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A numerical study on orthokinetic agglomeration in stirred tanks

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Abstract

A numerical study on the scale-up behaviour of orthokinetic agglomeration in stirred tanks is presented. Large Eddy flow simulations were performed to obtain an accurate description of the turbulent flow encountered in stirred vessels, equipped with either a Rushton or a pitched blade turbine. Simultaneously, the convection-reaction equation for the particle number concentration is solved. Equal resolutions were used for the flow simulations and the particle concentration equation. Agglomeration was incorporated by making use of the nonlinear agglomeration model proposed by Mumtaz et al. [Trans. Inst. Chem. Eng. 75 (1997) 152]. Reactor performance for vessel sizes in the range of 1 to 10 000 l was simulated. Three scale-up rules (viz. constant *Re* number, specific power input, and impeller tip speed) were investigated. It was found that impeller shape, vessel size, and *Re* number have a profound effect on reactor performance.

Keywords: Orthokinetic; Agglomeration; Turbulence; Modelling; Stirred tanks

1. Introduction

Precipitation (or reactive crystallization) is a common process step to obtain solid products in pure form. Usually, reactants are mixed in a stirred vessel to generate a supersaturated mother liquor. From this liquor, a solid phase may be formed by nucleation and growth. Aside from these primary mechanisms, agglomeration can act as a secondary mechanism: particles may collide and form clusters. Although particle agglomeration is known to drastically alter the particle size distribution (PSD) of a crystalline product, this mechanism is usually discarded in reactor design. This is mainly because the details of the agglomeration mechanism are poorly understood. It is therefore difficult to define a proper scale-up rule for this process.

The complexity of orthokinetic (or shear-induced) agglomeration is caused by the strong coupling of this mechanism to fluid flow. The flow in stirred tank reactors is notorious for its complexity, since it is usually turbulent, transient due to impeller movement and inherently three dimensional. An additional complication is that the local energy-dissipation rate can vary orders of magnitude between the impeller swept region and the bulk region of a tank. The shear rate, which is linked to the dissipation rate, is therefore also a pronounced function of the position in the tank. Aside from the nonlinearities found in stirred-tank flow, the agglomeration kinetics itself is highly nonlinear. In 1917, von Smoluchowski [2] derived a relation for the particle collision rate in a two-dimensional laminar shear flow. This relation shows a linear dependency of the collision rate on the applied shear rate. It is known from experiments, however, that this linear relation does not describe agglomeration at high shear rates: the collision efficiency decreases at increasing shear rate, yielding a zero agglomeration rate at high shear rates. The first paper presented in literature that takes this collision efficiency into account was from Mumtaz et al. [1].

In this work, an attempt has been made to account for the effect of local hydrodynamic conditions in a stirred vessel on orthokinetic agglomeration. A computer code, based on the lattice-Boltzmann method, is used to simulate the turbulent flow in a stirred vessel [3]. An eddy-viscosity model is incorporated in the code to be able to do large eddy simulations (LES) for highly turbulent flows. Agglomeration is incorporated by tracking the particle concentration in time. Particles are convected through the domain at the resolved velocity given by the LES simulation. The local flow conditions are used to make agglomeration happen: the local shear rate computed by the lattice-Boltzmann scheme

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is used to calculate the local agglomeration rate constant, as proposed by Mumtaz et al. [1]. This procedure is described in detail in Refs. [4–6].

The abovementioned procedure is used to compute the relative reactor performance with respect to agglomeration upon scale-up. The flow field induced by a standard Rushton turbine and a pitched blade turbine, at vessel sizes of 1 to 10 000 l, are considered. Three engineering rules are investigated for scale-up: constant *Re* number, constant mean power input, and constant impeller tip speed. The results show that both microscale effects (e.g. the shear rate at the Kolmogorov scales), and macroscopic effects (e.g. large-scale particle transport), play a role in the overall agglomeration performance of a reactor. These effects cannot be kept constant at the same time upon scale-up. Also, it can be seen that interpretation of experimental stirred-tank data is far from trivial. This paper will cover the modelling aspects of particle agglomeration in computational fluid dynamics (CFD) and show the implications of the common scale-up rules on reactor performance.

2. Theory and numerical setup

2.1. Kinetics

Since the early work of von Smoluchowski [2], it has been known that particles with a size of around 10 μm are susceptible for agglomeration due to fluid shear. For monodisperse particles, the collision rate constant is given by:

$$\beta_c = \frac{4}{3}\dot{\gamma}d^3 \tag{1}$$

Although particle collisions play an important role in the agglomeration mechanism, Eq. (1) is not able to fully describe it. It is known from experiments that the agglomeration rate falls to zero at high shear rates due to the decreasing contact times and increasing viscous forces acting on the agglomerates. In Ref. [1], the shear rate dependence of the agglomeration rate constant β_0 for calcium oxalate monohydrate in a two-dimensional planar shear flow was investigated numerically. A representation of this dependence is given in Fig. 1. As can be seen, the rate constant shows a maximum value around a shear rate of about 10 s^{-1}. For industrial applications, simple shear flow has limited value. To link kinetics based on a simple shear situation to (more practical) stirred-tank flow, relations like Eq. (2) are commonly used:

$$\dot{\gamma} \approx \sqrt{\frac{\varepsilon}{\nu}} \propto \sqrt{\frac{Po N^3 D^2}{\nu}} \tag{2}$$

The main objection to Eq. (2) is the volume averaging that is applied; i.e., a global value for the shear rate is derived from the total power input in the vessel. It is known that the energy dissipation rate ε is very unevenly distributed over the vessel [3]. The nonlinear nature of the agglomeration kinetics may render this averaging procedure unreliable. To overcome the possible errors introduced by volume averaging, this paper will solve the kinetics at a resolution equal to the flow equations. A computational fluid dynamics (CFD) tool is used to solve the flow field in stirred vessels. The local flow information derived from the flow simulations is used to determine the local kinetics. By solving the evolution of the particle number density simultaneously, the local and instantaneous agglomeration rate is computed.

2.2. Flow solver

It is the aim of this paper to study the influence of fluid flow on orthokinetic agglomeration in detail. To be able to do this, an accurate description of the flow field is needed. To properly predict the overall agglomeration rate of a reactor, it is insufficient to develop a model in terms of volume and time averaged quantities [4–6]. Particles do not experience averaged flows, but rather local and instantaneous hydrodynamic conditions. In this work, the reactor performance is derived from transient, three-dimensional flow calculations. An eddy-viscosity model [7] is incorpo-

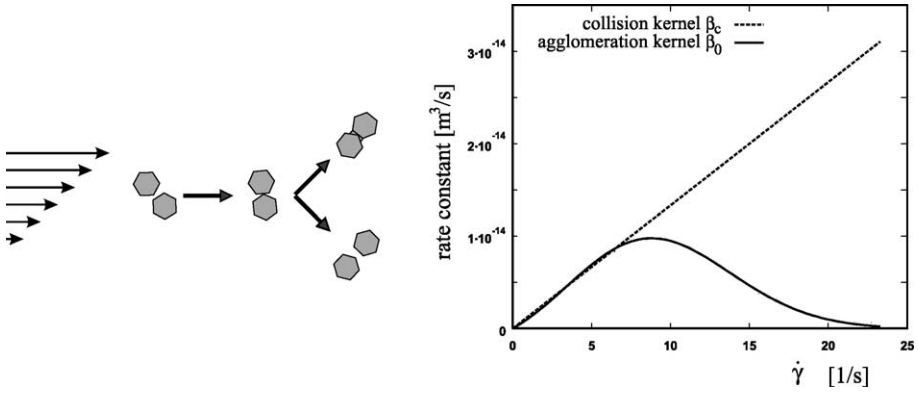

Fig. 1. Particles collide due to a fluid shear rate (left). Although the collision rate is linear with shear rate, the agglomeration rate will fall to zero at high shear rates (right). The agglomeration kernel β_0, computed for $CaO_x \cdot H_2O$, was taken from Ref. [1].

rated for turbulence modeling (i.e. large eddy simulations) in high Reynolds number situations.

The LES technique decomposes the flow equation into a resolved (grid scale) and an unresolved (subgrid scale) contribution. No additional modeling is needed for the large-scale flow structures. An SGS turbulence model incorporates the effect of the small-scale structures on agglomeration.

The flow solver is based on the lattice-Boltzmann algorithm [3], and is fully parallelized. The agglomeration reaction is incorporated by solving an additional convection-reaction equation for the particle number concentration. The particles are assumed to behave as passive tracers in the simulations: particles do not experience gravity and move with the resolved fluid velocity. The agglomeration rate constant is derived from the local effective shear rate derived from the flow simulations.

2.3. Converting kinetics to three-dimensional flow

To model agglomeration in LES simulations, the agglomeration rate constant that was determined for a two-dimensional shear flow has to be converted to an intrinsic three-dimensional turbulent flow. Dimensional analysis suggests that an effective shear rate can be linked to a local energy-dissipation rate:

$$\dot{\gamma} \propto \sqrt{\frac{\varepsilon}{\nu}} \tag{4}$$

However, the proportionality constant needs to be specified. Also, it should be kept in mind that in three-dimensional flow, it is difficult to define 'a' proper shear rate. In Ref. [8], the collision rate of inertialess particles in a rapidly sheared homogeneous turbulent flow is derived. In this paper, the eigenvalues of the rate of strain tensor are used to determine the actual collision rate constant. The procedure used in our paper is to match the collision rate given by Mei and Hu [8], to the collision rate by von Smoluchowski. This yields an equivalent two-dimensional shear rate for the intrinsic three-dimensional flow field. From the equivalent two-dimensional collision rate, the agglomeration rate constant from Ref. [1] is derived. The benefit of this method is that a decomposition of agglomeration due to GS and SGS motion can be made. Although this method is computationally slightly more demanding, it allows for accounting for resolved and unresolved scale agglomeration in a physically more correct way [6].

2.4. Numerical setup

Vessel sizes from 1 to 10 000 l are investigated. A standard six-blade Rusthon turbine ($D = D_{tank}/3$) and a four-blade pitched blade turbine ($D = D_{tank}/3$, 45° angle, pumping downward) are used. The vessels were equipped with four baffles ($D_{tank}/10$).

Three scale-up rules were investigated: scale-up at constant *Re* number, constant specific power input and constant impeller tip speed. The 100 l RT case at an Re-number of 20 000 was taken as a base case.

The reactor performance was derived from the time evolution of the particle number concentration in the vessel. The number concentration was fitted to the rate law for size-independent agglomeration:

$$\frac{dm_0}{dt} = -\frac{1}{2}\hat{\beta}_0 m_0^2 \Rightarrow m_0(t) = \frac{1}{0.5\hat{\beta}_0 t + \frac{1}{m_{00}}} \tag{5}$$

with $\hat{\beta}_0$ the reactor-averaged estimates of β_0. The dependence of $\hat{\beta}_0$ on flow conditions and vessel sizes was used to study the scaling behaviour of agglomeration. Most simu-

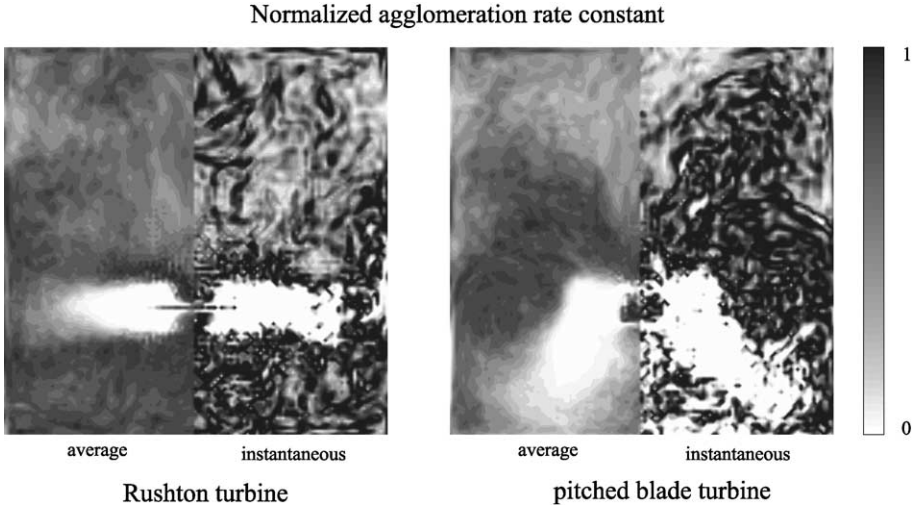

Fig. 2. Normalized agglomeration rate constant in a vertical plane between the baffles in a stirred vessel, equipped with a Rushton turbine (left) and a pitched blade turbine (right). Values are normalized by the maximum of β_0. Both the time-averaged and an instantaneous realization are depicted.

lations were performed on a 120 × 120 × 120 grid. For high *Re* number simulations ($Re>10^5$), a resolution of 180 × 180 × 180 grid nodes was used. A total of 34 cases, at various reactor sizes, impeller shapes and *Re* numbers, were simulated.

3. Results

To show the influence of the local nature of the energy dissipation rate in a stirred vessel, the values of the agglomeration rate constant in a vertical plane between the baffles are depicted in Fig. 2. Regions of high and low β_0 can be observed. The instantaneous pictures show large gradients in rate constant. Due to this effect, the particle number decrease will strongly vary as a function of the position in the tank. Consequently, large gradients in particle concentration arise. This indicates that the assumption of ideally mixed particles may be invalid. The average pictures show a large difference in the size and magnitude of the relatively low and high β_0 region for the RT and the PBT. This difference in macroscopic behaviour causes unpredictable scale-up behaviour, even if the specific power input is kept constant.

Data for scale-up at constant *Re* number and constant specific power input (Fig. 3) show irregular scale-up behaviour. In case of scale-up at constant *Re* number, both the RT and the PBT show a distinct maximum in observed rate constant at a vessel size of 100 l. This is caused by the fact that the mean energy dissipation rate will decrease at increasing vessel sizes. In reactors smaller than 100 l, the mean ε (and thus the mean shear rate) is so large that the right side of Fig. 1 is dominant. This is in agreement with the experimental observation that laboratory scale reactors do not agglomerate. For vessels larger than 100 l, shear rates are, on average, small, which results in agglomeration rate constants taken from the left part of the Mumtaz curve. This also yields a lower reactor averaged agglomeration rate constant.

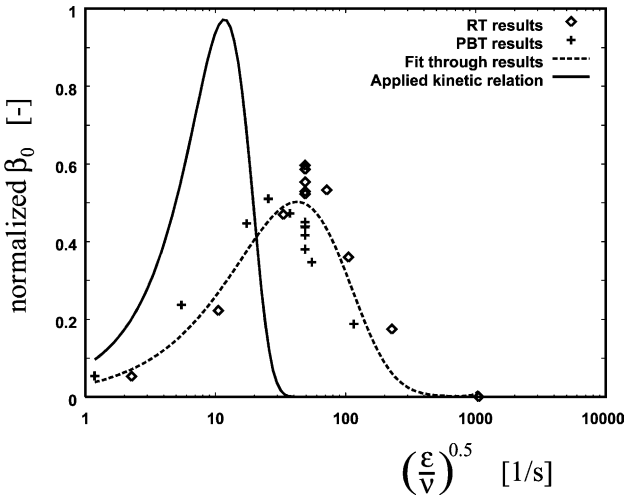

Fig. 4. A comparison between the applied kinetic relation and the kinetics derived from simulation results of two impeller geometries at various *Re* numbers.

Scale-up at constant specific power input shows a more constant reactor behaviour. The trends (negative slope for RT, positive slope for PBT) may be caused by differences in macroscopic timescales, important for, e.g. macroscale particle transport. The difference in impeller geometry is accounted for by the *Po* number in Eq. (2). Apparently, a residual effect, coupled to the differences in macroscopic flow field exists. The differences in impeller geometry can therefore not be explained by the difference in *Po* number only, as is implicitly assumed when Eq. (2) is used.

The numerical results can be presented in a way common to real-life experiments: the 'measured' agglomeration rate constants (i.e. $\hat{\beta}_0$ in Eq. (5)) are plotted against the volume average (mean) shear rate of the reactor (Fig. 4). Several interesting observations can be made. Although the statistics in numerical work are much better than can be expected in experimental work, the scatter in the data is still large. This scatter is caused by the differences in hydrodynamic conditions. If a curve is fitted through the numerical data, a

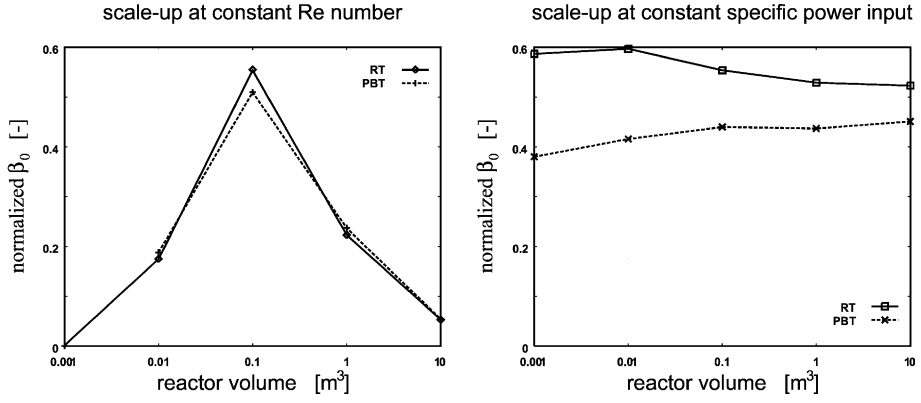

Fig. 3. Normalized agglomeration rate constant for an RT and a PBT. The rate constants are normalized by the maximum of Fig. 1. The left figure shows the agglomeration behaviour for scale-up at constant *Re* number (*Re* = 20 000), the right figure for scale-up at constant specific power input ($\varepsilon = 2.39 \times 10^{-3}$ m^2 s^{-3}).

curve similar to Fig. 1. is found. The fitted curve has a much lower maximum value for β_0. Furthermore, the maximum is shifted towards higher shear rates. Apparently, the nonlinear effects in the total process tend to shift the maximum agglomeration rate to higher volume average shear rates. Interestingly, an objection to the kinetic relation by Mumtaz et al. [1] was the fact that the optimum shear rate was predicted at much lower shear rate values than commonly found in stirred tank experiments (see, e.g. Ref. [9]). Fig. 4. shows that detailed hydrodynamic effects may be responsible for this effect. It also shows that it is very difficult to reconstruct the underlying agglomeration kinetics from stirred tank experiments. Based on the averaged reactor performance only, one cannot reconstruct the actual kinetic relation. Additional (detailed and local) flow information is needed to account for the nonlinear coupling of the various mechanisms described earlier.

4. Concluding remarks

A numerical technique to simulate agglomeration performance has been developed. The technique shows a strong coupling between fluid flow and agglomeration. Both particle transport and a spatial distribution in energy dissipation rate are responsible for irregular scale-up behaviour. A dramatic effect on agglomerator performance is the influence of impeller geometry. Only taking into account the *Po* number of an impeller fails to explain the observed differences in agglomeration behaviour between an RT and a PBT.

The conversion of the two-dimensional agglomeration kinetics proposed in Ref. [1] to the three-dimensional turbulence as encountered in an STR was studied in detail. A model that properly accounts for agglomeration due to velocity gradients at the resolved and the unresolved flow scales is incorporated in the LES simulations. Although this technique is slightly more computationally demanding, we believe that this model is physically more correct than a model based on estimating the local shear rate from $\sqrt{\varepsilon/\nu}$ only.

One of the major assumptions in our approach is that the agglomeration process is taking place at constant supersaturation, i.e. in a chemostatic environment. The reason for this is that no kinetic relation is available for β_0 as a function of shear rate *and* local supersaturation. In batch-type experimental work, the supersaturation usually decreases in time. As a consequence, the differences in agglomeration behaviour of the different flow systems as observed in our simulations may become stronger if the effect of the time evolution of the supersaturation is taken into account.

Some numerical issues regarding the results presented are worth mentioning. The total simulation time for this paper was about 1 CPU year. To obtain real grid independence, computational domains of 180^3 or larger are needed, which would mean an increase of at least a factor of 5 for computational resources. This was not feasible at this stage.

The results in this paper do show, however, that the agglomeration mechanism is very sensitive to small-scale flow phenomena and that high-resolution simulations are therefore necessary. Increasing the numerical resolution would decrease the SGS model contribution and therefore give better results. Higher resolutions would also allow for a more detailed description of the impeller geometry. The method does give insight in the trends in reactor performance, however. It is the authors' opinion that these type of simulations may contribute to better reactor design in the near future.

Nomenclature

d	particle diameter, m
D	impeller diameter, m
m_0	zeroth moment of PSD, m^{-3}
m_{00}	initial value of m_0, m^{-3}
N	impeller rotational speed, rev s^{-1}
t	time, s
β_c, β_0	collision, agglomeration kernel, m^3 s^{-1}
$\hat{\beta}_0$	observed agglomeration kernel, m^3 s^{-1}
ε	turbulent energy dissipation rate, m^2 s^{-3}
$\dot{\gamma}$	shear rate, s^{-1}
ν	kinematic viscosity, m^2 s^{-1}
CFD	computational fluid dynamics
GS	grid scale
LES	large eddy simulations
PBT	pitched blade turbine
Po	power number
PSD	particle size distribution
Re	Reynolds number
RT	Rushton turbine
SGS	subgrid scale

References

[1] H.S. Mumtaz, M.J. Hounslow, N.A. Seaton, W.R. Paterson, Trans. Inst. Chem. Eng. 75 (1997) 152–159.
[2] M. von Smoluchowski, Z. Phys. Chem. 92 (1917) 156.
[3] J.J. Derksen, H.E.A. Van den Akker, AIChE J. 45 (1999) 209–221.
[4] E.D. Hollander, J.J. Derksen, O.S.L. Bruinsma, G.M. van Rosmalen, H.E.A. van den Akker, Proceedings of the 10th European Conference on Mixing, 2000, p. 221.
[5] E.D. Hollander, J.J. Derksen, O.S.L. Bruinsma, G.M. van Rosmalen, H.E.A. van den Akker, Chem. Eng. Sci. 56 (2001) 2531–2541.
[6] E.D. Hollander, J.J. Derksen, L.M. Portela, H.E.A. van den Akker, AIChE J. 47 (2001) 2425–2440.
[7] J. Smagorinsky, Mon. Weather Rev. 91 (1963) 99–164.
[8] R. Mei, K.C. Hu, J. Fluid Mech. 391 (1999) 67–89.
[9] M. Van Leeuwen, Precipitation and mixing, PhD thesis, Delft University of Technology, 1998.