. CFD has been widely used in other branches of engineering but is a relatively recent addition to the toolbox of the distillation modeler, as will be evident from Table 1, which shows that to date there have been relatively few contributions to this aspect of distillation modeling. CFD has become practically important only in the last few years as computer power increased and methods of solving the CFD equations advanced sufficiently; there will certainly be much work in this area in the future.

The key to a proper (CFD) model is the estimation of the momentum exchange, or drag coefficient between the gas and liquid phases. In the absence of sound theoretical models, empirical correlations for the average gas fraction on the tray are used to estimate the drag coefficient. CFD simulations of sieve trays of 0.3 and 0.9 m in diameter operating in the bubbly flow regime, carried out by Krishna and van Baten<sup>43</sup>, demonstrate the chaotic, three-dimensional character of the flow and the existence of fluid circulation patterns in all three dimensions. These CFD simulations underline the limitations of other – simpler – approaches wherein the flow is assumed to be two-dimensional or where the interaction of the liquid phase with the gas phase is either ignored completely or simplified too greatly. An advantage of the CFD approach is that geometry and scale effects are properly encapsulated. They also demonstrate that CFD can be used to model the flow on trays supporting structures containing catalyst pellets, as might be needed in, for example, a reactive distillation column<sup>43</sup>. The application of CFD to the estimation of tray efficiencies has recently been considered by You<sup>44</sup> (using a 2D model that assumes the phenomena found by Krishna and van Baten are not important on large trays) and by Rahimi et al.<sup>45</sup> The inclusion of mass transfer in these latter CFD models relies on the use of standard (and sometimes inapplicable) mass transfer rate equations and theoretical or

empirical models for the mass transfer coefficients (e.g. a penetration type model in reference 45).

A few studies in which CFD has been used to model the flows over packing elements have also appeared. The paper by Hoffman et al.<sup>46</sup> is of particular interest because they their simulations show film break-up and rivulet flow in systems that may have multiple liquid phases.

### THREE PHASE DISTILLATION

Three-phase distillation remains relatively poorly understood compared to conventional distillation operations involving just a single liquid phase. It is important to be able to correctly predict the location of the stages where a second liquid phase can form (to determine the appropriate location for a sidestream decanter, for example). The very limited quantity of experimental data available for three phase systems suggests that efficiencies are low and highly variable with between 25% and 50% being not uncommon. Equilibrium stage models are widely used<sup>4</sup>; Cairns and Furzer<sup>47</sup> explicitly warn against incorporating Murphree efficiencies into the equilibrium stage model for 3-phase systems, although Müller and Marquardt<sup>48</sup> find that an efficiency modified EQ stage model to be perfectly adequate for their column for the dehydration of ethanol using cyclohexane. Nonequilibrium models for systems with more than two phases now have been developed by several investigators.<sup>49-52</sup> Experimental work that can be used to evaluate these models is, however, relatively scarce.<sup>47,52-53</sup>

### MASS TRANSFER COEFFICIENTS AND INTERFACIAL AREA

The inclusion in the model of the mass transport equations introduces the mole fractions at the interface. It is conventional in chemical engineering treatments of interphase mass transfer to assume that the mole fractions on opposite "sides" of the interface are in equilibrium with each other. This assumption has served us well in that it allows us to use the familiar equations of phase equilibrium to complete the model but it evades the question of the true nature of the interface. Developing models of a phase interface is very complicated and it is for pragmatic reasons that we have stayed away from this particular problem. It seems to be adequate to assume equilibrium at the interface; the limited evidence available suggests that it is a good assumption and the more sophisticated models simply are too complicated to include in process engineering models. In practice mass transfer coefficients and the equally important interfacial area (two parameters that frequently are combined) may be computed from empirical correlations or theoretical models.

The *AIChE Bubble Tray Design Manual* published in 1958 presented the first comprehensive procedure for estimating the numbers of transfer units in distillation. For many years this work represented the only such procedure available in the open literature; the work of organizations such as Fractionation Research Incorporated (FRI) was available only to member companies. Other comprehensive procedures for trays appeared in the 1980s (readers are referred to Kister<sup>54</sup> and Lockett<sup>31</sup> for details). Detailed physical

models based on the idea that bubbles rise in plug flow through the liquid have considerable value for the insight they provide into mass transport in distillation (see, again, Lockett<sup>31</sup> and Garcia and Fair<sup>55</sup> for a more recent application of these ideas). It is also possible to use the model parameters (bubble size, bubble rise velocity, and froth height) as parameters in a column simulation model that can be tuned to fit composition data so that mass transfer models can accurately model real distillation processes. This is preferable to fitting column performance data to efficiencies.

Table 1 shows that papers on mass transfer in distillation and absorption continue to be published. In fact, the number of papers on mass transfer is about twice the number of papers on tray efficiency. One of the more recent papers is an exceptionally comprehensive survey of correlations for the mass transfer coefficients and interfacial area in packed columns by Wang et al.<sup>56</sup> that cites over 120 papers dating back to the 1920s and discusses the ways in which each correlation depends on **physical properties**, operational parameters such as flow rates, and **equipment design** details. It is hard to argue with the request by Wang et al. for more fundamental studies to help us understand the basic phenomena at work in packed columns. What is missing from their review is any guidance on what correlations to use under what circumstances. A similar review of the methods available for estimating mass transfer coefficients (aka Numbers of Transfer Units) on trays would also be welcome. A closer look at the literature on performance correlations would reveal a serious lack of work on methods for estimating mass transfer coefficients, interfacial areas, capacity and pressure drop for systems with multiple liquid phases and in reactive distillation columns. Some of the performance correlations for reactive distillation packings (few in number in any case) are contradictory. This is the one aspect of reactive distillation modeling that warrants further study. The aforementioned work of the group of Wozny in Berlin is leading the way in studies of three-phase systems but we are still a long way from having performance correlations that can be used with confidence in our design and simulation models.

## PHYSICAL PROPERTIES

The only physical properties needed for an equilibrium stage simulation are those needed to estimate K-values and enthalpies; these same properties are needed for nonequilibrium models as well. Enthalpies are required for the energy balance equations; vapor liquid equilibrium ratios are needed for the calculation of driving forces for mass and heat transfer. The need for mass (and heat) transfer coefficients means that nonequilibrium models are rather more demanding of physical property data than are equilibrium stage models.

While, as noted above, papers on thermodynamic models continue to be published at a great rate, the number of papers dealing with other physical and transport properties is much lower. There is considerable room for improvement in our ability to model all transport properties, especially in liquids and high pressure gases. Surface and interfacial tension of mixtures is perhaps the property particularly in need of better predictive methods, as this property has a significant role to play in packed column hydrodynamics (and liquid-liquid extraction). Improved correlations of viscosities and diffusion

coefficients in liquid mixtures also would be welcome, as would be additional data. Krishna and coworkers<sup>57–58</sup> are using molecular dynamics simulations to investigate the composition dependence of binary diffusion coefficients in liquid mixtures and high pressure fluids. One hopes that these simulation studies will lead us to correlations that could be used in column simulation and design models.

## EQUIPMENT DESIGN

In addition to mass transfer coefficients and interfacial area, rate-based simulation models (as well as standard column design procedures) require methods to estimate the capacity and pressure drop of the chosen internal. Correlations for all of these essential quantities exist in the open literature for the older tray and packing types<sup>31,54</sup> (although a case could be made that many of these correlations are fundamentally unsound and extrapolate incorrectly). Table 1 shows that there is a continuing stream of papers on the performance of column internals, although an increasing number of these are the papers on CFD that also were caught by the same query (see for example, the perspective on structured packing of the future by Spiegel and Meier<sup>59</sup>). However, capacity and pressure drop correlations are not (yet) available in the open literature for some of the more modern internals designs. WoS and CA reported no papers that mention ULTRAFAC<sup>TM</sup> and CONSEP<sup>TM</sup>; there were, however, 26 papers that mentioned the older Mellapak<sup>TM</sup> and 5 that referred to Optiflow<sup>TM</sup> packings (although in few cases do the papers provide performance correlations).

## CONCLUSION

Readers of the distillation literature could be forgiven for thinking that this field is dominated by modelers (this author being one of them). While there are many papers that provide data (quite often, sad to say, in a form that renders it useless for other investigators), the majority do not, preferring to deal with one of more aspect of modeling distillation (or absorption). This is a reflection of the ubiquity of computers and the relative difficulty of conducting actual experiments. But if our models are to have any validity then experimental work is essential, a fact not lost on those that work in thermodynamics.

Within the last two decades a new way of simulating multicomponent distillation operations has come of age. These *nonequilibrium* or *rate-based* models abandon the idea that the vapor and liquid streams in a distillation column are in equilibrium with each other. The idea of modeling distillation as a mass transfer rate based operation is hardly new, however. In the 1920s E.V. Murphree went so far as to say: “the use of the general [mass transfer] equation in rectifying column problems would cause the calculations to become very much involved, and it is therefore not considered feasible for practical purposes.” Nowadays, such calculations not only are feasible, there are circumstances where they should be regarded as mandatory.

Of course, models based on *equilibrium stage* concepts will not be abandoned, nor is there any need to do so. For design of new columns in which the column configuration is

not fixed, it is best to start with the EQ model to determine the configuration, optimum reflux etc.

There will be very few (if any) attempts to develop completely novel computer-based methods for solving the equilibrium stage model equations of the equilibrium stage model. There is currently little incentive to do so. Incremental improvements in the computer methods used to solve the nonequilibrium stage model will, however, continue to be made.

To validate *any* column model it is necessary to measure composition profiles; by no means an easy task (especially for packed columns). Such data is, however, essential; product compositions are useless for testing column models; almost any model – including simple black boxes – can be validated with such data. We do not now have (and are unlikely ever to have) data of sufficient quality to allow us to do any better than is possible now with an appropriate column simulation model. Already it is possible to predict the performance of real distillation and absorption columns to within “reasonable doubt”. If the favored model (be it EQ, NEQ or CFD) does not provide sufficient accuracy, then it is possible to tune the model by adjusting certain parameters: efficiencies in equilibrium stage models or the more fundamentally sound choices of bubble size, rise velocity, and dispersion height (for example) in a nonequilibrium model.

All three classes of model currently depend crucially on our ability to estimate mass transfer coefficients, interfacial area, pressure drop, and capacity. Thus, improvements to all models can most easily be obtained by developing new and improved correlations for these key performance parameters. Such correlations should be based on fundamental models and they should behave themselves (i.e. extrapolate properly to the extremes of both low and high flow). CFD may perhaps be useful here in suggesting the proper form such correlations should take. New correlations should be based on data taken under unsteady state conditions. Steady state data is invaluable, but insufficient to allow us to model with confidence the dynamic behavior of real columns. Dynamic models will be used increasingly often in the future. More studies on 3-phase systems would be very welcome, but not modeling studies; what is needed is more experimental work to better understand the flows of multiple liquid phases over packings and on trays and composition profiles that will allow us to validate column simulation models.

There will continue to be improvement in CFD models of the flows on distillation trays. At some point we will be able to add the equations that describe mass and energy transfer across the phase interfaces in these complex multiphase flows. It is to be hoped that these models provide insight into the hydrodynamic (and mass transfer) behavior of our designs and provide guidance as to how we might improve our equipment designs. That these models have the potential to be useful in tray design should, however, no longer be in doubt.

There will be further development of models for predicting thermodynamic and transport properties based on molecular dynamics (MD) and simulations. We look forward to being able to predict with the needed accuracy the properties of the kinds of mixtures that we actually do distill in our real columns.

Indeed, it is not hard to imagine that there will come a time when it is possible to simulate an entire distillation process using a combination of CFD with MD for the property estimation. Such simulations might be expected to take many months (on a multi-processor computer of 2006) and those of us that take delight in long and complicated simulations (such as this author) will be very happy.

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