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# Markov-chain modelling and experimental investigation of powder-mixing kinetics in static revolving mixers

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## A B S T R A C T

This study aims to develop a general model that is able to describe powder flow and mixing in static mixers, regardless of the type of mixer or the mixing configurations. The process model is based on a homogeneous Markov chain describing the flow of each component through the mixing zone by a series of interconnected cells. It accounts for the number of mixing elements and their disposition in the mixer, as well as particle segregation via different transition probabilities. Some simulations are given to emphasize this particular aspect. Other outcomes of the model include the number of passages to reach a required mixture quality, as well as the asymptotic distribution of components. A laboratory static mixer of revolving type was designed specially for this study. It comprises up to 10 mixing sections, and its high internal voidage favours free flow of the powder. Segregating and non-segregating mixtures have been used to test the model and adjust unknown parameters. The model gives very satisfying results. In particular, it is able to account for the oscillating character of mixing kinetics due to particle segregation. It is also suggested that these parameters could be linked separately to powder flowability and mixing element characterization.

## Keywords:

Static mixer  
Mixing  
Markov chains  
Model  
Mixture quality

## 1. Introduction

Powder mixing is an important operation for many different industries as it adds significant value to the product. The term mixing is applied to operations which tend to reduce non-uniformities or gradients in the composition, properties or temperature of material in bulk. Such mixing is accomplished by the movement of material between various parts of the whole mass [1] under classical convection–dispersion transport mechanisms.

The technical process of mixing is performed by many different types of equipment available on the market. In tumbler mixers, the achievement of a mixture is obtained by the rotation of a drum containing the products to be mixed. This type of machine is typically used in batch mode, with a wide variety of drum designs, including storage containers and sometimes “home-made” designs. Because this relatively free particle motion can cause segregation, tumbler mixers are usually preferred for cohesive products. Convective powder mixers are closer in design to fluid or paste blenders. A convective powder mixer consists of an impeller rotating in a drum that contains the particles, which causes the displacement of these particles to regions in which they would never have gone by

free motion. For this reason, such mixers are recommended for free-flowing powders. Impeller types are extremely diverse: ribbons, paddles, blades mounted on a frame, orbiting screws, etc. Convective mixers can be operated either in batch and continuous mode. Horizontal or vertical impeller configuration, as well as different rotational speeds, can cause frictional flow or fluidised flow, can help alleviate particle cohesion, or cause particle de-agglomeration and sometimes grinding.

In static mixers, the mixing effect is provoked by the particulate flow through a mixing zone, which can be considered as a porous media, in a tube-shaped vessel. Although there are a wide variety of static mixers, we shall focus on those with multiple passages of material through the mixing zone. In these mixers, process optimisation involves searching for the minimum number of material passages through the mixing zone required to give the desired mixture quality. The absence of moving parts means that such mixers have extremely low energy consumption, and also makes them very versatile. Such static mixers are positioned between continuous mixers and batch mixers in a closed volume so that they combine the advantages of both operating principles. In addition, although batch loading reduces the throughput, it significantly improves the feeding precision, which is very important in many industries, such as the pharmaceutical or agro-food industries.

Mixture quality can be analysed using different approaches, for example those described in [2–4], through the help of standard

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deviation or variance with reference to the average concentration of a component in the whole volume. Most of the time, it is necessary to sample the mixture and therefore obtain an estimate of this statistical data. The size of the samples may be that of an end-used property (for example the mass of a pharmaceutical tablet) or that required to meet an industrial standard (three times the mass of a tablet, as needed by the FDA). In the present study, this problem will not be considered, as the whole volume of a binary mixture will be directly divided into samples and the mass concentration of the key component determined in each sample to find the variance of the mixture.

Modelling of particulate flow has received a lot of attention over the past 15 years, basically through the generalisation of distinct element models (DEM). These are able to model collective particle motion via a mechanistic representation of particle–particle and particle–wall contacts and interactions [5–7]. The main difficulty lies in considering the overall complexity of the process, including particle shape, size, surface, distribution of properties, particle number, etc., whilst avoiding a significant increase in computation time. This, together with the problem of dealing with the amount of data generated, has strongly moderated the interest of such models for process simulation and control. Therefore, the tendency is much more to find a way of linking such microscopic models with models that are more efficient at higher process scales. Markov-chain models belong to this category of mathematical tool. We have recently described and reviewed their applicability to particulate processes [8,9].

This Eulerian approach observes and describes variation of global process properties while particles are crossing a fixed volume during the flow. The advantage of the Markov chains is that they can work with finite volumes and discrete time intervals, making it possible to describe what happens at the input of the finite volume and at its output without necessarily determining the internal processes. Moreover, it does not require limitations, which we usually set to find analytical solutions to a problem. In the present work, we shall develop a general Markov-chain framework for modelling particulate flow in static mixers of different types and operational principles. This will be applied to the case of an experimental mixer with several particulate materials, with the aim of predicting mixer parameters that provide reasonable mixing regimes and reduce segregation influence. In addition, our interest also lies in finding out what sort of experimental work needs to be done in order to identify the model parameters.

## 2. Materials and methods

### 2.1. Static mixer considerations

As indicated above, a laboratory static mixer was specially designed for the present research. Its mixing zone is a rectangular tube, in which screws are inserted as mixer elements (see Figs. 1 and 2). These are placed as mixing sections consisting of a set of five screws, the whole mixing zone involving 10 mixing sections over its length. The feeder and the collector are completely identical boxes with hand-pulled insertions, making it possible to form the initial configuration and take samples at the bottom. The boxes can be exchanged so that turning them upside down imitates mixer revolution, placing the present mixer in the category of alternately revolving static mixers. A complete description of mixing mechanisms and mixing regimes in such mixers can be seen in [10,11]. Basically, we can consider that two flow regimes are about to occur in a static mixer: free flow and dense flow. Free-flow regime corresponds to dilute flow and implies that particle–particle interactions are negligible as compared to particle–wall and particle–mixing element interactions. These act as defectors of the flow and induce

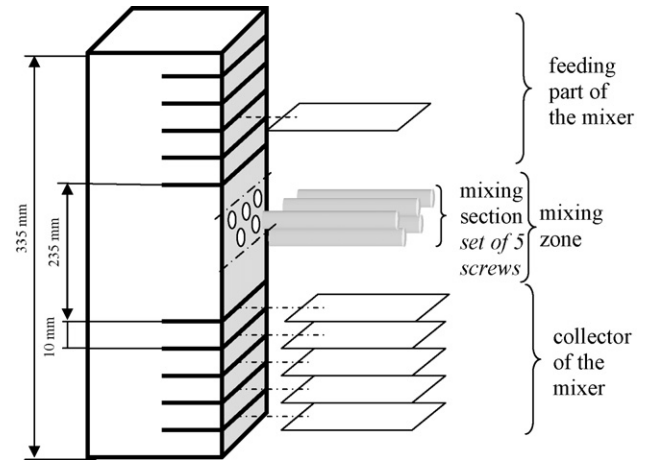


Fig. 1. The laboratory static mixer showing the insertions for sample definition.

various possible trajectories for the particles so that the general particle motion can be considered as stochastic. In concentrated flow, particle–particle interactions are superimposed because higher mass flow rates or higher compacity of the packing reduces the volume available for flow, but the basic stochastic behavior remains the same. In all cases, mixing occurs by convection due to the force

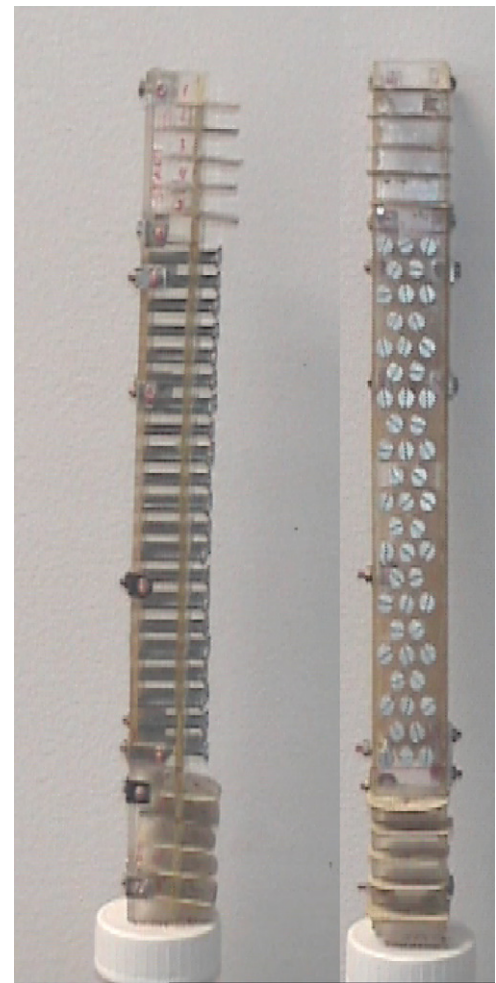
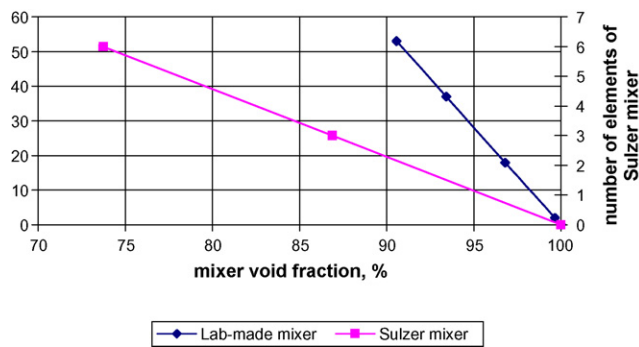


Fig. 2. Side views of the laboratory static mixer showing the mixing sections (set of five screws).



**Fig. 3.** Internal voidage of the static mixer used as a function of the number of mixing section (set of five screws). Comparison with a commercial static mixer.

of gravity and dispersion due to particle–particle, particle–wall and particle–mixing element interactions.

As an initial approach, a static mixer can be considered as a porous medium through which particles will flow downwards. The consideration of medium void fraction is therefore a good way of comparing mixers. Fig. 3 shows how the voidage of the mixer depends on the number of static mixer elements installed in the mixing zone, as well as on the type (shape, size, etc.) of these elements. As a comparison, data concerning a commercial apparatus (Sulzer Chemtech SMF DN 25) has been superimposed. This may help for the interpretation of the mixing results because it will also reflect what flow regime a mixer operates in. When comparing these two mixers, it is clear that the Sulzer mixer has a higher void fraction range than the laboratory mixer, which is more likely to work at free-flow. When adding or removing mixing elements (up to 6 for a total mixer length of 180 mm), the Sulzer mixer is expected to change the operational regime from free flow to dense (frictional) flow because the available flow volume can change significantly. On the other hand, the laboratory static mixer should work within one single flow regime, as long as excessive mass flows are not considered.

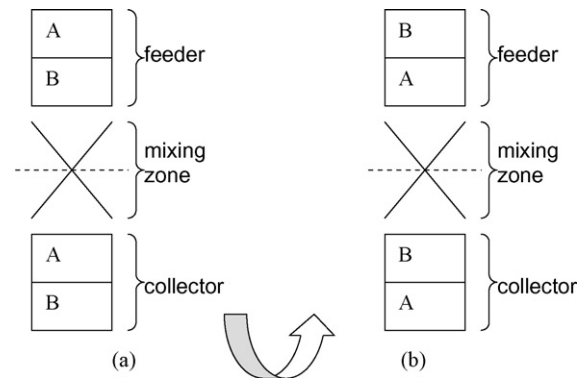
## 2.2. Methods of experimentation and materials

In order to investigate different flow behaviors, several materials were considered. Some characteristics of the materials are given in Table 1. The difference in diameter of the components, measured by sieving, is fairly evident. Using different pairs of materials can help investigate how static mixers operate with components differing in density or particle size distribution. In the present study, we will investigate mixtures consisting of couscous and sugar, as well as of millet and semolina. Because it has a particle size ratio close to 6, this last mixture is potentially a segregating mixture.

Before conducting any mixing experiments, the components are placed in the feeding section so as to occupy each of the five initial states (“macrostates”). These states can be defined by placing the hand-pulled insertions through the cross-section of the feeder, which allows the initial mixing quality to be described. After the insertions are removed, the flow starts, induced by gravity. The mixing elements deviate the downward plug flow so that

**Table 1**  
Some physical characteristics of the particulate solids used in this study.

Material	$d_{10}$ ( $\mu\text{m}$ )	$d_{90}$ ( $\mu\text{m}$ )	$d_{50}$ ( $\mu\text{m}$ )	Particle density
Millet	1700	2400	1900	1.410
Sugar	530	780	680	1.559
Couscous	1020	1550	1180	1.440
Semolina	200	480	330	1.470



**Fig. 4.** Scheme of operation of the laboratory static mixer (a, at the beginning of the process; b, after revolution).

the components mix in that region before arriving in the collector. Insertions are again placed in the collector to remove the content of each section. Components are then separated by an 800  $\mu\text{m}$  sieve for couscous/sugar or semolina/millet mixtures. This allows calculation of the mass fraction of one component in each section, and then calculation of the variance of the mixture at this scale of scrutiny. The apparatus is then revolved and the second particle passage occurs in the mixing section, following a “first in–first out/last in–last out” procedure (see Fig. 4). Therefore, we can complete the measurement procedure according to the number of mixer rotations we are interested in. Experiments were done for the following conditions:

- Number of revolutions of the mixer: 1, 2, 3, 4, 5, 6, 9, 12, 15, 19, 20.
- Number of mixing sections: 0, 1, 2, 4, 10.
- Each test was repeated three times, the mean values being retained.

As a consequence, 330 pieces of experimental data were obtained and used to model the mixing process for both pair of products.

## 3. Markov-chain modelling

### 3.1. General concepts and tools

Markov-chain modelling consists in representing the evolution of a system that can occupy several states, with the help of conditional probabilities. For example, a particle (system) can belong to different size intervals (states), and can experience grinding in a mill. The size-reduction process can be viewed as a stochastic process, the rule of passage from one size interval to another in a certain time interval being described as a Markov chain [12]. The same basic ideas can be used to describe chemical reaction kinetics or residence time distribution, as discussed by Tamir [13]. In powder technology, Markov chains have been specifically applied to model mixing and particulate flow [14–18].

The theory of Markov chains operates with two key tools: the state vector  $S(n)$  after  $n$  transitions of the system, and the matrix of transition probabilities  $M$ , in which probabilities determine possible transitions between the states. The evolution of the process, as well as the distribution of the system between the states can be described by

$$S(n+1) = S(n)M \quad (1)$$

Therefore, if the initial state or the system is known, the above relation allows calculation of any possible future state, even if  $M$



depends on  $n$  or on  $S(n)$ . For example in grinding, the particle size distribution (PSD) in a batch operation can be calculated at time  $t$  knowing the PSD at time  $t - \Delta t$  and the matrix of transition, even if this matrix is time-dependent or PSD dependent. This makes the Markov-chain approach to grinding more general than the classical breakage and selection functions approach.

Static powder mixers were modelled by Markov chains during the seventies. Fan and co-workers [19], and then Wang and Fan [20] represented the state of the particulate system as several macrostates defined for the feeder and the collector by insertions that were removed to let the powder flow. A key component was chosen and the matrix of transition probabilities of this component connected these states after one passage of particles through the mixing zone. After restoring the matrix, it was possible to calculate the distribution of components at the bottom for any number of passages, assuming the linearity of the process. This first black-box model was valid only for the mixing zone and the components the experimental data were obtained for. The same authors [21] also undertook more detailed decomposition of the process by presenting the total transition matrix as a product of matrices related to smaller time steps, when these matrices allowed transitions of a tracer only to the neighbouring cells (states). However, this approach led to the same matrix as in the previous paper.

While this approach constituted a valuable pioneering work, its lack of generality in the model formulation has limited its audience and applicability. In addition, it did not take into account particle segregation which is likely to occur because of gravity particle flow. Very interesting experimental data was recently published by Dalloz-Dubrujeaud et al. [22] on the mixing of two components in a rotating vertical tube. A specially designed electrical capacitance sensor allowed on-line measuring of the concentration distribution inside the mixer, i.e., describing the transient process and its asymptotic state. Unfortunately, no attempt to propose a mathematical model of the process was undertaken or published.

### 3.2. Model development

In the chain models described above, one transition of the system was equal to one passage in the mixing zone, whatever the flow in this zone. This seriously limits predictability. Our main idea is that a static mixer of this kind may be represented as a continuous mixer with a feed acting within a limited time interval. The present model will therefore be a model of the flow of each type of particle through the mixing zone, and will be dependent on the nature of this zone (number of mixing elements, type of elements, etc.). It can be considered as an evolution of the models presented so far for static powder mixers, from “black” to “grey” box model.

Let us consider a vertical mixer of tube type with two components A and B at the top of it (Fig. 5). The central part of the tube is a mixing zone that may contain mixing elements, whatever their type, number or combination. At the very initial state, A and B are completely separated and occupy the feeding zone. Let us divide its total volume into 10 sections (samples), for example: 5 for A and 5 for B. In the present case, the scale of scrutiny is the “size” of one of these sections (or “macrostates”). Both materials flow through the mixing zone and are collected at the bottom of the tube, occupying approximately the same volume as at the top. Each sample in the collector can contain both components A and B, mixed up to a certain scale of segregation that may be inferior to the scale of scrutiny of the macrostate sample. The present model will try to represent the filling process of the collector, which is due to particle residence time distribution or flow through the mixing zone.

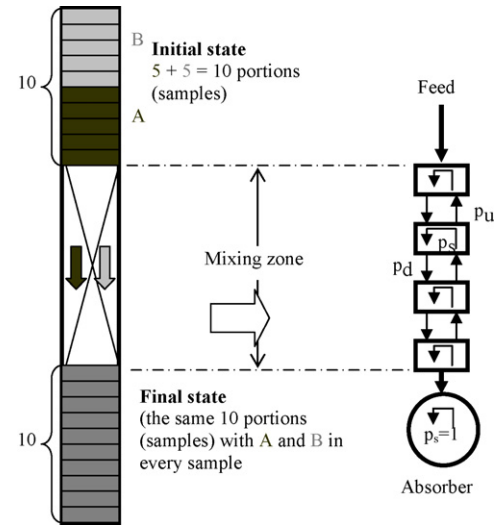


Fig. 5. General scheme of the Markov chain flow model.

The mixing zone can be presented as a series of cells connected by particulate flow, for example four cells as in Fig. 5. These cells can correspond to mixing elements inserted into the mixing zone, or can be chosen arbitrarily to define the zone as several spatial sections. The time step  $\Delta t$  chosen should be small enough to ensure that particles can transit no further than to a neighbouring cell, so that flow appears as a series of perfectly mixed cells with internal exchange. Consider an observation of this system during  $\Delta t$ . The mass fraction of a particle staying in the first cell can be viewed as a probability  $p_{s1}$  of staying in cell 1 during  $\Delta t$ . The mass fraction of a particle transiting from cell 1 to cell 2 during this time interval corresponds to the probability  $p_{d1}$  of downward transition between these cells. Similarly, the probability of upward transition from cell 2 to cell 1 will be denoted as  $p_{u2}$ . All these probabilities can be recorded in the following matrix of transition probabilities:

$$\mathbf{M} = \begin{bmatrix} p_{s1} & p_{u2} & 0 & 0 & 0 \\ p_{d1} & p_{s2} & p_{u3} & 0 & 0 \\ 0 & p_{d2} & p_{s3} & p_{u4} & 0 \\ 0 & 0 & p_{d3} & p_{s4} & 0 \\ 0 & 0 & 0 & p_{d4} & 1 \end{bmatrix} \quad (2)$$

The last cell corresponds to the collector, or absorbing state, for which the probability of staying is equal to 1. Of course, every column of the matrix should meet the condition of normalisation:

$$p_{ui} + p_{si} + p_{di} = 1, \quad i = 1, \dots, 5 \quad (3)$$

Because of gravity and high voidage of the mixing medium which limits the phenomenon of wall rebound, particle flow is basically taking place downwards. For instance, and as a first approach, upward transitions can be neglected in the present problem. Therefore,  $p_{di} = 1 - p_{si} = p_i$ ,  $i = 1, \dots, 5$ . In addition, probability  $p_i$  can be seen as the following product of probabilities:

$$p_i = \alpha_i p \quad (4)$$

where  $p$  corresponds to the transition probability without mixing elements, and  $\alpha_i$  is a coefficient of “delay” caused by the presence of mixing elements in the cell  $i$ . This allows the effect of different types of mixing elements to be taken into account, as well as any possible combination of these, and of course zones of “flow relaxation”, without mixing elements. In this latter case,  $\alpha_i$  is equal to 1, but  $p$  is still dependent on the time step  $\Delta t$ . The general formulation

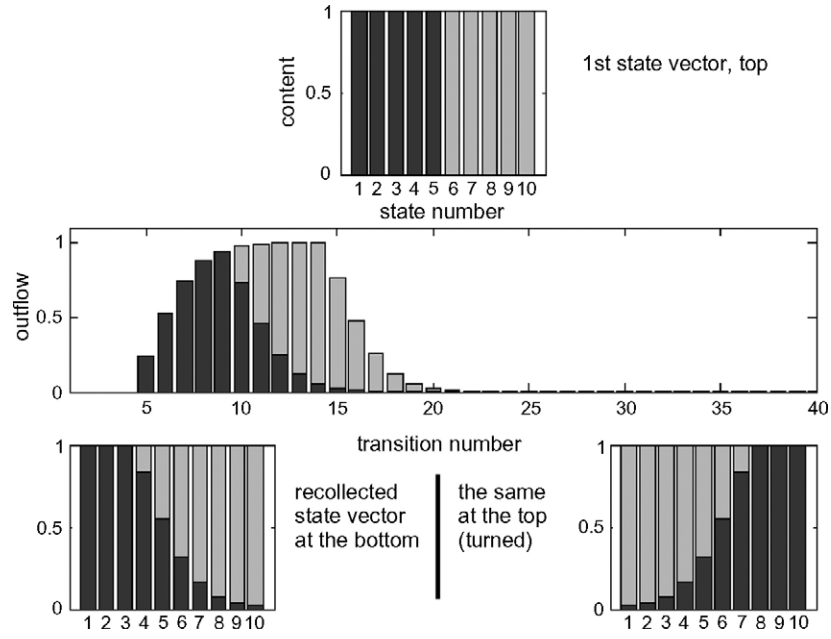


Fig. 6. Evolution of the state vector during the first passage in the mixer.

of the transition matrix is therefore:

$$\mathbf{M} = \begin{bmatrix} 1 - \alpha_1 p & 0 & 0 & 0 & 0 \\ \alpha_1 p & 1 - \alpha_2 p & 0 & 0 & 0 \\ 0 & \alpha_2 p & 1 - \alpha_3 p & 0 & 0 \\ 0 & 0 & \alpha_3 p & 1 - \alpha_4 p & 0 \\ 0 & 0 & 0 & \alpha_4 p & 1 \end{bmatrix} \quad (5)$$

For example, if all mixing elements are of the same type, and are only placed in the first and last cell, the resulting matrix will contain two possibly unknown parameters:

$$\mathbf{M} = \begin{bmatrix} 1 - \alpha p & 0 & 0 & 0 & 0 \\ \alpha p & 1 - p & 0 & 0 & 0 \\ 0 & p & 1 - p & 0 & 0 \\ 0 & 0 & p & 1 - \alpha p & 0 \\ 0 & 0 & 0 & \alpha p & 1 \end{bmatrix} \quad (6)$$

It may also be thought that  $p$  mainly depends on particle flowability, or settling velocity in the particle mixture, and that  $\alpha_i$  depends only on the mixing element type, at least from the point of view of its packing characteristics. Therefore, if two transition matrices  $\mathbf{M}_A$  and  $\mathbf{M}_B$  are to be used to describe the mixing process of two components of type A and B, they may be built with the same values of  $\alpha_i$ . However, we will not consider this as an assumption in the present work.

### 3.3. Process dynamics and simple simulations

The state of the process can be characterized by the state vector, which is the column vector with five elements. It represents the distribution of the amount of a given component over all the states at a fixed moment in time:

$$\mathbf{S} = \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \end{bmatrix} \quad (7)$$

This vector should also be written for both components A and B. The evolution of the state vector, related to the distribution of

particles over cells, including the collector, can be described by the matrix equation:

$$\mathbf{S}^{k+1} = \mathbf{M}(\mathbf{S}^k + \mathbf{S}_f^k) \quad (8)$$

where  $\mathbf{S}_f^k$  is a vector describing the arrival of components in the mixing zone at every transition. This would allow any type of inflow to the process to be simulated, including staged feeding, sinusoidal feeding, perturbations, etc. But insofar as the feed is introduced into the first cell of the mixing zone, all elements of  $\mathbf{S}_f^k$  are equal to zero except the first, which is

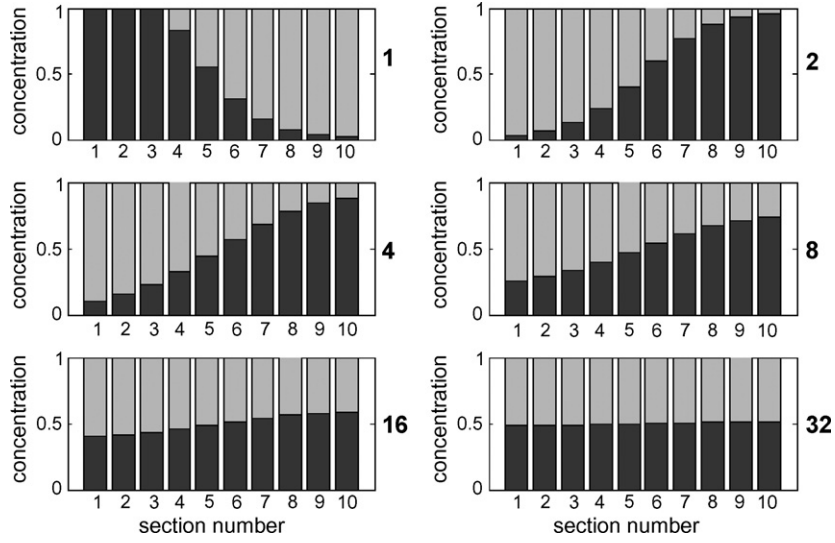
$$S_{fA1}^k = u(k) - u(k - 6), \quad (9)$$

$$S_{fB1}^k = u(k - 6) - u(k - 11) \quad (10)$$

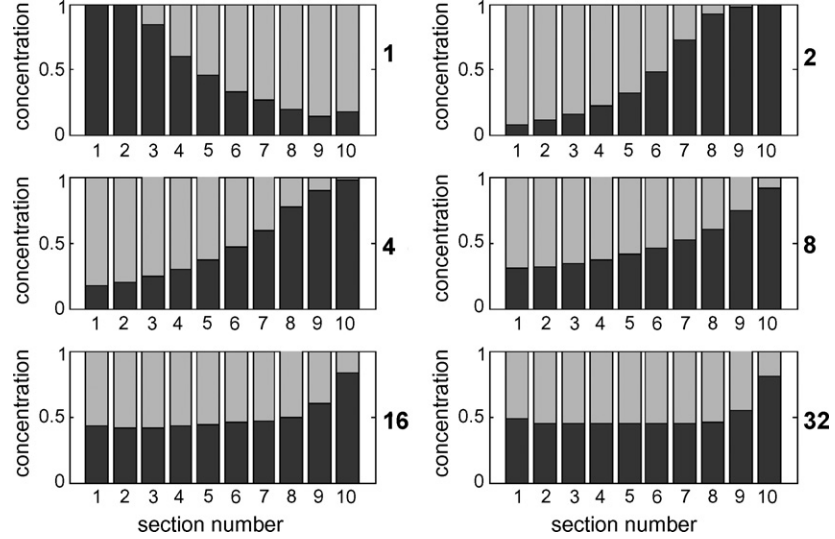
where  $u$  is the unit step function. Eqs. (9) and (10) show that component A enters the mixing zone during the first five transitions, and component B enters during five transitions beginning with the 6th.

The components approach the outlet of the mixer according to their own residence time distribution (RTD). The state  $S_5^k$  describes the cumulative collection of a component in the absorber, i.e., at the bottom of the tube, and the differences  $S_5^k - S_5^{k-1}$  describe the outflow of the component at every time step, i.e., the RTD histogram. The graph of the outflows from the mixing zone for identical transition matrices for A and B, with  $p=0.7$  and  $\alpha=1$ , is shown in Fig. 6. In this figure, the vertical axis represents the volume content of particles of both components in a section of the collector.

This allows the simulation of the filling process of the collector with A during the first 9 transitions, then with a mixture of A and B during the following transitions, according to the values of  $p$  and  $\alpha$ . Then the collector must be subdivided into the 10 original macrostates to serve as the feeder for the next passage. This procedure needs to account for the outflow transitions that are concerned with different macrostates in the collector. The cumulative curve for the mixture is to be divided into the intervals (samples) according to the scale of scrutiny, and then the content of A and B is to be calculated in every sample. The state vector that is obtained (a) characterizes the mixture state in terms of macrostates, which



**Fig. 7.** Concentration distribution in the collector after several revolutions for non-segregating mixture ( $p_A = p_B = 0.7$ ).

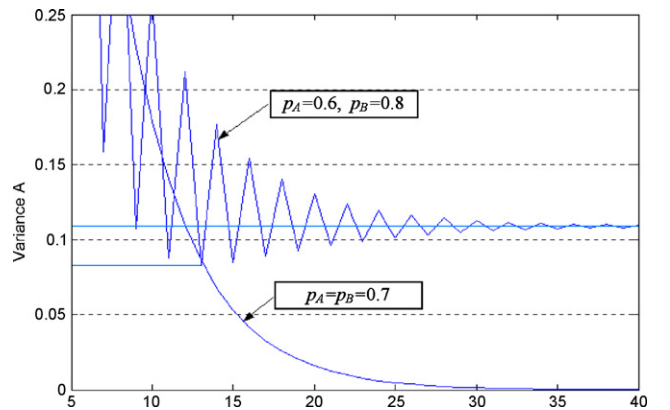


**Fig. 8.** Concentration distribution in the collector after several revolutions for a segregating mixture ( $p_A = 0.6, p_B = 0.8$ ).

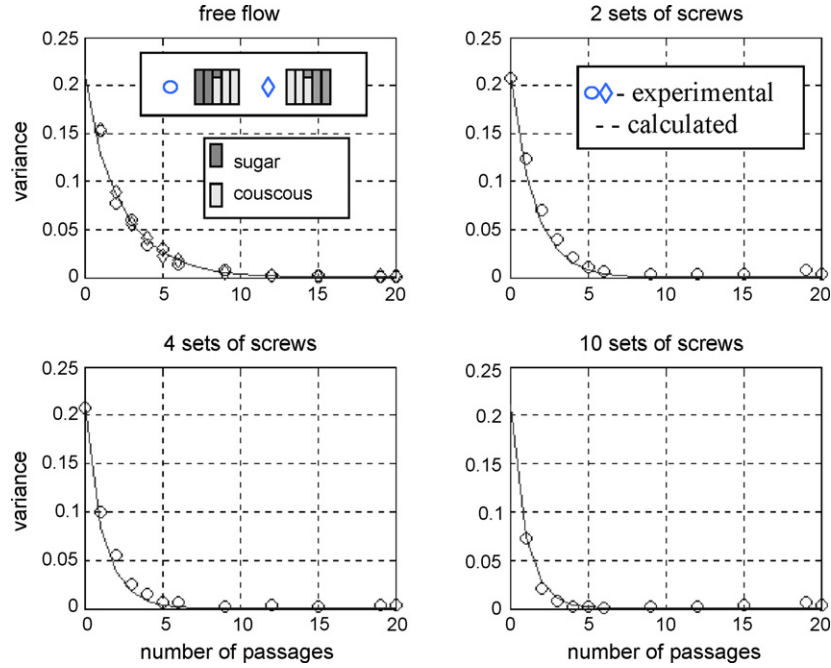
can be measured, and (b) becomes the feed vector for modelling the next passage being turned upside down.

Using the Markov chain model for the mixing zone, we can obtain the dynamics of the filling process of the 10 sections of the collector, and calculate the evolution of the overall variance of the mixture with the number of passages. This can be seen in Fig. 7 for  $p_A = p_B = 0.7$  and  $\alpha_A = \alpha_B = 1$ , for different numbers of passages. Obviously, for identical matrices for A and B, the asymptotic distribution is homogeneous and the final variance of the mixture is equal to zero (see also Fig. 9).

The evolution of the state vector for different matrices  $\mathbf{M}_A$  and  $\mathbf{M}_B$  with  $p_A = 0.6, p_B = 0.8$  and  $\alpha_A = \alpha_B = 1$  is shown in Fig. 8. The asymptotic distribution is already not homogeneous here, i.e., a perfectly homogeneous state can never be reached for the mixture. Fig. 9 shows the evolution of the mixture homogeneity presented by the variance of the component A in the macro states in the collector. The behaviour of the evolutions differs strongly for identical and different transition matrices. The variance decreases monotonously for identical matrices, and is asymptotically equal to zero. In the case of different matrices, the asymptotic distribution is



**Fig. 9.** Kinetics of mixing for segregating and non-segregating mixtures (cases of Figs. 7 and 8).



**Fig. 10.** Kinetics of mixing of sugar in couscous as measured experimentally and as calculated by the model, for different mixing configurations (circle, couscous at top; diamond, couscous at bottom).  $p_{\text{sugar}} = 0.91$ ,  $p_{\text{couscous}} = 0.91$ ,  $\alpha = 0.89$ .

approached through oscillations, so that after a certain number of passages, the mixture can be more homogeneous than the asymptotic state. This curve qualitatively corresponds to the experimental data published in [22], or previously by Poole et al. [23] or Gyenis [24].

#### 4. Experimental results and modelling

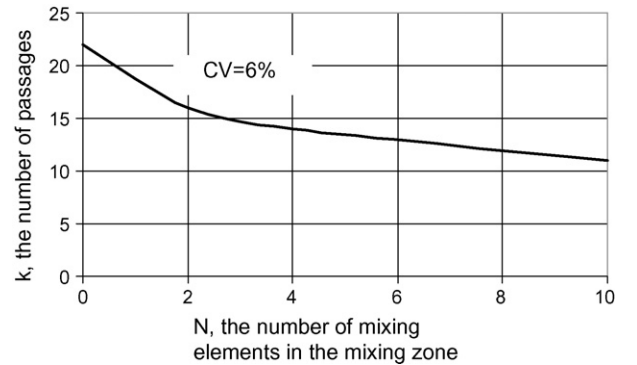
##### 4.1. Non-segregating particle mixture case

Fig. 10 refers to the influence of the number of mixing sections (sets of screws) and to the initial state on the variance evolution based on one of the components in the collector, as obtained experimentally for sugar and couscous. The upper left graph shows the kinetics of the process, the mixing zone being empty (without screws). When adding mixing sections in the tube, the kinetics of mixing improves, i.e., the variance decays quicker. However, the final state is largely independent of the number of mixing sections. This is not a surprise since mixer voidage does not change significantly in the range 0–10 mixing sections. In addition, it can be seen that the initial configuration has almost no influence on the process kinetics, i.e., the matrix is state independent, and the process is linear. The fact that the asymptotic distribution is close to the homogeneous one, but also that no oscillations were observed, indicates that the transition probabilities may be close for both components. The corresponding matrix of transition probabilities is presented as an  $11 \times 11$  matrix: 10 columns for the possible mixing sections and 1 for the absorbing state.

In order to identify the model parameters, we used the least square method for the error between the experimental and calculated distributions of concentration of the key component in the collector. For this, we first considered the data obtained with an empty mixing zone (i.e., without static mixing elements) to find the values of the transition probabilities  $p$ . The coefficient of delay  $\alpha$  was then determined by using these values of  $p$  for the experiments in which mixing sections were inserted. The reliability of the model was therefore tested for the whole set of presented data, assuming

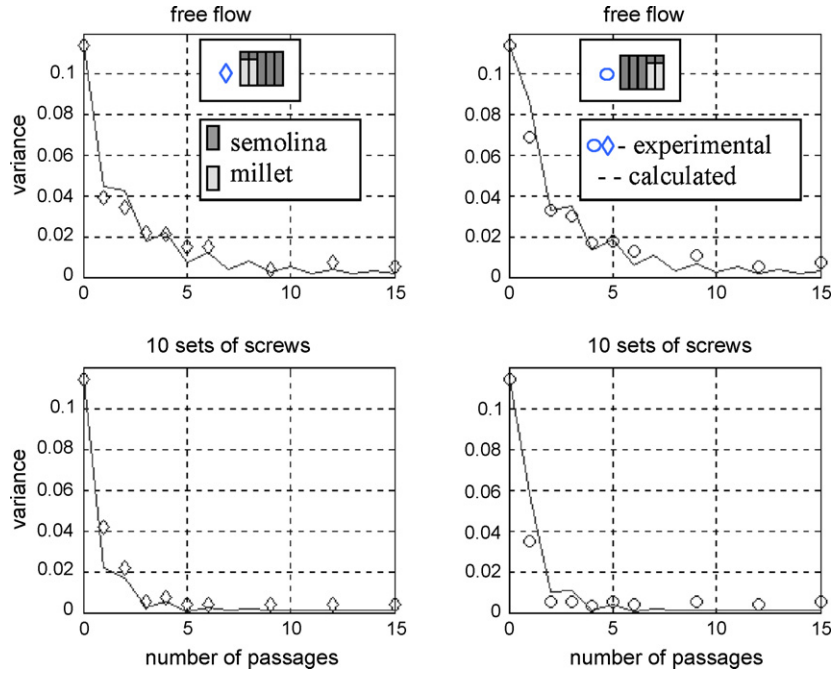
the same coefficient of delay  $\alpha$  for both the component and for all mixing configurations (initial component loading and initial disposition of the mixing sections). The curves in Fig. 10 correspond to the best model fit and was obtained with the following parameters:  $p_{\text{sugar}} = p_{\text{couscous}} = 0.91$  and  $\alpha = 0.89$ . Therefore, only two adjustable parameters can be considered to capture all process configurations and can be included in the matrix notation (Eq. (5) for each product). As for the data obtained, no segregation was predicted by the model. It can be argued that the difference in particle size is not so important, and probably counterbalanced by the difference in particle specific gravity which is favourable to sugar particles.

The influence of the number of mixing elements on the homogeneity of the mixtures can be observed from Fig. 11. As the predicted final state corresponds to a variance equal to zero, the standard value of 6% for the coefficient of variation was considered as a point of comparison. The increase in the number of mixing sections (or elements) leads to a quicker attainment of the target homogeneity, almost in a linear way. This could in turn be explained in terms of mixer internal void fraction, however experiments with other types of mixing section should be performed to confirm this hypothesis.



**Fig. 11.** Number of mixing elements and number of passages necessary for a target CV value of 6%.





**Fig. 12.** Kinetics of mixing of millet in semolina as measured experimentally and as calculated by the model, for different mixing configurations ( $p_{\text{millet}} = 0.94$ ,  $p_{\text{semolina}} = 0.896$ ,  $\alpha = 0.89$ ).

#### 4.2. Segregating particle mixture case

Fig. 12 shows the same type of results obtained with millet and semolina. As previously, increasing the number of screws allows quicker decay of the variance. On the other hand, it can be seen that the initial loading order of the component has an influence on mixture quality after a fixed number of passages through the static mixer. But the most important aspect lies in the oscillations that can be observed in the decay of the variance. This led us to consider different probabilities for the components, in accordance with the simulations presented above. The best fit was obtained with the following values of the model parameters:  $p_{\text{millet}} = 0.94$ ,  $p_{\text{semolina}} = 0.90$ , and  $\alpha = 0.89$ . The size ratio between the particles, which is close to the percolation threshold, induces a high degree of segregation that the mixer is not able to reduce significantly. In particular the target value of 6% on the coefficient of variation could not be reached in any case.

The value of  $\alpha$  was kept as an adjustable parameter in the procedure, but the fact that it remained the same as for the precedent case confirms that the mechanism of delay can be considered as independent of the materials investigated. In other words, it can be seen as an intrinsic characteristic of the mixer and its type of mixing elements. This suggests that once the link “probability  $p$  versus material properties” has been elucidated, maybe through flowability measurements, the whole process can be modelled, simulated, and optimized through mixing element design and disposition.

As was mentioned above, the matrices  $\mathbf{M}_A$  and  $\mathbf{M}_B$  are different in general cases but according to the accepted assumptions they are: (1) constant with time (homogeneous chain); (2) state independent, i.e., do not depend on concentration of A and B (linear chain). This last point is the main actual limitation of the model. If one component differs significantly from the other one in size and/or density, it can have additional resistance to the motion through the media, which depends on the concentration of one component in the other. In other words, the transition probabilities for A can be dependent on the concentration of A in the mixture, as well as the nature of the other component. This phenomenon

is ignored at the moment but will be taken into account in future work. Another limitation is that we suppose that there is no flow and therefore no mixing during the transition phase of mixer rotation, which is known to occur, at least if the revolution procedure is slow.

#### 5. Concluding remarks

In this work, we have proposed a model based on the theory of Markov chains for simulation of the mixing process in static mixers. As opposed to other models, the present one simulates bulk particle flow and takes into account the nature of the mixing zone. It has been applied for the case of a specially developed revolving apparatus, and for materials differing in size and densities, so that segregation was about to appear. A primary algorithm of model parameter identification was suggested. The results of the experiments proved the adequacy of the model developed and allowed to identify its unknown parameters. These have been extracted from a wide range of experimental data and are relatively few to describe the whole kinetics of the process, which gives a certain confidence in their values. In addition, it is suggested that they could probably be linked to material property and mixing element characterization (respectively through  $p$  and  $\alpha$  values).

The model has shown its ability to describe the main aspects of the process, including segregation and oscillating mixing kinetics. This particular effect has never been captured by a model up to now. An important idea is also that the mixing process can be described by linear models, even in the case of segregation, insofar as the mixer constantly works within one flow regime. However, it is probable that the actual model will need to be improved to take into account particle interactions and frictional flow regime that are likely to occur with a more concentrated flow. This will require considering state-dependent transition probabilities, and non-linear Markov chain modelling. Also, other aspects, such as particle shape, multi-component mixtures, different mixing element designs, mixer shape or revolution procedure are worthy of investigation.

## Appendix A. Nomenclature

$d_{10}, d_{50}, d_{90}$  characteristic diameters of the particles ( $\mu\text{m}$ )

$\mathbf{M}, \mathbf{M}_A, \mathbf{M}_B$  transition matrices

$p, p_s, p_d, p_A, p_B, p_i$  transition probabilities

$S(k), S_f$  state vectors

$S_i$  elements of state vector  $S$

$u$  unit step function

$\alpha, \alpha_A, \alpha_B, \alpha_i$  coefficients of delay as defined by the model

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