Precise and Fast Computer Simulations of the Dynamic Mass Transfer Behaviour of Liquid-Liquid Agitated Contactors

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ABSTRACT

Algorithms for solving the population balance equations for the transient drop volume (v) and solute concentration (c) distributions and the dispersed phase hold-up of a continuous flow liquid-liquid system, with simultaneous drop coalescence and breakage, are very complex and make heavy demands on computing time, of the order of m^4 (m being the number of discrete classes used). This paper simplifies and accelerates our already fast, recently developed algorithm, for the most common situation where a full description of the above bivariate (v and c) behaviour is not required. The mathematical foundations of the algorithm are developed and it is shown that meaningful, precise and very fast ($\propto m^2$) dynamic simulations of the full drop size distribution and of the width of the solute concentration distribution within each drop size fraction may be achieved in less than 8% of the real process time for a continuous flow stirred vessel, using an ordinary 486DX2/66MHz microcomputer. Besides the excellent time performance of the algorithm, the other important feature is that, as the full size-concentration distribution does not need to invoked or computed, a substantial economy in working memory is also achieved. Actual dynamic simulations of mass transfer and reacting systems have been performed. Limitations of space only compel us to restrict the discussion to mass transfer systems. The applicability of these techniques to real control situations is also highlighted.

INTRODUCTION

In earlier works, one of the authors [Ribeiro (1995), Ribeiro *et al.* (1995)] has presented direct numerical solutions of the unsteady-state drop population balance equations, describing the transient behaviour and also the limiting asymptotic steady-state of interacting liquid-liquid dispersions in single continuous or batch stirred vessels. Hydrodynamics alone, as well as a complete description of the full trivariate drop properties distribution in mass transfer conditions (drop volume, solute concentration and age), have both been addressed. Mathematical models for breakage and coalescence [Coulaloglou/Tavlarides (1977)] and mass transfer [Cruz-Pinto (1983)], as well as the numerical procedure used, have been given in detail by Ribeiro (1995), who showed that the algorithm provides precise and fast simulations of the evolution of drop sizes, solute concentrations and extraction efficiencies, also being able to portray the dispersion's behaviour after step or pulse changes in the main process variables typical of industrial practice: flow rates (residence time and phase ratio), dispersed phase feed drop size distribution and inlet solute concentration. The numerical calculations are carried out by an adequate phase-space discretization, in which drops can reside only in cell sites, and time is also quantized by discrete values. With this simulation model, execution time is approximately proportional to $(m_v \times m_c)^{4/3}$ and $(m_v \times m_c)^2$, respectively, for the rigid and the oscillating mass transfer model predictions, where m_v and m_c stand for the number of grid cells along the volume and the concentration co-ordinate axis, respectively. When rigid drops are assumed, we have shown [Ribeiro (ibid.)] that the execution time for the simulation of the hole start-up period of

the contactor is as fast as the real process, when running on a DEC 300/500 AXP machine. Using the oscillating drop model to describe mass transfer reduces the execution time by an order of magnitude, as the mass transfer performance does not depend in this case on drop age, and the study may then be carried out with just the bivariate volume-concentration distribution.

In the present work, we show that a modification of the above simulation model, using monovariate drop volume distributions, together with the mean and the standard deviation of the solute concentrations in each volume cell, requires execution times (on a 486DX2/66MHz microcomputer) well within the real process time, thus enabling its use in control of liquid-liquid contactors in real mass transfer processes.

THE SIMULATION MODEL

In previous works [Ribeiro (1995), Ribeiro *et al.* (1995)], assuming the oscillating drop model for mass transfer, we used a bivariate drop volume-solute concentration distribution to describe the dynamics of the dispersed phase drop population and the mass transfer rates between the two phases of a perfectly mixed homogeneous continuous flow stirred-tank contactor, where both drop coalescence and break-up take place. In the numerical procedure, drop volume v and drop concentration c are discretized in classes of mean drop volume v_i ($i=1, \ldots m_v$) and mean solute concentration c_j ($j=1, \ldots m_c$), and the drop population is defined by an n_{ij} matrix, each element representing the mean number of drops per unit dispersion volume with mean drop volume v_i and mean solute concentration c_j. At every time step, Δt, the algorithm starts by evaluating the convective movement of drops in the phase-space concentration axis due to mass transfer. Next, it calculates the mean number of drops created and destroyed in each class due to breakage (n^{bb} and n^{db}), coalescence (n^{bc} and n^{dc}), feed (n^{bf}) and exit (n^{de}). The execution time for these calculations is proportional to $m_c \times m_v$ for feed and exit, to $m_c \times m_v^2$ for breakage, and to $m_c^2 \times m_v^2$ for the coalescence process, which on its own is responsible for 99% of the total execution time. At last, the new matrix at $t+\Delta t$ is such that

$$n_{ij}(t+\Delta t) = n_{ij}(t) + (n_{ij}^{bb} + n_{ij}^{bc} + n_{ij}^{bf}) - (n_{ij}^{db} + n_{ij}^{dc} + n_{ij}^{de}) \qquad (1)$$

The present algorithm is new in that it substitutes solute concentration mean and standard deviation for the solute concentration distribution used in the previous one. The information available about the solute concentration distribution within the drop population is less than in the previous work but, in nearly all industrial processes, there is no need for more than the mean and the standard deviation. The drop population may thus be described, though approximately, by:

1. a vector n_i, representing the mean number of drops per unit dispersion volume within each volume class i of mean drop volume

$$v_i = \sum_k v_{ik} / n_i \quad , \qquad (2)$$

where v_{ik} stands for the volume of drop k in class i, k varying from 1 to n_i;

2. a vector c_i, representing the mean solute concentration in each volume class i,

$$c_i = \sum_k v_{ik} c_{ik} / v_i \quad , \qquad (3)$$

where v_{ik} is as in 1. above and c_{ik} is the solute concentration of drop k in class i;

3. a vector σ_{ci}, representing the standard deviation of the solute concentration in each class i,

$$\sigma_{ci} = \sum_k v_{ik}(c_{ik} - c_i)/v_i \qquad (4)$$

At every time step, this new algorithm starts by computing the current values of vectors c_i and σ_{ci}, that are modified by mass transfer during each time slice, Δt, of the computation. When mass transfer may be described by the oscillating drop model [Cruz-Pinto (1983)], the drop solute concentration c may be obtained, for each drop ik, by

$$c_{ik}(t+\Delta t) = c^* - \left[c^* - c_{ik}(t)\right] e^{-\frac{\Delta t}{\tau_i}} \quad , \qquad (5)$$

where c^* is the drop solute concentration in equilibrium with the continuous phase and τ is a time constant, that depends on drop size and mass transfer parameters ($1/\tau = 6\,K_{od}/d$).

Using equation (5) and the τ value corresponding to the mean drop volume of class i, the new values of c_i and σ_{ci} may be derived from (3) and (4) above, giving

$$c_i(t+\Delta t) = c^* - \left[c^* - c_i(t)\right] . e^{-\frac{\Delta t}{\tau_i}} \qquad (6)$$

and $$\sigma_{ci}(t+\Delta t) = \sigma_{ci}(t) . e^{-\frac{\Delta t}{\tau_i}} \quad . \qquad (7)$$

Next, the algorithm calculates the number of drop death events by breakage, coalescence and exit from the vessel in each drop volume class, and subtracts it from n_i. The remaining drops keep their values of c_i and σ_{ci}, as well as the new-borns, because mass transfer is here assumed not to occur during interactions. Birth events by breakage originate different classes of daughter droplets; the mean solute concentration and standard deviation within each volume class equal the corresponding values of the parent drop at the instant of breakage. The group of new-born drops (r) resulting from coalescence of a pair of drops of groups a and b, must be described by their characteristic values: n_r, v_r, c_r, σ_{cr}. When one drop of group a coalesces with one of group b giving one drop of group r the following relations apply:

(i) the volume of the resulting drop is the sum of those of both drops from a and b:

$$v_{rk} = v_{ak} + v_{bk} \quad . \qquad (8)$$

(ii) the resulting drop solute concentration is given by

$$c_{rk} = \left(v_{ak} c_{ak} + v_{bk} c_{bk}\right) / v_{rk} \quad . \qquad (9)$$

Using relations (8) and (9) and definitions (2) and (3), the mean volume and mean solute concentration for the group r may be shown [Regueiras] to be:

$$v_r = v_a + v_b \qquad (10)$$

and $$c_r = \frac{v_a . c_a + v_b . c_b}{v_a + v_b} \quad . \qquad (11)$$

The standard deviation may not be obtained from (4), (8) and (9), unless a simplifying assumption is made: all drops in group a have the same volume ($v_{ak}=v_a$) and all drops in group b also have the same volume ($v_{bk}=v_b$). On this assumption, the standard deviation of group r is given by:

$$\sigma_{cr} = \frac{\sqrt{v_a^2 . \sigma_{ca}^2 + v_b^2 . \sigma_{cb}^2}}{v_a + v_b} \quad , \qquad (12)$$

that is a reasonable approximation, specially when very small drop class sizes are taken, as we do in this work.

During each time slice Δt, several groups of drops enter the vessel, each with a number of drops proportional to its contribution to the feed drop volume distribution. The mean solute concentration and the standard deviation in all these groups are given as parameters to the algorithm. For example in our computations no solute is assumed in the dispersed phase feed.

After the resulting groups of drop breakage, coalescence and feed birth events at time step Δt are known, the intervening drops must be added to the corresponding groups of non-interacting drops.

For such pairs of joining groups a and b resulting in a single group r, the following relations can be deduced from the definitions (2), (3) and (4) without any simplifying assumptions [Regueiras]:

$$n_r = n_a + n_b \quad , \tag{13}$$

$$v_r = \frac{n_a . v_a + n_b . v_b}{n_r} \quad , \tag{14}$$

$$c_r = \frac{n_a v_a c_a + n_b v_b c_b}{n_r v_r} \quad , \tag{15}$$

$$\sigma_{cr} = \sqrt{\frac{n_a v_a}{n_r v_r}\sigma_{ca}^2 + \frac{n_b v_b}{n_r v_r}\sigma_{cb}^2 + \frac{n_a v_a . n_b v_b}{(n_r v_r)^2}(c_a - c_b)^2} \quad . \tag{16}$$

When the joining groups have the same mean drop volume, equations (14), (15) and (16) simplify, giving:

$$v_r = v_a = v_b \quad , \tag{14'}$$

$$c_r = \frac{n_a c_a + n_b c_b}{n_r} \tag{15'}$$

and

$$\sigma_{cr} = \sqrt{\frac{n_a}{n_r}\sigma_{ca}^2 + \frac{n_b}{n_r}\sigma_{cb}^2 + \frac{n_a . n_b}{{n_r}^2}(c_a - c_b)^2} \tag{16'}$$

With this approach, the execution time becomes proportional to m_v for the feed and exit events, and to m_v^2 for the simulation of breakage and coalescence events.

RESULTS AND DISCUSSION

The most important feature of the present development is the ability of the new algorithm to simulate the dynamic behaviour of an agitated liquid-liquid dispersion in a very short time, without loss of precision. Results for the overall mean volume and mean solute concentration obtained with the present algorithm and the previous one have relative differences of less than 10^{-4}, even during pulse

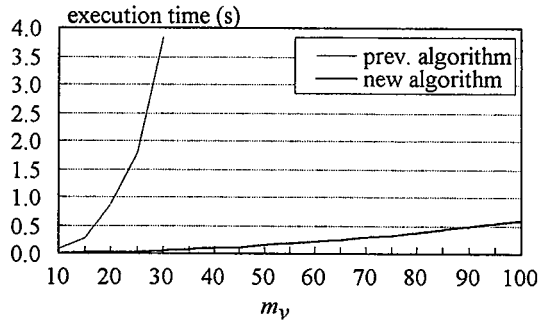

Figure 1: Execution time for each real time step (Δt) versus the number of logarithmic volume classes (m_v)

or step disturbances of the process variables.

Figure 1 shows the relation between the number of logarithmic volume classes m_v and the resulting execution time for each real time step for both the previous and the present algorithm. For the older algorithm, m_v is simultaneously the number of volume classes and the number of concentration classes. It is clear from this figure that, for the earlier algorithm, the execution time increases rapidly

and, when the number of classes exceeds 20, it becomes too high for any kind of simulation, except in very simple cases. Also it was not possible in this case, due to the great number of matrix elements and memory limitations, to test for more than 30 volume classes. For the new algorithm, however, execution times were easily obtained for up to 100 volume classes.

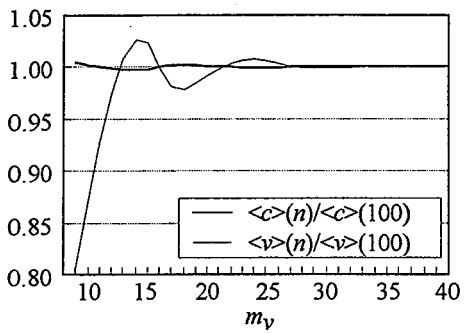

Figure 2: Effect of the number of volume classes (m_v) on the resulting mean outlet values of v and c

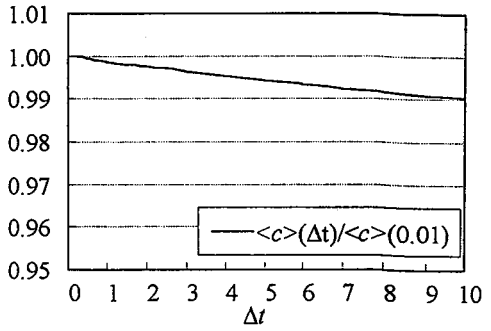

Figure 3: Effect of the time step Δt on the resulting value of the mean outlet concentration value <c>.

Figure 2 represents the mean outlet drop volume, <v>, and mean outlet concentration, <c>, divided by the corresponding values for 100 volume classes, plotted against the number of volume classes m_v, for m_v from 9 to 40. The error resulting from low values of m_v is negligible for <c> over the full range of m_v. For <v>, however, the errors are too high when m_v is lower than 15, do not exceed 2.5% for m_v from 15 to 20, 1 % for m_v from 20 to 28 and are entirely negligible for m_v greater than 28. The execution times for each real time step are, for these cases:

m_v	15	20	25	30
t (s)	0.0137	0.0239	0.0376	0.0538

Figure 3 represents the mean drop solute concentration divided by the value obtained for $\Delta t = .01$ plotted against the time step used in the calculation. The errors resulting from using time steps of less than 10 seconds do not exceed 1%.

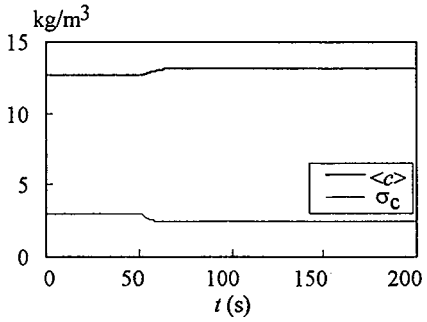

Figure 4: Computed response of the mean outlet solute concentration and corresponding standard deviation to a step change on mean feed volume (0.5×10^{-9} m^3 to 0.5×10^{-10} m^3)

Despite its simplified structure, the algorithm realistically predicts the dynamic mass transfer behaviour of the dispersion, after sudden changes into the process variables, as illustrated in Figure 4. It may be seen that, when the dispersed phase feed drops suddenly become smaller, the expected increase in the average solute transfer efficiency is accompanied by a decrease in the overall width of the solute concentration within the dispersed phase.

When evaluating the execution times of the new and previous algorithm, we used a 486DX2/66MHz microcomputer running DOS 6.2. The liquid-liquid system modelled was toluene-acetone-water, as in Guimarães (1989) and in Guimarães *et al.* (1990), with the following operating parameters:

residence time	$\theta = 60$ s
mean agitation power	$\varepsilon = 0.15$ W/Kg
drop volume range	$v_{min} = 10^{-12}$ m^3, $v_{max} = 10^{-9}$ m^3
feed drop distribution	$\langle v_{feed} \rangle = 0.5 \times 10^{-9}$ m^3, $\sigma_{vfeed} = 0.625 \times 10^{-10}$ m^3

CONCLUSIONS

1. A previously developed simulation algorithm for the dynamics of liquid-liquid dispersions has been modified and considerably accelerated, for potential use in process control situations.
2. If 0.5% errors are allowed in the solute concentration predictions, ratios of computation times/ real process times as low as 1% may be achieved, for the simulation of single-contact continuous flow liquid-liquid stirred vessels; memory requirements also have been reduced by a factor of 10, relative to previous simulation. This makes possible to consider the dynamic simulation of more complex contactors, such as extraction columns.
3. The detailed features of the dynamic behaviour of such systems are realistically portrayed after pulse or step changes in the process variables.
4. The algorithm is also applicable, and have already been applied, to reacting systems.

NOMENCLATURE

ca, cb, cr	mean drop solute concentration in groups *a*, *b* and *r*
m, mv, mc	number of discretization classes
va, vb, vr	mean drop volume in groups *a*, *b* and *r*
Superscripts	
bb	born by breakage
bc	born by coalescence
bf	born by feeding
db	destroyed by breakage
dc	destroyed by coalescence
de	destroyed by exiting

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