



Fluid Dynamics and Transport Phenomena

The space time CE/SE method for solving one-dimensional batch crystallization model with fines dissolution

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ABSTRACT

This article is concerned with the numerical investigation of one-dimensional population balance models for batch crystallization process with fines dissolution. In batch crystallization, dissolution of smaller unwanted nuclei below some critical size is of vital importance as it improves the quality of product. The crystal growth rates for both size-independent and size-dependent cases are considered. A delay in recycle pipe is also included in the model. The space–time conservation element and solution element method, originally derived for non-reacting flows, is used to solve the model. This scheme has already been applied to a range of PDEs, mainly in the area of fluid mechanics. The numerical results are compared with those obtained from the Koren scheme, showing that the proposed scheme is more efficient.

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1. Introduction

Crystallization is an important unit operation, often used to produce solids from liquids. It has a wide range of applications in chemical, pharmaceutical, material, and semiconductors industries. The process is proficient to provide high purity products and offers a potential to adjust the operating conditions for achieving desired product properties. Its advantages such as its high product purity and low operating costs, make it more desirable as compared to other separation processes such as extraction and distillation. It is important to understand and optimize the crystallization process for improving the product quality and for minimizing the production costs. This goal can be achieved by modeling and developing advanced control algorithms for online optimization of crystal size distribution. An accurate simulation of the distribution can be challenging as the distribution may extend many orders of magnitude in size and time [1].

The dissolution appears when a solution with crystals is warmed up, presenting a diminution in the crystal size distribution (CSD). The dissolution and crystallization are considered as opposite processes. In a batch crystallization process, dissolution of small crystals (fines) can improve the quality of a product. Normally, large size crystals are of more

interest in the industry. The dissolution of fines reduces undesirable small crystals and helps in achieving the desired CSD. Furthermore, it facilitates downstream processes such as filtration [2].

Population balance based modeling is considered to be the most useful approach for describing crystallization process along with several other chemical processes. The theory of population balances was introduced in 1960 [3,4] in the field of chemical engineering. Their wide range of application in industry has provoked the researchers to have high interest in the solution of population balance equations (PBEs), which are hyperbolic partial differential equations. Analytical solutions are possible only for a limited number of simple problems, so lots of efforts have been invested to develop appropriate numerical schemes, such as method of moments [5,6], method of characteristic [7,8], method of weighted residuals [9], the Monte Carlo method [10–12], finite difference scheme (FDS) [13,14], and high resolution finite volume schemes (FVS) [15,16].

In this article, a model is derived for the simulation of a one-dimensional batch crystallization process with dissolution of fines. A simplified dynamic model of ideally mixed batch crystallizer is considered here. It is assumed that fines completely dissolve at the end of recycle pipe attached to the crystallizer, see Fig. 1. The crystal growth rates can be size-dependent or size-independent and a delay in the recycle pipe is also integrated in the model. The space–time conservation element and solution element method is implemented for solving the resulting model. Numerous striking features of CE/SE method such as

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extremely low numerical dissipation and simplicity of construction makes the method very promising for computational fluid dynamics simulation.

2. One-dimensional Batch Crystallization with Dissolution of Fines

In this section, we give a mathematical model for the simulation of a batch crystallizer equipped with a fines dissolution loop, see Fig. 1. A simplified dynamic model of an ideally mixed batch crystallizer is considered. In the current situation, the crystallizer is connected to a recycling pipe. It is assumed that fines, taken from the crystallizer to the dissolution unit, dissolve completely before re-entering the crystallizer. It is also assumed that initially the pipe is filled with the same solution as in the crystallizer. Moreover, a delay in the recycle pipe is also incorporated in the model. In the one-dimensional case, the evolution of CSD $n(t, x) \geq 0$ is given by the population balance equation (PBE) (e.g. [4,17])

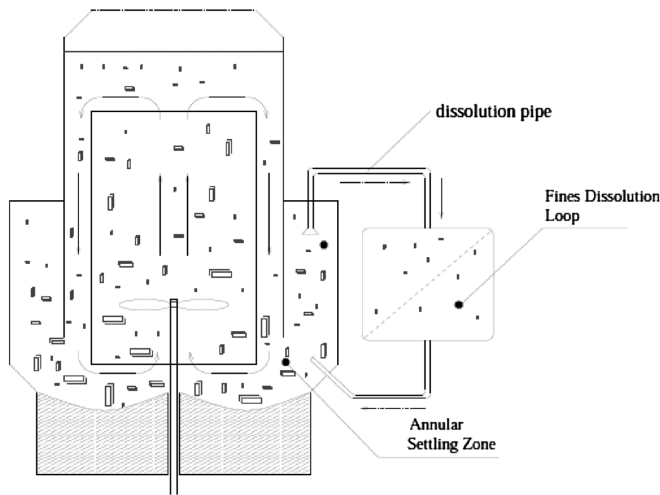


Fig. 1. Single-batch process setup with fines dissolution.

$$\frac{\partial n(t, x)}{\partial t} = -\frac{\partial(G(t, x)n(t, x))}{\partial x} - \frac{\dot{V}}{V_{\text{crz}}}h(x)n(t, x) + B_0(t)\delta(x-x_0), \quad (1)$$

$$n(0, x) = n_0(x), \quad (t, x) \in \mathbb{R}_+^2,$$

where $\mathbb{R}_+ := (0, \infty)$. Here, $n_0(x) \in \mathbb{R}$ denotes the CSD of seed crystals added at the beginning of the batch process, $G(t, x) \geq 0$ is the crystal growth rate along the characteristic directions x , $B_0(t) \geq 0$ is the nucleation rate at minimum crystal size x_0 , and δ is the Dirac delta distribution. V_{crz} is volume of crystallizer and $\dot{V}$ is the volumetric flow rate. The death function $h(x)$ describes the dissolution of small particles below some critical size. The i th moment of CSD is defined as

$$\mu_i(t) = \int_0^\infty x^i n(t, x) dx \quad i = 0, 1, 2, \dots \quad (2)$$

We consider the case of fines dissolution with time delay in the dissolution pipe. It is assumed that the crystallizer and the pipe are filled with same solution. The crystallizer is seeded by putting small crystals for starting the crystallization process. After commencement of the process of crystallization, small crystals along with the solution are taken to

the dissolution pipe. The solution from the recycle pipe comes back into the crystallizer after certain time. It is assumed that all solid particles in the solution dissolve in the dissolution unit because of heating. Now the solution in the pipe is cooled down to the crystallizer temperature before re-entering the crystallizer to avoid a flow of hot liquid into the crystallizer which will affect the crystallization process. Based on above assumptions, a balance for the liquid phase yields an ordinary differential equation for the solute mass of the form

$$\frac{dm(t)}{dt} = \dot{m}_{\text{in}}(t) - \dot{m}_{\text{out}}(t) - 3\rho_c k_v \int_0^\infty x^2 n(t, x) G(t, x) dx. \quad (3)$$

Here, ρ_c represents crystal density. Due to the dissolution of fines this equation has two mass fluxes. The mass flux $\dot{m}_{\text{out}}(t)$ taken out from the crystallizer into the dissolution unit is expressed as

$$\dot{m}_{\text{out}}(t) = w(t) \dot{V} \rho_{\text{solu}}(T), \quad (4)$$

The incoming mass flux $\dot{m}_{\text{in}}(t)$ is from the dissolution unit to the crystallizer, defined as

$$\begin{aligned} \dot{m}_{\text{in}}(t) = & \dot{m}_{\text{out}}(t - \tau_2) \\ & + \frac{k_v \rho_c}{V_{\text{crz}}} \dot{V} \int_0^\infty x^3 n(t - \tau_2, x) h(x) dx - \rho_c k_v (x_0)^3 B_0(t - \tau_2) \end{aligned} \quad (5)$$

where, $\tau_2 \geq 0$ represents the time of residence in the dissolution unit

$$\tau_2 = \frac{V_p}{\dot{V}}. \quad (6)$$

where, V_p is the pipe volume. The crystal growths is considered as

$$G(t, x) = k_g (S(t) - 1)^g (1 + \alpha_1 x)^{\alpha_2} := g_1(t) g_2(x), \quad (7)$$

where k_g is a constant of growth rate, exponent g stands for growth rate order, exponent α_1 is a constant representing size-dependency and supersaturation $S(t)$ can be described as

$$S(t, m) = \frac{w(t)}{w_{\text{sat}}} \quad \text{with} \quad w(t) = \frac{m(t)}{m(t) + m_{\text{solu}}(T)} \quad (8)$$

where, $w(t)$ denotes a fraction of mass while w_{sat} is the saturated fraction of mass at specified temperature. Normally, the rate of nucleation is

$$B_0(t) = k_b [S(t) - 1]^b \int_0^\infty x^3 n(t, x) dx. \quad (9)$$

In this equation, constant k_b is a rate of nucleation and b is its order. Naturally, the relations of growth and nucleation are empirical. Parameters k_g , k_b , g and b are normally derived from experiments [18,19]. Note that for $\tau_2 = 0$ this model reduces to the dissolution model without delay.

3. Numerical Method

In this section, the space-time CE/SE method is applied to solve the batch model, which was originally developed by Chang [21] for hyperbolic conservation laws. This scheme has been applied to a range of partial differential equations, mainly in the area of CFD. The CE/SE method has been successfully applied to various physical problems, thus, confirming its robustness and generality. This method is established to overcome the limitations of traditional numerical schemes, such as FDS, FVS and finite element method.

In single property variable Eq. (1) reduces to

$$\frac{\partial n}{\partial t} + \frac{\partial F}{\partial x} = Q, \quad (10)$$

where n is the number density function and $F(G, n) = G(t, x)n(t, x)$ is the flux function. Let t and x denote the coordinates of a two-dimensional Euclidean space-time (E_2) and $\mathbf{h} = (n, F, -Q)$ is the current density vector. By using Gauss divergence theorem, the corresponding integral conservation form of Eq. (10) is equivalent to the integral equation [21]

$$\oint_{S(v)} \mathbf{h} \cdot d\mathbf{s} = 0, \quad (11)$$

where $S(v)$ is the boundary of an arbitrary space-time domain V . Eq. (11) is restricted to the space time domain, the conservation element (CE), which permits the discontinuities of flow variables. The actual numerical integration is done directly on the solution elements (SEs). An SE is a different space-time region in which the flow variables are assumed to be smooth. Thus, the discretization of the flow variables with a prescribed order of accuracy can be performed.

Let Ω denote the set of grid points (η, j) with $\eta = 0, \pm \frac{1}{2}, \pm 1, \pm \frac{3}{2}, \dots$ and for every $\eta, j = \eta \pm \frac{1}{2}, \eta \pm 1, \eta \pm \frac{3}{2}, \dots$. With each $(\eta, j) \in \Omega$ one SE is associated. It is assumed that $SE(\eta, j)$ shades space-time region in Fig. 2. It includes the segments of horizontal and vertical lines and

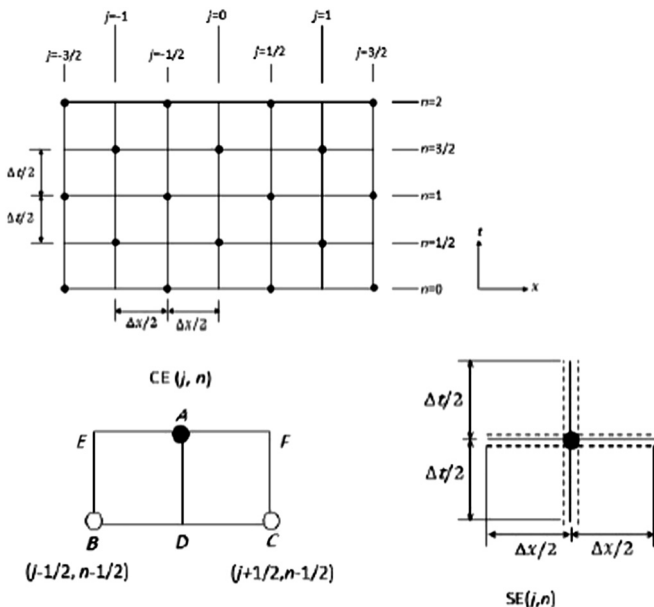


Fig. 2. CE/SE grid.

their close neighborhood. The actual size of the neighborhood is not a concern. At point (t, x) in SE, the approximation of $n(t, x)$, $F(t, x)$, and $h(t, x)$ are given as $n^*(t, x; \eta, j)$, $F^*(t, x; \eta, j)$, and $h^*(t, x; \eta, j)$, respectively.

Let

$$\begin{aligned} n^*(t, x; \eta, j) &= (n)_j^\eta + (n_t)_j^\eta (t - t^\eta) + (n_x)_j^\eta (x - x_j), \\ F^*(t, x; \eta, j) &= (F)_j^\eta + (F_t)_j^\eta (t - t^\eta) + (F_x)_j^\eta (x - x_j), \end{aligned} \quad (12)$$

where $(n)_j^\eta$, $(n_t)_j^\eta$, $(n_x)_j^\eta$, $(F)_j^\eta$, and $(F_t)_j^\eta$ are constants in $SE(\eta, j)$. They can be considered as the numerical analogues of $\frac{\partial n}{\partial x}$, $\frac{\partial n}{\partial t}$, $\frac{\partial F}{\partial x}$, and $\frac{\partial F}{\partial t}$ at (t^η, x^η) , respectively. Because of $h = (F, n)$ one can write

$$h^*(t, x; \eta, j) = (F^*(t, x; \eta, j), n^*(t, x; \eta, j)) - Q^*(t, x; \eta, j). \quad (13)$$

By definition $(F)_j^\eta$ is a function of $(n)_j^\eta$, $(F_x)_j^\eta$ is a function of $(n)_j^\eta$ and $(n_x)_j^\eta$, and $(F_t)_j^\eta$ is a function of $(n)_j^\eta$ and $(n_t)_j^\eta$. Moreover, it is assumed that for any $(t, x) \in SE(\eta, j)$, $n^*(t, x; \eta, j)$, and $F^*(t, x; \eta, j)$ satisfy Eq. (10), i.e.

$$\frac{\partial n^*(t, x; \eta, j)}{\partial t} + \frac{\partial F^*(t, x; \eta, j)}{\partial x} = Q. \quad (14)$$

According to Eq. (12), Eq. (14) is equivalent to

$$(n_t)_j^\eta = -(F_x)_j^\eta + Q. \quad (15)$$

As $(F_x)_j^\eta$ is a function of $(n)_j^\eta$ and $(n_x)_j^\eta$ Eq. (15) implies that $(n_t)_j^\eta$ is also a function of $(n)_j^\eta$ and $(n_x)_j^\eta$. Based on this result and Eq. (15) one can conclude that $(n_t)_j^\eta$, $(F)_j^\eta$, $(F_x)_j^\eta$ and $(F_t)_j^\eta$ are functions of $(n)_j^\eta$ and $(n_x)_j^\eta$. As a result $(n)_j^\eta$ and $(n_x)_j^\eta$ are the only independent discrete variables needed to be solved in the current marching scheme.

In Fig. 2, the rectangular non-overlapped regions represent the CEs. Consider its integral representation

$$\int_{\partial\Omega} n^* dx - F^* dt = 0, \quad (16)$$

where, $\partial\Omega$ is the boundary of Ω . On integrating over the rectangular region $\Omega_1 = [x_{i-1/2}, x_{i+1/2}] \times [t^\eta, t^{\eta+1/2}]$, where $\Omega = \Omega_1 \cup \Omega_2$, we obtain

$$\begin{aligned} (n)_j^\eta - (n)_{j+1/2}^{\eta+1/2} \pm \frac{\Delta x}{4} [(n_x)_{j+1/2}^{\eta-1/2} + (n_x)_j^\eta] \pm \frac{\Delta t}{4\Delta x} [(F)_{j+1/2}^{\eta-1/2} + (F)_j^\eta] \\ \pm \frac{\Delta t^2}{\Delta x} [(F_t)_{j+1/2}^{\eta-1/2} + (F_t)_j^\eta] = \frac{\Delta t \Delta x}{4} P_{tj-1/2}^{\eta-1/2} \end{aligned} \quad (17)$$

Note that, we have two Eq. (17) for two unknowns n_j^η and n_{j+1}^η . By adding and then subtracting the above two equations we have

$$\begin{aligned} (n)_j^\eta = \frac{1}{2} [(n)_{j-1/2}^{\eta-1/2} + n_{j+1/2}^{\eta-1/2} + (S)_{j-1/2}^{\eta-1/2} + (S)_{j+1/2}^{\eta-1/2}] \\ + \frac{\Delta t}{4} [Q_j^\eta + Q_{j+1}^\eta], \end{aligned} \quad (18)$$

and

$$\begin{aligned} \frac{\Delta x}{2} (n_x)_j^\eta = (n_{j+1/2}^{\eta-1/2} - n_{j-1/2}^{\eta-1/2}) - (S_{j+1/2}^{\eta-1/2} - S_{j-1/2}^{\eta-1/2}) \\ - \frac{\Delta t}{\Delta x} \left(\frac{\Delta t}{2} (F_t)_j^\eta - 2(F)_j^\eta \right) + \frac{\Delta t}{2} (Q_{j-1/2}^{\eta-1/2} + Q_{j+1/2}^{\eta-1/2}). \end{aligned} \quad (19)$$

The approximated spatial derivatives $(n_x)_j^\eta$ in Eq. (19) can be imprecise due to discontinuities. In this case, the solution can be very oscillatory and for a small Courant–Friedrichs–Lewy condition the solution

may become overly diffusive. To overcome this limitation, Chang [21] introduced the following limiting formulations

$$(n_x)_j^\eta = U_i((n_{ix-})_j^\eta, (n_{ix+})_j^\eta; \alpha). \quad (20)$$

Here $1 \leq \alpha \leq 2$ and

$$U_i(x_-, x_+; \alpha) = \frac{|x_+|^\alpha x_- + |x_-|^\alpha x_+}{|x_+|^\alpha + |x_-|^\alpha}. \quad (21)$$

Moreover,

$$(n_{ix\pm})_j^\eta = \pm \frac{(n_i')_{j\pm 1/2}^\eta - (n_i)_j^\eta}{\frac{\Delta x}{2}} (n_i)_j^\eta = (n_i)_{j\pm 1/2}^{\eta-1/2} + \frac{\Delta t}{2} (n_{it})_{j\pm 1/2}^{\eta-1/2}. \quad (22)$$

This concludes the derivation of the scheme.

4. Numerical Test Problem

In this section we considered a numerical test problem in order to validate our numerical schemes for the given model. The initial data are given as

$$n(0, x) = \frac{m_{\text{seeds}}}{k_v \rho_c \mu_3(0) \sqrt{2\pi\sigma}} \exp\left(-\frac{(x-\bar{x})^2}{2\sigma^2}\right), \quad (23)$$

where $x_0 = 0$ and $x_{\text{max}} = 0.005$ are the minimum and maximum crystal sizes respectively. The interval $[0, x_{\text{max}}]$ is divided into 300 grid points and the simulation time is 800 min. The temperature of the crystallizer is kept constant at 33 °C. The kinetic parameters are given in Table 1. The death function $h(x)$ is defined as

Table 1
Parameters for the test problem 1

Description	Symbols	Value	Unit
Growth rate constant	k_g	1.37×10^{-5}	$\text{m} \cdot \text{min}^{-1}$
Growth rate exponent	g_1	0.73	–
Nucleation rate constant	k_b	3.42×10^7	$\text{m}^{-3} \cdot \text{min}^{-1}$
Nucleation rate exponent	b	2.35	–
Density of crystals	ρ_c	1250	$\text{kg} \cdot \text{m}^{-3}$
Volume shape factor	k_v	0.029	–
Initial solute concentration (mass)	$m(0)$	0.09915	kg
Saturated mass fraction	w_{sat}	0.090681	–
Mass of seeds	m_{seeds}	2.5×10^{-3}	kg
Mass of solvent	m_{sol}	0.8017	kg
Density of solution	ρ_{sol}	1000	$\text{kg} \cdot \text{m}^{-3}$
Constant (Eq. (24))	σ	3.2×10^{-4}	m
Constant (Eq. (24))	$\bar{x}$	1.4×10^{-3}	m
Volume of the crystallizer	V_{crz}	10^{-3}	m^3
Volumetric flow rate	$\dot{V}$	2×10^{-5}	$\text{m}^3 \cdot \text{min}^{-1}$
Volume of the pipe	V_p	2.4×10^{-4}	m^3

$$h(x) = \frac{1}{\sqrt{2\pi}\sigma_1} \exp\left(-\frac{x}{\alpha\sigma_1}\right)^2, \sigma_1 = \frac{1}{\sqrt{2\pi}\sigma n_{\text{max}}} \quad (24)$$

where, $\alpha = 0.0011547$ and $n_{\text{max}} = 0.6$. Final crystal size distribution for size-independent growth and size-dependent growth is shown in Fig. 3,

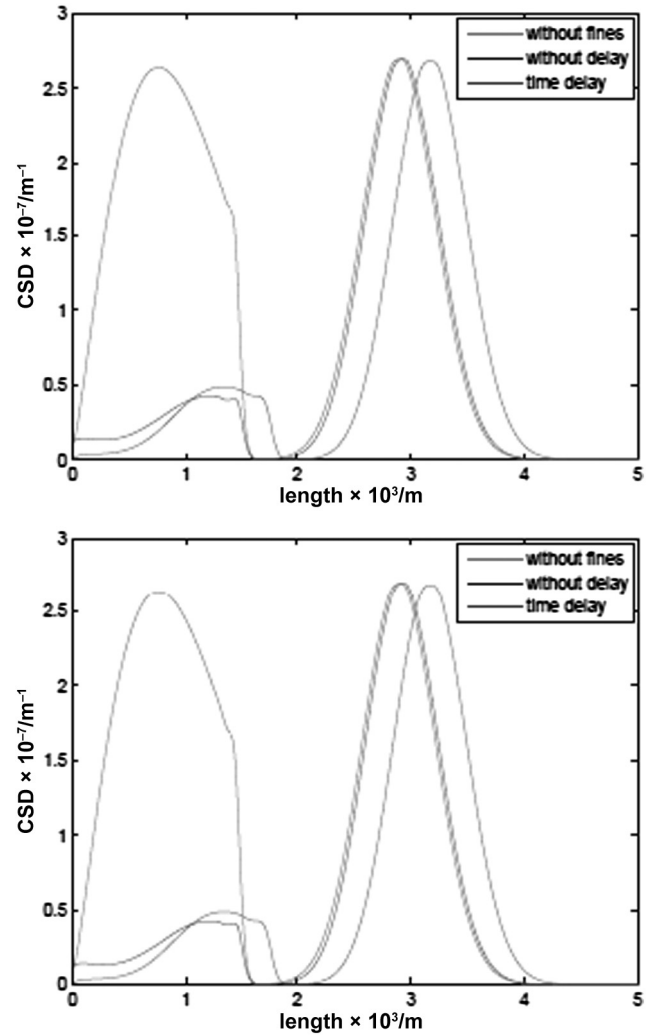


Fig. 3. Size-independent (top) and size-dependent (bottom) cases.

in which the final CSD for the model without fines dissolution, fines dissolution with and without time delay is compared. Without fines dissolution there is a large number of small unwanted nuclei which affect the product quality, while the dissolution unit dissolves the small crystal below some critical size and reduces the number of small crystals in the crystallizer. In the case of fines dissolution without time delay small crystals are dissolved as soon as they are introduced in the solution, so their effect on crystal growth rate is negligible. On the other hand, fines dissolution with time delay permits nuclei to grow for a certain time and the concentrated solution from dissolution unit get back to the crystallizer with a time delay. As a result the seed crystals grow at a faster rate. Figs. 4 and 5 compare the proposed scheme and the finite volume Koren scheme for fines dissolution with and without time delay for both size-independent and size dependent growth rates. The results with the same model are established by [20]. The numerical results for both the schemes are almost overlapping, but the current scheme gives better results for the proposed model.

5. Conclusions

In this paper, a mathematical model for one-dimensional batch crystallization process with fines dissolution was derived. The case study shows that the dissolution of smaller nuclei below some critical size helps in improving the product quality. Crystal growth rates are

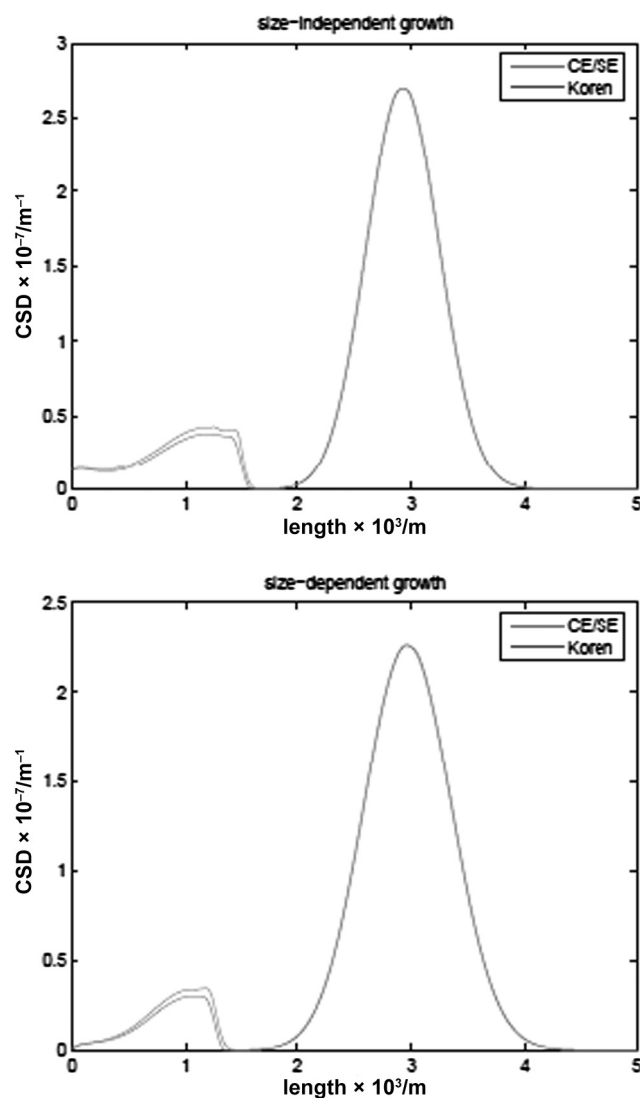


Fig. 4. Comparison of CE/SE and Koren for without time delay and size-independent (top) and size-dependent (bottom) growth.

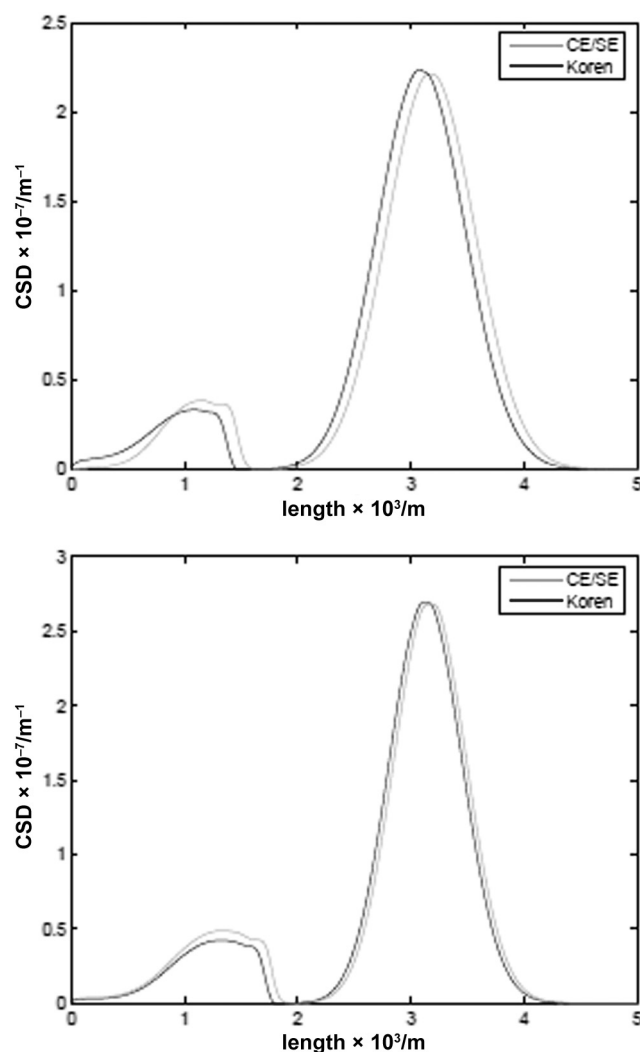


Fig. 5. Comparison of CE/SE and Koren for time delay and size-independent (top) and size-dependent (bottom) growth.

considered to be size-independent and size-dependent. Moreover, a delay in the recycle pipe is also incorporated in the model. The space time conservation element and solution element method is used to solve the resulting model. The numerical results show excellent performance of proposed numerical schemes for solving the current model.

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