New Approach to Refinery Process Simulation with Adaptive Composition Representation

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The established technique for simulation of refinery processes is the use of pseudocomponents. However, in order to increase the economical benefit of plant operation, it seems inevitable to include molecular information in petroleum mixtures characterization. This will lead to a strong increase of problem size. For this new class of models, there currently seems to be no special algorithms available. The classic pseudocomponent approach is compared with a newly developed solution strategy, which is explicitly developed to efficiently solve simulation problems with a high detail in composition representation. The new solution strategy is an adaptive multigrid method based on a wavelet–Galerkin discretization. With the wavelet–Galerkin discretization the model can easily be formulated on various levels of detail. In an iterative procedure the multigrid concept exploits these different formulations to construct correction-term approximations to the true solution. The discretization of these correction-term models is now done with a detail in composition representation that is determined by a residual-based adaptation strategy. The proposed method has been implemented for a simple 9-stage distillation column and tested for a variety of feed mixtures. In all investigated tests the proposed method proved to be superior to the conventional pseudocomponent approach in terms of accuracy and efficiency. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 633–645, 2004

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Introduction

The amount of matter processed in the petroleum industry exceeds that in any other branch of chemical processing. For example, in the year 2000 there were refinery capacities to process 4066 million tons of crude oil worldwide, while a total of 3500 million tons were actually consumed (Mineralölwirtschaftsverband, 2000). The second largest industry, the steel industry, processes less than a quarter of this amount (Katzer et al., 2000).

The particular economic importance of the petroleum processing industry has lead to great efforts throughout the last century to model and simulate refinery processes. In the beginning, the methods were mainly based on the evaluation of charts giving rule-of-thumb results for the design of distillation columns. Since a detailed analysis of crude oil was not accessible, the oil was characterized in terms of measurable bulk properties, which is still part of today's procedure. The experimental techniques for obtaining these properties are largely standardized. Most common are the determination of the total density and the characterization of the evaporation behavior by means of experimental procedures given by the American Society for Testing of Materials (ASTM). Differential distillation apparatuses are employed to measure temperature and the corresponding amount of distilled matter.

It is possible to use this characterization to derive certain sets of pseudocomponents, which reflect the measured behavior. The concept of using these pseudocomponents to describe the mixture was introduced early by Katz and Brown in 1933. After introduction of correlation based properties, pseudocomponents can be used like actual chemical compounds. However, this method did not gain wide acceptance until the tedious

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nature of the involved calculations had been effectively tackled with digital computers (Hariu and Sage, 1969). Like many other aspects of science, the modeling of refinery processes was also greatly affected by this rise of digital computers in the following decades. This development helped to create more sophisticated and rigorous models for all refinery processes.

The use of pseudocomponents to represent the composition of a petroleum mixtures is still common practice in the petroleum industry. Because of the successful application of pseudocomponent models in the past, researchers have focused more on determining the primary properties, such as critical properties and the acentric factor, to describe the thermophysical behavior more accurately than on developing completely new concepts for dealing with petroleum mixtures (alternative concepts such as continuous thermodynamics have not yet gained wide industrial acceptance). All major commercial simulation programs (Aspen Plus, HYSYS, Pro/II) (Aspen Plus and HYSYS are a trademarks of Aspen Technologies; Pro/II is a trademark of SIMSCI) can generate pseudocomponents in similar ways to carry out refinery process simulations.

Today, tightened environmental regulations put a lot of pressure on the refining industry by restricting the contents of specific components or component classes in fuels. Besides technical innovations, as, for example, in sulfur reduction technology, all model-based evaluations must increase their level of detail in order to determine the content of particular components with high accuracy.

However, the need to increase modeling details is not just a result of political regulations. The increase in the details of composition by means of molecular information also seems to be a very promising, if not the inevitable way to optimize all refinery processes. In a long-sighted article on the future development of refining, Katzer et al. (2000) stated: “We believe the refinery will change more in the next 20–30 years than it has in the last 70 years.” One of the key issues they raised is how to increase the level of composition detail. This will bring a paradigm shift toward considering refinery processes “more and more like today’s chemical plants.” With such a molecular level of modeling detail, it should be possible to track the path of each individual molecule as it is processed. This should allow us to get the most value out of any molecular species.

In the case of petroleum mixtures, the accurate modeling of heavy components, even if they only amount to a few percent, is crucial for the accurate modeling of the phase-equilibrium behavior (Neau et al., 1993). Thus, a detailed composition cannot easily be avoided if a model with highly predictive capabilities is desired. Considering refinerywide optimization, such a model with detailed composition would surely yield significant economic benefits.

Thinking of a rigorous, composition-based, and refinerywide model that has high predictability, it is clear that the sheer model size hinders an efficient solution on current computers. The reasons for this are not only the memory and processing power limitations. Models of this size become increasingly difficult to solve numerically, so that algorithmic improvements are as important as waiting for new computer generations. Without algorithmic improvements high-performance computers will only be able to tell you much faster that they could not find any solution to your problem.

Besides also stressing the need for models with detailed composition in his keynote lecture at FOCAPO’98, Michael P. Ramage (Ramage et al., 1998) focused on the changes in technical computing within the petroleum industry. To keep such large model sizes manageable, Ramage posed the demand for adaptive calculation schemes. Coarsening and refinement of modeling detail should be possible in order to satisfy constraints on accuracy and calculation time. This adaptivity should be an inherent feature of future calculation schemes, allowing different parts of the complete model to shrink and grow in order to provide just as much rigor as is needed to obtain the desired result.

Based on previous work by von Watzdorf (1998) and von Watzdorf and Marquardt (1997), a new simulation technology has been developed by Briesen and Marquardt (2003a), which seems promising to resolve some of the issues just reviewed. The objective of this new approach was to provide a sound, flexible, adaptive, and error-controlled framework for the simulation of complex multicomponent mixture processes. While Briesen and Marquardt (2003a) focused more on the mathematical background and the algorithmic framework, this article presents the application of the method to distillation column simulation and compares the new approach to pseudocomponent lumping. Therefore, this article investigates the performance of the new algorithm instead of giving the details of the algorithm itself. However, to get an understanding of the algorithm, a descriptive formulation is given. For the mathematical description of the algorithm, the reader is referred to the article just cited.

Characterization

Petroleum analysis

The characterization of a petroleum fraction largely depends on the available analytical data. There are numerous experimental techniques for analyzing petroleum fractions.

First, bulk properties are usually recorded. The measurement of bulk properties is generally quick and cheap to perform. These bulk properties, like density (or API specific gravity), viscosity, and molecular weight, do not provide any information on composition directly. But bulk property measurements are input data for many pseudocomponent generation schemes. The proper use of these bulk data can significantly improve the quality of the characterization.

Distillation curves are more informative than bulk property measurements. Again, there are many different procedures with standardized experimental setups and specifications. For example, D86 distillation, true boiling point distillation (TBP), and equilibrium flash vaporization (EFV) are very popular.

Because of its high resolution, gas chromatography (GC) is the method of choice for low boiling hydrocarbon mixtures. If properly calibrated, GC directly reveals the composition in terms of the chemical species. For higher boiling fractions, the separation gets increasingly difficult, since the number of components with similar retention behavior increases quickly.

Another way to access the composition on a molecular level is mass spectrometry (MS). MS becomes particularly powerful if it is coupled with one of the separation techniques just discussed. In particular, the coupling of gas chromatography and mass spectrometry (GC-MS) provides a detailed composition analysis of most of the low boiling components augmented with a separation in compound class: paraffins, olefines, naphtenes, and aromatics.

To determine the number of structural elements in a molecule, nuclear magnetic resonance spectroscopy (NMR) can be used. NMR spectroscopy can directly determine the amount of aromatic and aliphatic carbon, as well as hydrogen distributions. With this information NMR spectra can be used to derive the separation of the mixture into compound classes as well as directly access structural molecular information.

As analytical techniques are continuously improving, there is a trend in modeling petroleum processes to better exploit this analytical information, which leads to more detailed, hence much larger process models, as will be shown in the following sections.

Pseudocomponent generation

The use of pseudocomponents is the prevailing technique for characterizing petroleum mixtures for simulation purposes. All major commercial simulators (Aspen plus, HYSYS, Pro/II), which are commonly used for petroleum process simulation, follow this concept by generating a set of pseudocomponents on the basis of the available analytical data. The core of every pseudocomponent generation technique is the assignment of physical properties to the hypothetical components. A wide range of different methods can be used for this procedure, each one serving a special purpose. The highly heuristic nature of pseudocomponent generation has hindered the development of a *single* commonly accepted method.

Historically, the concept of pseudocomponents was developed under the name *integral method* quite some time ago (Katz and Brown, 1933). Hariu and Sage (1969) were the first to use a computer to use the pseudocomponent method to calculate a flash. This paved the way for the enormous, almost exclusive popularity of the pseudocomponent approach.

The experimental basis for pseudoization is usually a distillation curve analysis. As stated earlier, there are several different experimental procedures, all leading to different distillation curves. Nevertheless, pseudoization is mostly based on TBP curves. If a distillation curve other than TBP, such as the popular D86, is provided, one uses conversion correlations (see, for example, Daubert, 1994) to obtain a TBP curve first.

There are different schemes in the literature for selecting the pseudocomponents (see, for example, Sim and Daubert, 1980; Miquel and Castells, 1993). In commercial simulators it is common to choose boiling-point ranges in the TBP curve. The boiling point of a particular pseudocomponent is determined by some averaging procedure over the TBP curve. Using molecular weight and density information, the corresponding volume fraction is converted to the molar fraction of the pseudocomponent.

The property calculation for hydrocarbon mixtures is usually based on *equation-of-state* (EOS) models. Cubic equations of state, namely, the Peng-Robinson and the Soave-Redlich-Kwong equation, are used most frequently. To employ EOS-based property calculations, the critical properties and the acentric factor need to be estimated. The estimation of these properties is the most error-prone and “magic” part in the pseudocomponent lumping scheme. It is clear that the more input data provided (compound class analysis, viscosity, etc.), the more accurate the characterization will become. None of the many different estimation methods available (e.g., Lee and Kesler, 1975; Kesler and Lee, 1976; Riazi and Daubert, 1980; Zhang et al., 1998) is generally superior to the others. Recommendations on the choice of an appropriate method can be found in the API *Technical Data Book* (1992). Generally, the characterization, and consequently the model accuracy, largely depends on the experimental data available, the pseudocomponent method, and the number of pseudocomponents chosen (Carrier et al., 1989).

There are also methods for pseudocomponent characterization that do not follow the path just outlined. Eckert (1999) suggested a method to determine the composition of a petroleum mixture in terms of an introduced set of real chemical species that are likely to be present in the mixture. The method is based on the composition optimization of the substitute mixture in order to optimally reflect the measured EFV curve. Although this results in a set of actual chemical species, the method is classified here as a pseudocomponent method, because of the uncertainty about whether the chosen species are actually present in the mixture. But contrary to the pseudocomponent methods given earlier, it has the advantage that reactions can be modeled in a straightforward way.

Another lumping strategy based on mixing rules was presented by Leibovici et al. (1996) for the case of an existing detailed chemical analysis. With their algorithm they reduced the number of components from 150 identified chemical species to 26, 7, and 5. Employing proper mixing rules, Leibovici (1993) showed that the EOS for the lumped mixture is consistent with the detailed one. By applying delumping strategies to the results of a lumped-mixture simulation, one can also obtain an approximate solution for the full mixture (Leibovici et al., 1996; Rabeau et al., 1997).

Continuous mixture characterization

As with the pseudocomponent concept, the continuous mixture characterization is also quite old. In fact, it was the prevailing way of characterization (e.g., Bowman, 1949) before the pseudocomponent method gained popularity. The continuous characterization stems from the generalization of the standard distillation theory of that time to mixtures with an indefinite number of components.

Because it is much more usable on computers, however, pseudocomponent techniques have widely superseded the continuous representation. Since pseudocomponents were already discrete by nature, one did not have to be concerned with discretization of the continuous concentration distribution. However, von Watzdorf (1998) has shown that the pseudocomponent method is actually nothing but a collocation discretization of a continuous distribution.

The primary idea of the continuous mixture representation is to assume that the number of chemical species present in a petroleum (or other complex multicomponent) mixture is so large that it can be considered a continuous rather than a discrete distribution. If only a few discrete components are present, this obviously does not make much sense (see left of Figure 1).

However, as the number of components increases, one can see that the continuous distribution, $F(\xi)$, is also capable of reflecting the discrete description (see right of Figure 1). The value of the molar fraction of a particular component can always be determined by integrating the distribution $F(\xi)$ over the corresponding interval of the characterizing variable $\Delta\xi$

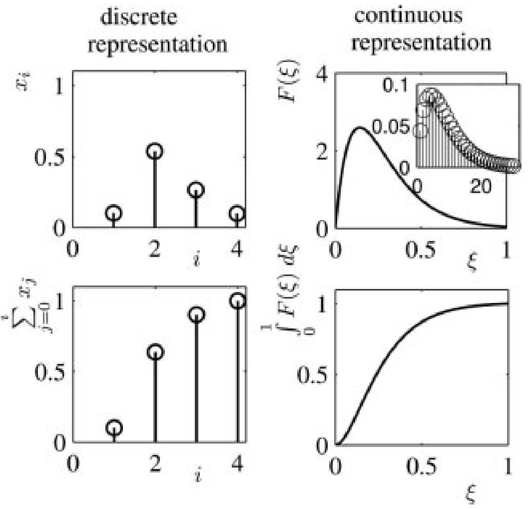

Figure 1. Discrete (left) and continuous (right) mixture characterization.

(this is what was done by early pseudocomponent techniques, giving them the initial name *integral methods*):

$$\int_{\Delta\xi_i} F(\xi)d\xi = x_i. \tag{1}$$

Generally, there are no limitations in the choice of the characterizing variable. For example, Bowman (1949) used the relative volatility as the characterizing variable. But equivalently any other property, such as normal boiling temperature or even a discrete component index for identified components, can be used. For convenience the values of the characterizing variable in this work will be scaled to the interval [0, 1]. For a finite interval of the characterizing variable, this can be achieved without loss of generality by a simple linear transformation. In the mid-1980s, researchers revisited the continuous representation concept to build a complete thermodynamic framework nowadays known as *continuous thermodynamics* (Rätzsch and Kehlen, 1983; Cotterman et al., 1985). Following the concepts of continuous thermodynamics, several technical problems such as flash calculations (Cotterman and Prausnitz, 1985; Chou and Prausnitz, 1986; Rätzsch et al., 1988), multicomponent distillation (Rätzsch et al., 1989), reservoir fluid simulation (Peng et al., 1987), and adsorption processes (Annesini et al., 1994), have been investigated. A drawback of these examples is that they all use statistical functions (e.g., gamma distribution) for the approximation of the concentration distributions. This approach significantly restricts flexibility, since only distributions with the appropriate shape can be represented adequately.

Molecular characterization

As in Leibovici et al. (1996), modern lumping strategies rely more and more on detailed experimental data. This is true for separation and seems inevitable for reaction process modeling (Hu et al., 2002). It seems to be a promising way to base all simulations (separation and reaction) not on two different sets of lumps, as is current practice, but to use the detailed experimental analysis directly in an appropriate representation. A unified composition representation would allow the consideration of a larger part of a refinery complex without inconsistencies, which may stem from frequent lumping and delumping along with the different unit operations. This may add significant value, particularly to refinerywide optimization. Such a composition representation also would be highly beneficial for integrated processes, since it enables the consistent modeling of, for example, reactive distillation.

Hu et al. (2002) suggested a matrix representation, which stems directly from the available experimental data. The advanced experimental methods usually characterize a mixture by means of molecular type and molecular size. With these two properties one can span two dimensions of a matrix that holds the flow rates of the particular molecular types and sizes. The rows of the matrix capture the size of the molecules represented by the carbon number (number of carbon atoms per molecule). The columns can hold any molecular type present in petroleum mixtures such as normal or isoparaffins (nP, iP), normal and isoolefines (nO, iO), naphtenic compounds with one or more rings (N, 2N, nN), aromatics with different numbers of aromatic rings (A, 2A, nA), and compounds with both organic and naphtenic rings (AN6, an aromatic with a six carbon atom naphtenic ring). The suggested matrix does not distinguish between structural isomers within one matrix entry, but since structural isomers currently can only be experimentally distinguished for a lower molecular weight range, this is not a serious drawback of the representation.

For property calculations the matrix representation is a suitable framework to employ group contribution methods. Since each entry in the matrix has the same structural groups, approaches like the UNIFAC group contribution method (Ruzicka et al., 1983) or the COSMO-RS quantum mechanics approach (Klamt and Eckert, 2000) are applicable, respectively, today or in the future.

If the matrix should provide high flexibility, one has to consider many matrix entries. To built a simulation of a separation unit, one certainly needs to reduce the complexity of the calculation, that is, by introducing a lumping scheme to generate a set of pseudocomponents. However, by introducing lumping and delumping in the process units, an inconsistent composition system again arises for the different process steps. The matrix representation then acts more like a common interface between different reaction and separation units. Nevertheless, the pseudocomponent lumping can easily be based upon the molecular information using appropriate mixing rules. Since properties other than just normal boiling temperature can be employed in addition to find components with similar behavior, this eventually is a much more fundamental approach, similar to the lumping scheme presented by Leibovici et al. (1996). Such lumping schemes based on molecular information should be clearly superior in their predictiveness to the introduction of purely fictitious pseudocomponents based on TBP analysis.

Model Formulation

Continuous model formulation

The simulation technology presented in this work is based on the idea used in continuous thermodynamics to represent the

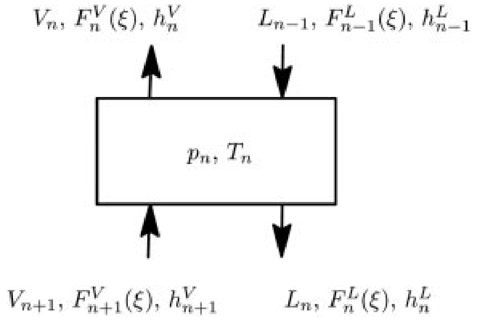

Figure 2. Flow convention and nomenclature for a standard distillation column tray model in terms of a continuous composition representation.

mixture by means of a (possibly highly irregular) distribution function instead of using a discrete representation of distinct components. Generally, such a distribution function can fully represent any composition information, including a detailed chemical analysis.

The main conceptual advantage gained by using a distribution function is to consider the model reduction problem as a discretization of a continuous problem. The issues of adaptivity, error control, and reliability of the solution cited earlier quite naturally arise in modern discretization techniques for differential-algebraic systems (see, for example, Brenan et al., 1996) and partial differential equations (see, for example, Vande Wower et al., 2001). Thus, many concepts developed from numerical mathematics can be adopted for the rather specific task of reducing the complexity of petroleum mixture process simulation.

In the previous section the continuous and the discrete (pseudocomponents, molecular) representations were introduced mainly from the viewpoint of characterization of hydrocarbon mixtures. This section will discuss the consequences that arise if these representations are used for process modeling. Using some standard simplifications and the flow conventions given in Figure 2 the continuously formulated equations for a simple tray of a distillation column are given as follows.

Function-valued equations

$$0 = V_{n+1}F_{n+1}^V(\xi) + L_{n-1}F_{n-1}^L(\xi) - V_nF_n^V(\xi) - L_nF_n^L(\xi), \quad (2)$$

$$0 = F_n^V(\xi) - K(F_n^V, F_n^L, T_n, p_n, \xi)\, F_n^L(\xi). \quad (3)$$

Scalar-valued equations

$$0 = V_{n+1} + L_{n-1} - V_n - L_n, \quad (4)$$

$$0 = V_{n+1}h_{n+1}^V + L_{n-1}h_{n-1}^L - V_nh_n^V - L_nh_n^L, \quad (5)$$

$$0 = \int_0^1 F_n^V(\xi)d\xi - 1, \quad (6)$$

$$0 = p_n - p_{n-1} - \Delta p, \quad (7)$$

$$0 = h_n^L - h_n^L(F_n^L(\xi), T_n, p_n), \quad (8)$$

$$0 = h_n^V - h_n^V(F_n^V(\xi), T_n, p_n). \quad (9)$$

The unknowns in this model are the flow rates (V_n, L_n) leaving the tray n, the liquid and vapor enthalpies (h_n^L, h_n^V), the pressure (p_n), the temperature (T_n), and the vapor and liquid phase composition distributions ($F_n^L(\xi)$, $F_n^V(\xi)$) on tray n. The vapor flow rate, V_{n+1}, and the liquid flow rate, L_{n-1}, including their intensive properties entering the tray, as well as the pressure, p_{n-1}, on tray n, can be considered as known quantities if a single tray is considered.

The component material balance (Eq. 2) and the vapor–liquid equilibrium (Eq. 3) are modeled using only one function-valued equation for each. For a discrete modeling approach these equations would be vector equations, concatenating one scalar equation for each (pseudo or real) component considered. Also the discrete phase-equilibrium constant becomes a continuous function $K(\xi)$.

The set of scalar-valued equations is essentially the same as it would be in the discrete case. If state functions like the enthalpy depend on composition, the corresponding continuous formulations (Eqs. 8 and 9) use the whole distribution function, which carries the complete composition information. Finally, the standard summation in the closure condition just needs to be replaced by the corresponding integration (Eq. 6). Every process model available in discrete representation can generally be rewritten without major effort in the continuous formulation (see the following section).

"Continuization" of the discrete problem

The current trend in modeling petroleum processes involves an increasingly detailed composition. This detailed, molecular information is in principle discrete. However, it is straightforward to set up a continuously formulated model representing exactly the same physical system description as for the discrete formulation containing the molecular information. The only condition that needs to be considered is Eq. 1. It poses the relation between the discrete molar fractions x_i of the ith discrete component and the distribution function $F(\xi)$ over the interval $I_i = [(i - 1)/n, (i/n)]$. Assuming a distribution function that is piecewise constant over the intervals I_i, a constant function value, F_{I_i}, can be determined by

$$x_i = \int_{(i-1)/n}^{i/n} F_{I_i}d\xi = F_{I_i}\Delta\xi_i = \frac{F_{I_i}}{n}. \quad (10)$$

A distribution function corresponding to an arbitrary set of discrete components can therefore always be written as

$$F(\xi) = F_{I_i} = x_in, \quad \xi \in I_i, \quad i = 1, \ldots, n. \quad (11)$$

By this evaluation every interval I_i is directly associated with a single component x_i (see Figure 3).

What is true for the composition representation is similarly valid for any other state function such as the continuous phase equilibrium function $K(\xi)$. A discrete set of phase-equilibrium constants can be "continuized" according to

$$K(\xi) = K_{I_i} = k_i, \quad \xi \in I_i, \quad i = 1, \ldots, n. \quad (12)$$

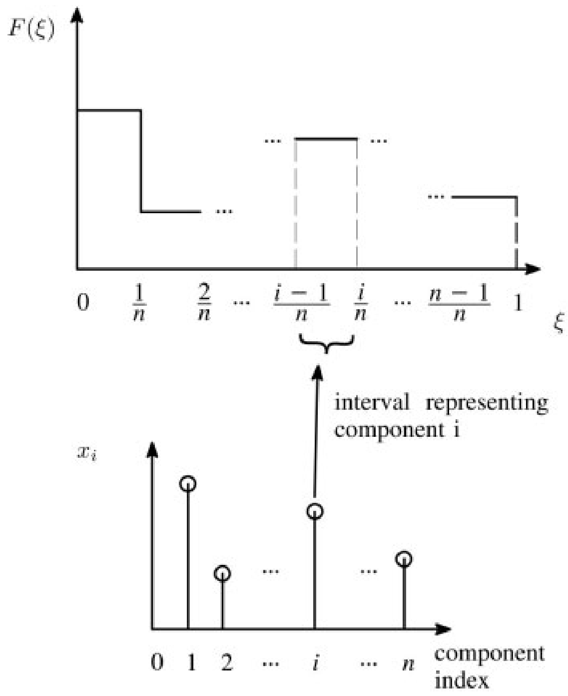

Figure 3. The "continuization" of a discrete composition representation.

Since for the K-values there is no integral equation (Eq. 1) to be satisfied, the discrete K-values do not even have to be scaled. The discrete K-values k_i are just associated with the interval $I_i = [(i-1)/n, (i/n)]$, which represents the discrete component i. This is generally possible no matter how the discrete K-values k_i have been calculated. Note that all continuized models contain exactly the same information as the discrete model, since all the performed operations again lead to piecewise constant functions.

With this procedure, however, the path of continuous thermodynamics is left, since the phase equilibrium constants may be calculated the same way as for a discrete mixture. Only the representation of the composition by a continuous distribution function, which can generally be highly irregular, is retained. In essence a "continuization" of a discrete problem is done. One might ask, why bother with the continuous formulation at all if it gives us only a different perspective on the same problem? But it is just this simple shift of view that allows the model reduction problem to be considered as a discretization problem. A similar shift of view has also been employed for the model order reduction for staged separation processes (Cho and Joseph, 1983a, b; Stewart et al., 1985). Instead of considering the stages of a column in a discrete manner, these authors introduced a partial differential equation to approximate the complete staged model. The concentrations of the components are then no longer discrete values on the stages, but are approximated by polynomial expressions over the column height.

The continuous model formulation will be used in this work even if the original model is discrete. Instead of considering the discrete model, the perspective is changed to obtain a compact continuous model formulation (see Figure 4). Discretization now introduces many degrees of freedom to derive reduced-order models. For particular "continuization" and discretization approaches (like the one used in this work), even the original discrete formulation can be reobtained. Considering the model reduction problem as a discretization problem generally opens up a variety of mathematical concepts available for adaptive model reduction.

Note that the use of a continuous composition representation does not automatically *imply* the use of continuous thermodynamics, since the properties can still be evaluated in the final discretized manner. On the other hand, it also does not *preclude* continuous thermodynamics, which again stresses the flexibility of the approach.

Model complexity

One of the primary objectives of this work is to compare the pseudocomponent modeling and simulation approach with the newly proposed simulation technology. In order to be able to compare both approaches, we need to find measures for the model complexity.

For pseudocomponents the number of used components is a direct measure of the model size. The pseudocomponents scale the model size by introducing equations for the composition relationships, such as the material balance and the phase equilibrium. Hence, in the context of pseudocomponents, it is reasonable to reduce the complexity of the problem by using as few pseudocomponents as possible to obtain a small problem size.

Considering a continuous model, the discussion of the complexity is different. The sets of composition equations in the continuous formulation reduce to only one now function-valued equation: Eqs. 2 and 3 need to be satisfied for each value of ξ, so there is no simple measure for the actual model complexity, such as the number of components in the pseudocomponent case. The question of complexity of the continuous formulation remains unanswered until a discretization scheme to facilitate a numerical solution is introduced. After discretization the complexity can be considered to be the number of equations emerging from each of Eqs. 2 and 3. In essence, the same model complexity for the discretized continuous approach and the pseudocomponent approach is equivalent to the equality of the total number of equations in both models. Although formally not correct, the model complexity in the discretized continuous model can be seen as an equivalent pseudocomponent number.

In this work, a wavelet-Galerkin discretization is used to obtain the discretized equations. The problem of the discretization of continuously formulated models with a wavelet-Galerkin discretization is discussed in more detail by von Watzdorf (1998) and Briesen (2002). A summary is presented elsewhere (Briesen and Marquardt, 2003a).

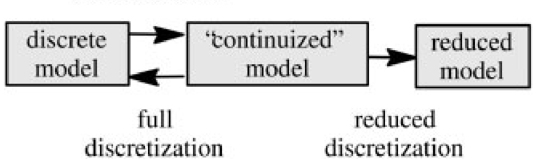

Figure 4. Model reduction by means of a discretization of a "continuized" problem formulation.

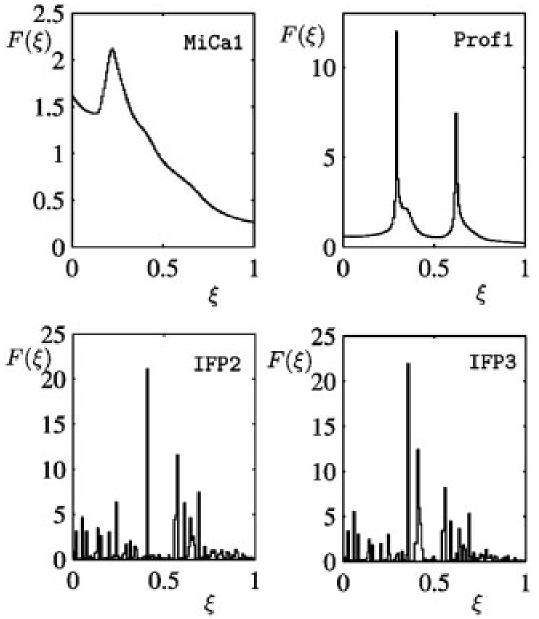

Figure 5. Feed distribution for the continuous characterization (upper plots) and detailed chemical analysis (lower plots).

Model example

As discussed earlier, the available characterization of a petroleum mixture can vary significantly. In order to show that the proposed method is not limited by the available experimental characterization, two extreme cases of characterization are considered. The minimum characterization necessary to derive a composition description and to employ a property calculation method is given by a distillation curve and the bulk specific gravity. Although this may hardly be satisfactory for a predictive simulation, it marks the minimal experimental information on which a simulation can *in principle* be built. The most detailed information that can be expected from an experimental analysis is the fully resolved composition of the mixture in terms of real chemical components.

Two example systems are considered for each of the two characterization types. The first set of data for the case of a minimum characterization is taken from Miquel et al. (1992). It is further denoted by `MiCa1`. The authors give a TBP curve with 11 data points spanning the boiling point interval from 270 K to 900 K. Generally, the few data points that are usually available from TBP experiments lead to quite smooth-fitting curves of these data. To be able to show how the proposed algorithm could handle a more detailed (such as continuously reported) TBP curve, a fictitious TBP curve denoted by `Prof1` is introduced. This curve shows "plateaus," which can be associated with the presence of some main components in the mixture. The data sets with the detailed composition analysis have been provided by Vacher (personal communication, 1998). These sets, denoted in the following by `IFP2` and `IFP3`, contain the detailed gas chromatographic analysis of two commercial gasolines. The shapes of all four feed distributions are given in Figure 5.

In all of the distribution functions presented, the components are arranged in order of increasing normal boiling temperature. Since the examples will focus on thermal separation processes, the vapor–liquid equilibrium is the main influence on the system behavior. The normal boiling temperature therefore qualifies as a characterization variable, since it can be seen as an indicator for the phase behavior of a component. However, this particular order of components is not mandatory. Generally, the components should be ordered according to similarity in the behavior which is decisive for the particular process. If there are different types of units in a flow sheet, this may necessitate reordering the components.

To derive a continuous composition representation from the TBP curves of the `MiCa1` and `Prof1` mixtures, a method proposed by Miquel and Castells (1993, 1994) was extended. Their method was directly adopted for the corresponding pseudocomponent calculations.

For the pseudocomponent simulations based on the detailed composition sets `IFP2` and `IFP3`, standard mixing rules have been applied to lump certain sets of components in pseudocomponents.

For the property calculations, namely, the phase-equilibrium constants and the enthalpies, simple correlations were used. The phase equilibrium constant was calculated on the basis of the Clausius-Clapeyron equation in combination with Trouton's rule, resulting in dependence only on the normal boiling temperature of the components (Vakili-Nezhaad et al., 2001). For the liquid and vapor enthalpy calculations, a correlation proposed by Moharam et al. (1998) was used. It allows us to calculate the enthalpies as a function of molecular weight, the Watson characterization factor, temperature, and pressure.

The example process investigated consists of a 9-staged distillation column with the feed tray on the fifth stage. The model equations for the standard trays are given in Eqs. 2–9. The top of the column is modeled as a total condenser, the bottom as a simple reboiler, and for the feed tray the balance equations are augmented by the appropriate expressions for the feed stream. The maximum composition detail considered is 128 components. This number of components was chosen for reference calculations, since the wavelet framework of the method naturally subdivides the domain in 2^n section. Thus, the reference model of the example comprises the total number of 2361 equations. The column is specified by the choice of a bottom product flow rate, P_{bot}, a pressure, p_{top}, at the top of the column, and a feed specification.

A more comprehensive description of the four example mixtures, the employed physical property calculation methods, and the column model can be found elsewhere (Briesen, 2002).

Adaptive Multigrid Solution Strategy

This section is intended to give the reader the main conceptual ideas of the proposed solution strategy in a largely nonformal manner. This should provide the reader with a qualitative understanding of the algorithm needed to discuss the simulation results. The explanation of the algorithm is rather simplified, so that not all the details of the method actually implemented are given here. In particular, the true character of the multigrid approach cannot be properly reflected in such a simplified description. For full information, the reader is referred to the expositions of Briesen (2002) and Briesen and Marquardt (2003a).

Multigrid approach

The algorithm is based on a continuous or "continuized" model formulation as introduced earlier. Steady-state models of thermal separation processes like the column (or just the tray) can be written according to the following general residual formulation

$$\boldsymbol{f}(\boldsymbol{F}(\xi), \boldsymbol{x}, \boldsymbol{p}) = 0, \tag{13}$$

$$\boldsymbol{g}(\boldsymbol{O}[\boldsymbol{F}(\xi)], \boldsymbol{x}, \boldsymbol{p}) = 0. \tag{14}$$

The arguments of these functions are the vectors $\boldsymbol{F}(\xi)$ of the state functions (continuous distribution functions), $\boldsymbol{x}$ of the state variables, and $\boldsymbol{p}$ of the parameters. The notation $\boldsymbol{O}[\boldsymbol{F}(\xi)]$ in Eq. 14 denotes that the vector $\boldsymbol{F}(\xi)$ of the state functions is not directly an argument of the vector function $\boldsymbol{g}$. The operator $\boldsymbol{O}[\,\cdot\,]$ maps the vector of state functions on a vector of scalar values. Obviously, Eqs. 2 and 3 are of the Eq. 13 type, and Eqs. 4–9 are of the Eq. 14 type.

Since continuously formulated models with practical relevance almost never can be solved analytically, a discretization scheme needs to be introduced to solve the problem. Since Eq. 14 is already algebraic, only Eq. 13 needs to be considered for discretization.

For discretization there is a wide variety of different methods available. As already mentioned, a wavelet-Galerkin discretization is used in this work. The major discretization feature of interest here is that discretization is always associated to a discretization grid determining the resolution of the discretization. In the wavelet-Galerkin discretization this grid is determined by a set of basis functions (Haar-wavelets). Since the state functions, the distribution functions, reflect the composition information, a discretization of this variable on a certain grid means a problem formulation with a certain level of detail in composition. This dependence of the discretization on the grid allows the formulation of models with high or low detail in a composition representation corresponding to the discretization on a high- or low-resolution grid, respectively. This flexibility is the main prerequisite for the use of multigrid methods, which today are among the most powerful tools known in numerical mathematics with a wide range of applications (Briggs et al., 2000).

The objective of the proposed algorithm is to determine an approximation of the solution in high resolution without actually solving a high-resolution model. To achieve this, the problem is decomposed resulting in a sequence of smaller problems, which are solved iteratively. The proposed multigrid algorithm is given on a very coarse level of detail in Figure 6. As with every iterative procedure, the algorithm first needs to be initialized with an initial guess for all the unknowns. Then a low-resolution model is solved to determine a correction of the initial guesses. Note that the concentrations *themselves* are not determined, but only a *correction* of the concentration on the coarse grid. The solution of this low-resolution correction model is much easier and faster than the solution of a large high-resolution model. After correcting the approximation, the residual error is compared against a user prescribed tolerance ε_{tol}. If the desired accuracy of the approximation is met, the algorithm can be terminated. If the prescribed accuracy is not yet met, another iteration needs to be performed.

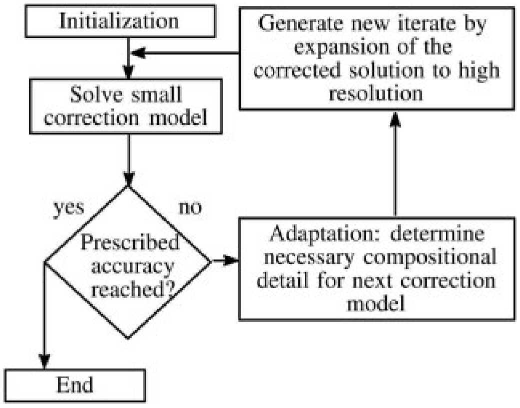

Figure 6. Proposed multigrid algorithm on a coarse, illustrative level of detail.

Adaptive grid selection

Adaptivity is one of the most important concepts included in the algorithm. In the adaptation step, the necessary composition detail for the next small correction model is determined. Thus, it can be assured that concentrations, for which the approximation is already good, do not have to be considered in the next loop, since they do not need further correction. Therefore, besides the accuracy of the approximate solution and the savings in computation time, the adaptively generated grid is of major interest. The discussion of the adaptation grid for the following exemplary simulations will reveal that the adaptation algorithm is capable of determining a composition detail that reflects the desired accuracy, the particular chemical system, and the process behavior.

Expansion of the correction term

Multigrid methods require expansion of the correction term for low resolution to the high resolution. In the terminology of multigrid methods, this procedure is called *prolongation.* This prolongation can be seen as an interpolation of the reduced grid correction to the detailed grid.

How this prolongation is realized is a degree of freedom of multigrid methods. In the proposed algorithm the detailed discretized system is linearized at the current iteration. The solution of this linear system thus gives only the interpolated solution. With some problem-specific tuning, the prolongation can be realized quite efficiently. The efficiency of the prolongation is of major importance for the overall efficiency of the algorithm.

A high-resolution estimate of the solution is obtained with one completed iteration loop, at the cost of a small nonlinear model and a moderately sized linear model.

Problem-specific extensions

Briesen and Marquardt (2003a) have developed the algorithm in a general manner and have illustrated it with a simple flash model. Some part of the algorithm can always be tuned by problem-dependent extensions. The extensions for the considered distillation column example can be constructed in analogy to the flash example presented in the article just cited. Specifically, step 4 of basic algorithm 1 given in Briesen and Mar-

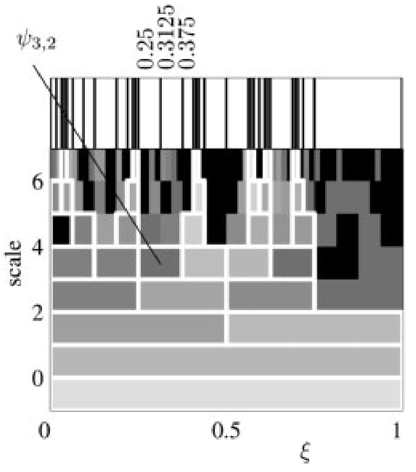

Figure 7. Discretization visualization by means of a grid plot in comparison to the scale-location plot.

quardt (2003a), which performs the prolongation by a linearization of a high-resolution model, is modified. By analogy to the flash model, the prolongation is performed separately for each tray of the distillation column. In the adaptation procedure in step 3.4 of the basic adaptation algorithm 3 in Briesen and Marquardt (2003a), the discretization grids are chosen to be the same for the discretization of the material balance and the phase equilibrium on each tray.

Results and Discussion

Adaptation behavior

In a one-stage flash process, adaptation only requires the identification of *one* set of basis functions necessary to properly reflect the actual process problem. In a multistage process like the 9-stage distillation column investigated in this work, an additional potential of adaptivity becomes important. In the adaptive framework the composition does not have to be represented with the same detail on every tray of the column. In fact, it is highly desirable to have different composition representations for the different trays. Since it is the primary objective of the column to separate a mixture into heavier and lighter components, the composition on the trays will be much different. For example, the light end of the distribution does not need to be modeled in great detail in the bottom of the column, since it does not actually reach the bottom, and therefore it does not contribute to the phase behavior.

This is contrary to the pseudocomponent approach where the composition description is fixed for all trays, thus necessitating the heavy components also to be calculated at the top of the column, even if they are no longer present in the fluid on the top tray. Although this is not strictly correct, the adaptive strategy can be considered to be a method in which each tray has its own set of pseudocomponents tailored to reflect the tray-specific phase behavior in an optimal manner.

A scale-location plot is usually used to visualize a set of wavelet basis functions. Each of the patches in Figure 7 corresponds to a distribution coefficient of the wavelet expansions. The horizontal axis gives the localization of the corresponding wavelet in the domain $\xi \in [0, 1]$. The scale j of the Haar-wavelet basis function

$$\psi_{j,k} = 2^{j/2}\psi(2^j - k), \tag{15}$$

with

$$\psi = \begin{cases} 1, & 0 \le \xi < 0.5, \\ -1, & 0.5 \le \xi < 1, \\ 0, & \text{else}, \end{cases} \tag{16}$$

is represented on the vertical axis. The brightness of the patches corresponds to the absolute value of wavelet distribution coefficients.

However, it is inconvenient for this visualization to represent more than one set of basis functions. Since, for the column example, one of the main features is the difference in the sets for the different trays, another plot that reflects this feature is needed.

Figure 7 shows the connection between the scale-location plot and a "bar code" type plot, which will be referred to as the grid plot. Since the representation of a function in the Haar-wavelet basis always results in a function with step changes at certain locations, the discretization grid can be represented by marking only these locations. If, for example, the basis function $\psi_{3,2}$ is active in a certain set, the approximated distribution will change its value at $\xi = 0.25$, 0.3125, and 0.375. If this marking is done for all the active basis functions, a grid plot reflecting all ξ-locations where the distribution possibly changes its value is obtained. Considering one of these bar codes for each tray gives a grid plot for the whole column, in which the discretization for the different trays can be identified easily, as will be seen in the following figures.

Figure 8 shows the bottom and the top product compositions for one selected adaptive simulation with the feed `MiCa1`.

For comparison, a reference solution has been calculated. This reference is obtained with a simulation using 128 components. In Figure 8 the reference solution is given as a bold gray line. From this exact solution, one sees that the column performs a rather sharp split into components with $\xi > 0.3$

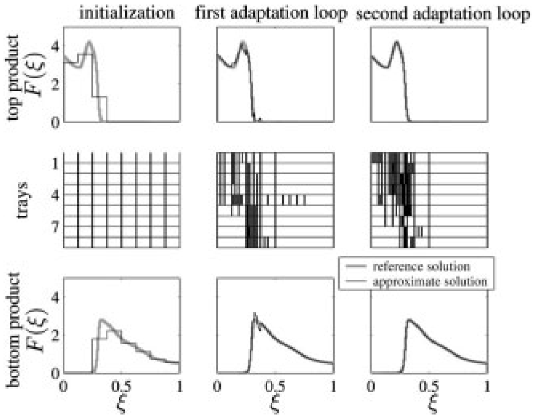

Figure 8. Results for an adaptive column simulation with a smooth feed distribution (Specifications: feed composition `MiCa1`; feed flow: 100 kmol/h; feed pressure: 1 bar; feed temperature: 300 K; top pressure: 1 bar; reflux ratio: 1; bottom flow: 50 kmol/h; residual error tolerance $\varepsilon_{\text{tol}} = 0.02$).

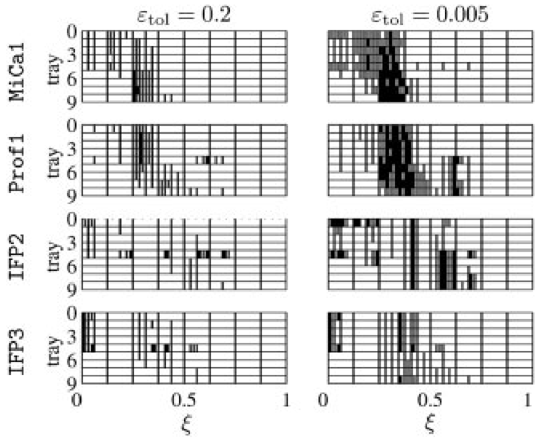

Figure 9. Grid plots for column simulations for different feed specifications with different error constraints.

corresponding to normal boiling temperatures larger than 457.3 K. These components are removed from the bottom of the column, whereas the lighter components are removed from the top.

To obtain an initial approximation, eight basis functions were chosen for the initial step. The grid plot in the first column shows the bar codes for each of the column trays given on the vertical axis. The grid is uniform over the whole column, dividing the ξ-domain in eight equally spaced intervals corresponding to the eight basis functions used on each tray.

As expected the initial iteration does only provide a coarse approximation of the top and the bottom product distributions. In a first adaptation step, a new set of basis functions is selected to correct the initial approximation. Obviously, the approximation for the heavy end is better than for the light components. Therefore, the grid mainly is refined for values of ξ smaller than 0.5. However, on the fifth tray, which is the feed tray, some basis functions for $\xi > 0.5$ are selected because of an unsatisfactory closure of the material-balance equation.

There is an obvious structure in the grid, which directly corresponds to the physics in the column. The interval of ξ in which the resolution is refined moves from small values of ξ to larger ones as we move from the top to the bottom of the column. Since the components are arranged by increasing normal boiling temperatures, this perfectly reflects the purpose of the column. The composition representation for the light-end components is refined in the top, while it is refined in the bottom for the heavier components. Note that we do not have to model components in detail where they do not contribute to the behavior.

Even after the first adaptive iteration, a significant deviation of the approximation from the exact solution is visible, making another iteration necessary. The second adapted grid again shows the same trend of modeling lighter components in greater detail in the top. The second iterative correction then yields an approximation that fulfills the specified residual error constraint of $\varepsilon_{tol} = 0.02$ and is visually indistinguishable from the exact solution.

Note that the obtained solution is on the full grid. For the case of a feed specification in terms of a large number of true components, such as the `IFP` sets, this means that an approximate solution is gained for *all* components. This would facilitate the simulation of any further processing of the top or the bottom product. On a flow-sheet level a consistent composition description in great detail is gained. However, the actual simulations of the different units could be done with an adaptively reduced composition complexity according to the accuracy requirements and the behavior of the particular unit.

Scalable model size

The adaptive multigrid method is also capable of providing solutions on various levels of detail. Figure 9 shows the adaptively generated grid plots for different error constraints and variations of the feed specification. The grids shown are the grids accumulated from all adaptation steps. In each of the grids we can see the general trend that the light-end components are refined in the top and the heavy components are refined in the bottom of the column. Obviously, a finer grid is needed if the error constraint is tightened.

In contrast to pseudocomponents, the error-controlled solution means that no model reformulation is necessary if the model has to be solved in greater detail. Instead of specifying a number of pseudocomponents mainly from experience or heuristic rules, the method allows us to directly specify the accuracy up to which the model has to be solved. Of course, the availability of a detailed and validated model is a prerequisite for this feature.

Change of column specification

Until now we have discussed how the physical behavior in the column and how the change in the accuracy requirement influence the adaptively generated discretization grids. To conclude the investigation on the discretization grid for the column, a change in the column specification is investigated.

Figure 10 shows the resulting top and bottom products as well as the accumulated grid plots for adaptive simulations with different bottom flow specifications. For the bottom flow

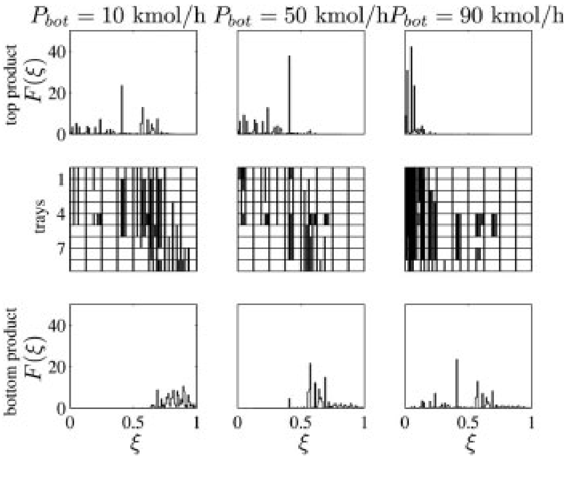

Figure 10. Results for adaptive column simulations with a detailed composition for different bottom flow settings.

Specifications: feed composition `IFP2`; feed flow: 100 kmol/h; feed pressure: 1 bar; feed temperature: 300 K; top pressure: 1 bar; reflux ratio: 1; bottom product flow: {10, 50, 90} kmol/h; residual error tolerance $\varepsilon_{tol} = 0.02$.

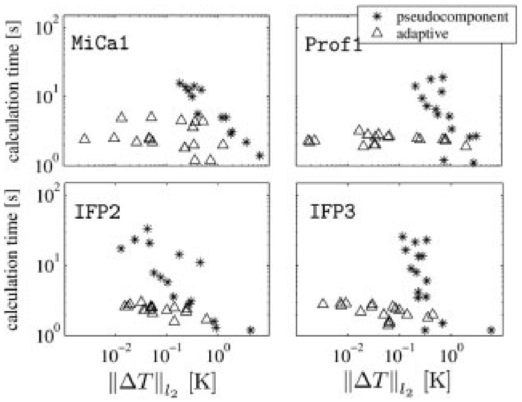

Figure 11. Calculation times for pseudocomponent and adaptive calculations plotted vs. the corresponding error in the column temperature profiles.

Specifications: feed flow: 100 kmol/h; feed pressure: 1 bar; feed temperature: 300 K; top pressure: 1 bar; reflux ratio: 1; bottom flow: {70, 80, 90} kmol/h; for adaptive multigrid approach: residual error tolerance ε_{tol} = {0.2, 0.1, 0.05, 0.02, 0.01, 0.005}; for pseudocomponent approach: model complexity: {8, 16, 24, 32, 40, 48} pseudocomponents.

rate P_{bot} = 10 kmol/h, only the very heavy fraction of the `IFP2` feedstream is removed from the bottom tray, while the top product is very similar to the feed distribution. In the corresponding grid plot the three lowest trays show a similar grid that directly reflects the need for representing the bottom product distribution function. From the feed tray to the bottom of the column, the grid is selected mainly to correct the main peaks of the distribution.

Corresponding to the increased removal of the bottom product, the plots in the center of Figure 10 show that the high-resolution zone has shifted toward smaller values of ξ. Finally, if the main part of the stream is removed from the bottom tray, there are mainly the light-end components that need to be modeled in great detail, since only the very light end of the components is actually separated.

Computation time and accuracy

Besides information on the current approximation error, the main purpose of an adaptive algorithm is to reduce the model complexity in order to save computation time. Figure 11 shows the calculation time (all the calculations in this work were performed with a SUN SPARCstation 10, 60-MHz SuperSPARC, 128 MB) needed to achieve a certain accuracy for the adaptive method and the pseudocomponent calculations.

To judge the accuracy of the solutions on a "macroscopic" level, the error norm of the temperature profiles over the trays has been chosen

$$\|\Delta \boldsymbol{T}\|_{l2} = \|\boldsymbol{T} - \boldsymbol{T}^{\text{ref}}\|_{l2} = \sqrt{\sum_{i=1}^{9} (T_i - T_i^{\text{ref}})^2}. \qquad (17)$$

The data presented in Figure 11 are obtained by simulations with a set of different bottom flow specifications. Furthermore, for the adaptive and the pseudocomponent simulation, the accuracy constraint ε_{tol} and the number of pseudocomponents respectively, has been varied. The figures reveal that the accuracy for the adaptive simulations is generally better, though the results have been obtained faster. Note that the solution of the pseudocomponent model was obtained by solving the model equations simultaneously with the same nonlinear solver as was used in the adaptive simulations. Since the performance of a nonlinear solver strongly depends on the initial guesses, it should be pointed out that equivalent initial guesses have been chosen for both the pseudocomponent and the adaptive calculations.

Of course, there are ways to enhance the performance of the solution of the pseudocomponent model. For example, the inside-out algorithm (Boston and Britt, 1978) is known to be faster than the Newton-type algorithm. However, inside-out techniques could also be implemented in the adaptive scheme in order to reduce calculation time further.

From a practical point of view, the results in Figure 11 are of only minor significance. In almost all cases investigated the error in the temperature is quite small. The temperature accuracy therefore should be seen as a parameter revealing the generally superior accuracy of the adaptive model solution.

If the error in the composition is considered, the results get more significant. Figure 12 shows the calculation times needed to obtain a composition with a certain accuracy. For the pseudocomponents, the results are "continuized" in the sense mentioned earlier to be able to evaluate the function norm:

$$\|\boldsymbol{F}(\xi) - \boldsymbol{F}^{\text{ref}}(\xi)\|_{L2} = \sqrt{\int_0^1 (F(\xi) - F^{\text{ref}}(\xi))^2 d\xi}. \qquad (18)$$

Especially for the feeds `IFP2` and `IFP3`, for which a detailed analysis was available, it is clear that even the compositions obtained by a 48 pseudocomponent model do not accurately describe the highly irregular distribution functions. Therefore,

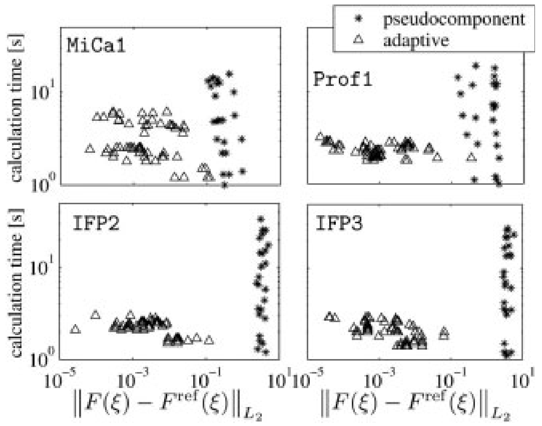

Figure 12. Calculation times for pseudocomponent and adaptive calculations plotted vs. the corresponding error in the composition.

Specifications: feed flow: 100 kmol/h; feed pressure: 1 bar; feed temperature: 300 K; top pressure: 1 bar; reflux ratio: 1; bottom flow: {50, 60, 70, 80, 90} kmol/h; for adaptive multigrid: residual error tolerance ε_{tol} = {0.2, 0.1, 0.05, 0.02, 0.01, 0.005}; for pseudocomponent approach: model complexity: {8, 16, 24, 32, 40, 48} pseudocomponents.

the accuracy in composition improves only little, even for increased calculation times. Because of the logarithmic scale, the improvement cannot even be seen. If the number of pseudocomponents would be increased to values larger than 48, the accuracy would not increase much until the order of the full model size with 128 components would be reached. The error for the 128 pseudocomponent simulation would, of course, be zero without having to spend infinite calculation time, as the plots may indicate at first sight.

The results are similar for the continuous feed distributions `MiCal` and `Prof1`, which do not have the burden of high irregularity. At least the improvement of accuracy for the pseudocomponent calculations with increasing calculation time can be detected even in the logarithmic scale. But the arrangement of the data points is still rather "vertical," which means that even if the calculation time provided is significantly increased, only a slight improvement in the composition results is obtained. The data points for the adaptive calculation form a more "horizontal" pattern. To increase the accuracy of an adaptive calculation by orders of magnitudes, only a little more time needs to be provided.

The results presented reveal that the proposed method qualifies for simulation problems where a highly detailed description of the composition is desired. For calculation of "less detailed" information, such as a column temperature profile, pseudocomponent methods may be similarly effective. But as outlined earlier, the trend in modeling petroleum processes points to a more detailed composition representation, to fully exploit the benefits of each molecular species.

Conclusions and Future Perspectives

Today, the information gained from the improved analytical techniques for petroleum fraction characterization is already far too comprehensive to be used directly for the simulation and optimization of petroleum plants. Currently, lumping procedures are utilized to generate sets of pseudocomponents, which should be able to reflect the physiochemical behavior of the original system. Contrary to this approach, the inclusion of a composition representation on a molecular level seems to be the only way to fundamentally enhance the predictive capabilities of models for petroleum processes (Ramage et al., 1998; Katzer et al., 2000). These molecular-based models will certainly pose new challenges to simulation packages. The number of components to be considered will exceed by an order of magnitude the current level of detail of roughly 20–40 pseudocomponents for the simulation of separation processes. In addition, accounting for the high level of process integration from a refinerywide point of view, the model sizes will increase far beyond the current level. Currently, there seem to be no specialized simulation techniques available that exploit the particular behavior of petroleum mixture processes in order to provide fast and reliable solution of these models.

By adopting multigrid strategies, the method presented can very quickly and robustly solve models with high composition detail. One feature of the method is to exploit the benefits of an adaptive composition representation for solving petroleum process problems. Instead of solving the complete process on the same large level of detail, only the composition detail actually needed is considered.

The main focus in the discussion of the results was on the adaptation behavior. The adaptively generated composition detail could always be perfectly matched with the physical behavior of the process. Taking advantage of this adapted composition representation, the proposed strategy was shown to be superior with respect to accuracy and computation time requirements compared to a conventional pseudocomponent approach.

However, the method cannot provide improvement in accuracy with respect to the plant–model match. Of course, a bad process model cannot be improved by any model-reduction scheme or a solution strategy. But provided that a good, detailed model (e.g., on the molecular level) is available, the technique can facilitate the quick and robust solution as well as a scaling of the model size to meet various accuracy criteria. Therefore, the model can be used at various degrees of accuracy to meet different objectives. For example, to screen many design alternatives, a fully rigorous model may not be necessary, whereas the most promising alternatives should be checked against each other in greater detail. In real-time applications the accuracy may instead be limited by a specified calculation time, which can also be handled within the given framework. The solution is then just calculated up to the degree of detail allowed by the specified calculation time.

Besides the reduced computation time, an increased solution robustness can be expected. Since the proposed algorithm first generates an initial solution on a coarse grid, the model formulations on the adapted and more detailed grid can be solved more robustly than directly solving the model with high composition detail.

Since both the process problem and the property calculation method used are quite simple, the results should be interpreted on a methodical level. To prove the technical applicability, industrial benchmark problems need to be set up. Compared to the simple model in this work, these benchmarks would certainly involve more complex flow sheets and property calculation methods. A single-unit process has been considered in the example presented. However, the problem of exchanging composition information has already risen implicitly. The information exchange between two units can only be viewed as the information exchange between two trays of a distillation column. Therefore, the extension to flow sheets set up by a number of connected units should, in principle, not pose any problem. Actually, when connecting more than one unit, the method should be able to show additional benefits. Since the adaptation realizes optimal composition representation for each of the particular units without loosing the full detailed composition information, a consistent representation over the complete flow sheet should be possible.

Besides the extensions to obtain more realistic models, the extension to other than steady-state processes poses additional conceptual challenges. However, preliminary studies for dynamic simulation (Briesen and Marquardt, 2003c), steady-state optimization (Briesen and Marquardt, 2003b), and reactive processes (Briesen and Marquardt, 2000) show at least the compatibility of the approach presented.

The discussions presented in this work only consider examples processing hydrocarbon mixtures, because of the impressive economical importance of the refinery industry. However, the framework of the method is rather general and could possibly also improve simulation of other multicomponent mixture processes. The tailoring necessary to guarantee an efficient solution strategy is very problem dependent and cannot yet be foreseen.

Literature Cited

API Technical Data Book-Petroleum Refining. American Petroleum Institute, Washington, DC (1992).

Annesini, M., M. Giona, and F. Gironi, "Continuous Model for Complex Mixture Adsorption," *Ind. Eng. Chem. Res.,* **33**(11), 2764 (1994).

Boston, J., and H. Britt, "A Radically Different Formulation and Solution of the Single-Stage Flash Problem," *Comput. Chem. Eng.,* **2**, 109 (1978).

Bowman, J., "Distillation of an Indefinite Number of Components," *Ind. Eng. Chem.,* **41**(9), 2004 (1949).

Brenan, K., S. Campbell, and L. Petzold, *Numerical Solution of Initial-Value Problems in Differential-Algebraic Equations*, North-Holland, New York (1996).

Briesen, H., *Adaptive Composition Representation for the Simulation and Optimization of Multicomponent Mixture Processes*, VDI-Verlag, Düsseldorf (2002).

Briesen, H., and W. Marquardt, "Adaptive Model Reduction and Simulation of Thermal Cracking of Multicomponent Hydrocarbon Mixtures," *Comput. Chem. Eng.,* **24**, 1287 (2000).

Briesen, H., and W. Marquardt, "An Adaptive Multigrid Method for the Steady-State Simulation of Petroleum Mixture Separation Processes," *Ind. Eng. Chem. Res.,* **42**, 2334 (2003a).

Briesen, H., and W. Marquardt, "A Real-Time Optimization Strategy for Petroleum Processes with Successive Adaptive Model Refinement," *Proc. FOCAPO 2003*, Coral Springs, FL, p. 431 (2003b).

Briesen, H., and W. Marquardt, "Adaptive Multigrid Solution Strategy for the Dynamic Simulation of Petroleum Mixture Processes: A Case Study," *Proc. Process Systems Engineering 2003*, Kunming, China, p. 406 (2003c).

Briggs, W., V. Henson, and S. McCormick, *A Multigrid Tutorial*, SIAM, Philadelphia, PA (2000).

Carrier, B., M. Rogalski, and A. Péneloux, "Choice of Pseudocomponents for Flash Calculations of Petroleum Fluids," Tech. Rep. Laboratoire de Chimie-Physique, Faculté des Sciences de Luminy, Marseille, France (1989).

Cho, Y., and B. Joseph, "Reduced-Order Steady-State and Dynamic Models for Separation Processes—Part I. Development of the Model Reduction Procedure," *AIChE J.,* **29**(2), 261 (1983a).

Cho, Y., and B. Joseph, "Reduced-Order Steady-State and Dynamic Models for Separation Processes—Part II. Application to Nonlinear Multicomponent Systems," *AIChE J.,* **29**(2), 270 (1983b).

Chou, G., and J. Prausnitz, "Adiabatic Flash Calculations for Continuous and Semicontinuous Mixtures Using an Equation of State," *Fluid Phase Equilib.,* **30**, 75 (1980).

Cotterman, R., R. Bender, and J. Prausnitz, "Phase Equilibria for Mixtures Containing very Many Components. Development and Application of Continuous Thermodynamics for Chemical Process Design," *Ind. Eng. Chem. Process Des. Dev.,* **24**(1), 194 (1985).

Cotterman, R., and J. Prausnitz, "Flash Calculations for Continuous or Semicontinuous Mixtures Using an Equation of State," *Ind. Eng. Chem. Process Des. Dev.,* **24**(2), 434 (1985).

Daubert, T., "Petroleum Fraction Distillation Interconversions," *Hydrocarbon Process*, 78 (1994).

Eckert, E., "Non-Traditional Characterization of Petroleum Mixtures in Terms of Selected Components," *Collect. Czech. Chem. Commun.,* **64**, 571 (1999).

Hariu, O., and R. Sage, "Crude Split Figured by Computer," *Hydrocarbon Process*, (1969).

Hu, S., G. Towler, and X. Zhu, "Combine Molecular Modeling with Optimization to Stretch Refinery Operation," *Ind. Eng. Chem. Res.,* **41**(4), 825 (2002).

Katz, D., and G. Brown, "Vapor Pressure and Vaporization of Petroleum Fractions," *Ind. Eng. Chem.,* **25**(12), 1373 (1933).

Katzer, J., M. Ramage, and A. Sapre, "Petroleum Refining: Poised for Profound Changes," *Chem. Eng. Process.*, 41–51 (2000).

Kesler, M., and B. Lee, "Improve Prediction of Enthalpy of Fractions," *Hydrocarbon Process*, 153 (1976).

Klamt, A., and F. Eckert, "COSMO-RS: A Novel and Efficient Method for the a Priori Prediction of Thermophysical Data of Liquids," *Fluid Phase Equilib.,* **172**, 43 (2000).

Lee, B., and M. Kesler, "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States," *AIChE J.,* **21**(3), 510 (1975).

Leibovici, C., "A Consistent Procedure for the Estimation of Properties Associated to Lumped Systems," *Fluid Phase Equilib.,* **87**, 189 (1993).

Leibovici, C., E. Stenby, and K. Knudsen, "A Consistent Procedure for Pseudo-Component Delumping," *Fluid Phase Equilib.,* **117**, 225 (1996).

Mineralölwirtschaftsverband, Kraftstoffe der Zukunft, (2000).

Miquel, J., and F. Castells, "Easy Characterization of Petroleum Fractions (Part 1)," *Hydrocarbon Process*, 101 (1993).

Miquel, J., and F. Castells, "Easy Characterization of Petroleum Fractions (Part 2)," *Hydrocarbon Process*, 99 (1994).

Miquel, J., J. Hernández, and F. Castells, "A New Method for Petroleum Fraction and Crude Oil Characterization," *SPE Reservoir Eng.*, 265 (1992).

Moharam, H., A. Braek, and M. Fahim, "A Simple Method of Estimating the Enthalpy of Petroleum Fractions," *Ind. Eng. Chem. Res.,* **37**(12), 4898 (1998).

Neau, E., J.-N. Jaubert, and M. Rogalski, "Characterization of Heavy Oils," *Ind. Eng. Chem. Res.,* **32**(6), 1196 (1993).

Peng, D.-Y., R. Wu, and J. Batycky, "Application of Continuous Thermodynamics to Oil Reservoir Fluid Systems Using an Equation of State," *AOSTRA J. Res.,* **3**, 113 (1987).

Rabeau, P., R. Gani, and C. Leibovici, "An Efficient Initialization Procedure for Simulation and Optimization of Large Distillation Problems," *Ind. Eng. Chem. Res.,* **36**(10), 4291 (1997).

Ramage, M., M. Sood, J. Pita, C. Siletti, A. Sapre, S. Vasantharajan, and D. Mosher, "The Petroleum Industry of the 21st Century: The Enabling Role of Technical Computing," *Proc. FOCAPO 1998*, Snowbird, UT (1998).

Rätzsch, M., and H. Kehlen, "Continuous Thermodynamics of Complex Mixtures," *Fluid Phase Equilib.,* **14**, 225 (1983).

Rätzsch, M., H. Kehlen, and J. Schumann, "Flash Calculations for a Crude Oil by Continuous Thermodynamics," *Chem. Eng. Commun.,* **71**, 113 (1988).

Rätzsch, M., H. Kehlen, and J. Schumann, "Computer Simulation of Complex Multicomponent Hydrocarbon Distillation by Continuous Thermodynamics," *Fluid Phase Equilib.,* **51**, 133 (1989).

Riazi, M., and T. Daubert, "Simplify Property Predictions," *Hydrocarbon Process*, 115 (1980).

Ruzicka, V., A. Fredenslund, and P. Rasmussen, "Representation of Petroleum Fractions by Group Contribution," *Ind. Eng. Chem. Process Des. Dev.,* **22**(1), 49 (1983).

Sim, W., and T. Daubert, "Prediction of Vapor-Liquid Equilibria of Undefined Mixtures," *Ind. Eng. Chem. Process Des. Dev.,* **19**(3), 386 (1980).

Stewart, W., K. Levien, and M. Morari, "Simulation of Fractionation by Orthogonal Collocation," *Chem. Eng. Sci.,* **40**(3), 409 (1985).

Vakili-Nezhaad, G., H. Modarress, and G. Mansoori, "Continuous Thermodynamics of Petroleum Fluids Fractions," *Chem. Eng. Process.,* **40**, 431 (2001).

Vande Wower, A., P. Saucez, and W. Schiesser, eds., *Adaptive Method of Lines*, Chapman & Hall/CRC, Boca Raton, FL (2001).

Von Watzdorf, R., *Adaptive Multiskalenverfahren für die Modellreduktion von thermischen Vielstofftrennprozessen*, VDI-Verlag, Düsseldorf (1998).

Von Watzdorf, R., and W. Marquardt, "Fully Adaptive Model Size Reduction for Multicomponent Separation Problems," *Comput. Chem. Eng. Suppl.,* **21**, S811 (1997).

Zhang, J., B. Zhang, S. Zhao, R. Wang, and G. Yang, "Simplified Prediction of Critical Properties of Nonpolar Compounds, Petroleum, and Coal Liquid Fractions," *Ind. Eng. Chem. Res.,* **37**(5), 2059 (1998).

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