Ninth International Conference on CFD in the Minerals and Process Industries
CSIRO, Melbourne, Australia
10-12 December 2012

STUDY OF THE DISPERSED PHASE BEHAVIOR IN A PULSED COLUMN FOR OXALATE PRECIPITATION IN AN EMULSION

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ABSTRACT

An original process of continuous precipitation in emulsion in a pulsed column is under study. A thorough understanding of the behaviour of the droplets inside the column helps to achieve process optimization and is the purpose of this paper. Two approaches are undertaken with this aim. The Lagrangian one allowed us to measure experimentally the residence time distribution of the droplets inside the column and then to simulate their trajectories using a CFD code ANSYS-Fluent®. The simulation results according to this model were in good agreement with the experiments. An Eulerian approach, on the other hand, will allow us to account for the droplets population evolution with the occurrence of coalescence and breakage phenomenon. This approach was firstly undertaken on a test case, in order to identify the problem issues and specific requirements, before implementing the Population Balance Equation and CFD coupling to our own system. The model details and first results are discussed.

NOMENCLATURE

ρ relative density
μ dynamic viscosity
σ Interfacial tension
k kinetic energy
ε turbulence dissipation
A pulsation amplitude
F pulsation frequency

INTRODUCTION

An alternative to the current method of reprocessing spent nuclear fuel would be to co-extract the actinides then to co-precipitate them in a single step. With this aim, we are studying a new process based on continuous oxalic precipitation in emulsion using a pulsed column. The novelty of this process, for which the feasibility has already been demonstrated (Borda *et al*., 2011), lies in the containment of the reagents in drops of aqueous phase dispersed in an inert continuous organic phase (figure 1). The precipitation occurs inside the aqueous drops after they coalesce. The pulsed column is used as a liquid contactor. The process has therefore the double advantage of: *i)* implementing a well-known technology of the nuclear industry, and *ii)* ensuring the confinement of the sticky precipitates by the inert organic diluent (Tetrapropylene Hydrogen, TPH).

A thorough understanding of the precipitation mechanisms and their interactions with the particular hydrodynamic conditions prevailing around the liquid drops in the apparatus is essential for process optimization. In this context, modeling and numerical simulation are powerful tools complementary to the experiments in order to study both the dispersed liquid phase behavior within the pulsed column (*i.e.* drops residence times and collision frequency) and the mixing of the reactants within the drops.

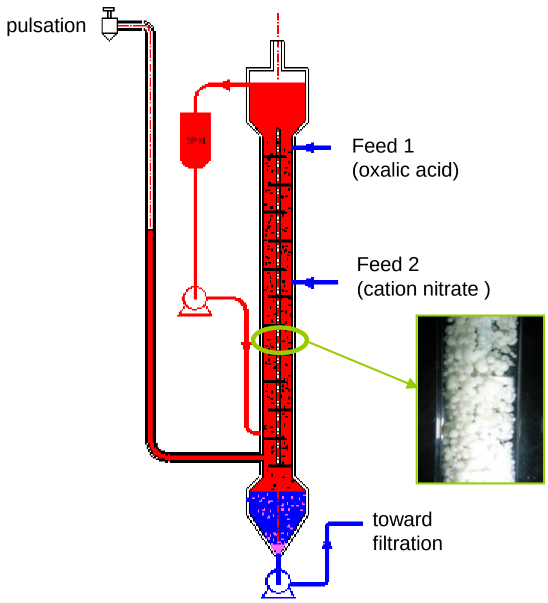

Figure 1: Cerium oxalate precipitation in pulsed column. Sketch of the pulsed column (left) and photo of the solid phase enclosed in aqueous drops (right).

Modelling of a disc and doughnut pulsed column: state of the art

Different experimental and numerical studies have been conducted to comprehend the monophasic flow in a disc and doughnut pulsed column. Experimental studies by Laulan (1981), Oh (1983) and Buratti (1988) were focused on the velocity field inside the column using different experimental techniques under a certain range of

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experimental conditions. Those studies demonstrated a spatial periodic behavior of the flow inside the column and an axial symmetry. Angelov *et al.* (1990) have confirmed those results. They have demonstrated that the whole flow inside the column could be represented by one compartment (disc-doughnut-disc or doughnut-disc-doughnut), showing that the flow is independent from the boundary conditions. Oh (1983), Angelov (1990) and Legarrec (1993), in their numerical studies, have assessed the influence of the pulsation frequency and amplitude and the geometric parameters on the flow. Aoun Nabli (1995) has firstly validated the *k-ε* standard turbulence model on stationary flow *(i.e.* without accounting for the pulsation) by comparing his simulation results with the drop pressure measurements performed by Leroy (1991). He then studied the pulsed flow by comparing his simulation results with the axial dispersion coefficient measured by Oh (1983) and Buratti (1988). Aoun Nabli (1995) has proposed a numerical correlation for the most important parameters of the flow based on the *k-ε* standard turbulence model (pressure drop, axial dispersion coefficient, turbulent dissipation…). More recently, Bujalski et al (2006) have measured the velocity field inside the column by the PIV and LDV techniques. They compared their results with simulations conducted with the low Re *k- ε* turbulence model. The influence of the gap between the doughnut and the column wall was discussed as well.

The biphasic flow was also studied, mostly in a Lagrangian approach. Bardin-Monnier (1998) has studied droplets trajectories using a video technique. The author has compared her numerical results with the experimental ones. The influence of important flow parameters and different forces on the calculation of the droplets residence times was discussed. A population balance approach was used by some authors to study the behavior of the dispersed phase in the column (Casamatta (1980), Dimitrova *et al.* (1988)).

While they have been conducted under flow conditions (pulsation frequency and amplitude) that are different from our case, the conclusions of these studies allowed us to make some general assumptions for our work. In the biphasic studies, the coalescence was neglected, although this phenomenon is essential in our application as it is the trigger of the precipitation reaction taking place inside the droplets. As a result, we are obliged to perform our own experimental measurement and numerical modeling to model our application. We have used the literature results to validate, in some cases, some components of our model.

THE PRESENT WORK

The present study is focused on the behavior of the aqueous droplets flowing in an organic continuous phase inside the column.

Experimental setup

The experimental setup (figure 2) is described in detail by Randriamanantena *et al.* (2010). The column diameter is 50mm, equipped with disc and doughnut internals. The disc diameter is 43.5mm and the doughnut diameter is 25mm. The distance between a disc and a doughnut is 25mm. The column is pneumatically pulsed and can work with frequencies ranging from 0.5 to 2 Hz. The column is jacketed to avoid optical deformations.

Residence time measurements

On one hand, the droplets residence time and velocities were determined experimentally by means of an optical approach consisting of a high speed camera (frame rate 125 Hz; resolution 728×512 pixels) combined with a backlight system (figure 2 and figure 3).

Figure 2: Experimental set-up for drop trajectory measurements

Figure 3 Example of drops visualization within the column (left) and 45° view on the mirror (right)

Aqueous droplets of various diameter (1mm ≤ dp < 4mm), colored with methylene blue, were investigated in a continuous organic phase (hydrogenated tetra propylene, TPH). The phase system properties are given in table 1. Droplets diameters reproducibility was ensured by weighing a certain number of droplets before each series of measurements. The standard deviations were found to be between 2 and 10% from the desired diameter. The residence time of the droplets was determined for at least 300 droplets for each experimental condition.

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Component	ρ	μ (Pa.s)	σ (N.m^{-1})
TPH	0.76	1.26 10^{-3}	43 10^{-3}
Water + Methylene blue	1	10^{-3}	

Table 1: Phase system physical properties

Different pulsation intensities, which is defined as the product of the pulsation amplitude and frequency $A \times f$, were also studied (1cm/s, 2 cm/s). The separate effect of pulsation amplitude and frequency was also assessed.
The experimental results were found to be in agreement with previously published results (Bardin-Monnier, 1998), showing a decrease of the droplet residence time with the pulsation intensity, $A \times f$, and the droplet diameter as illustrated on figures 4 and 5. We have also demonstrated that the frequency and amplitude of pulsation have a separate effect on the mean residence time, this point being not considered in the previous studies.

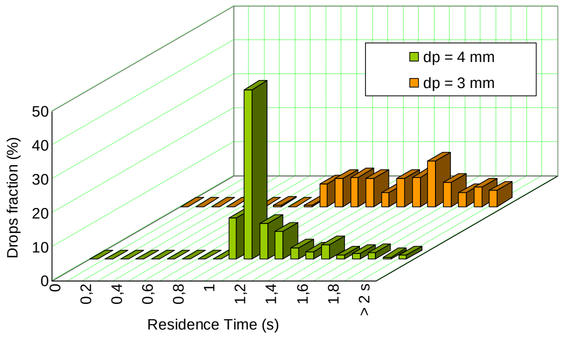

Figure 4 Measured residence time distribution in a compartment for 3 and 4 mm drop diameter (A × f = 1.3 cm/s)

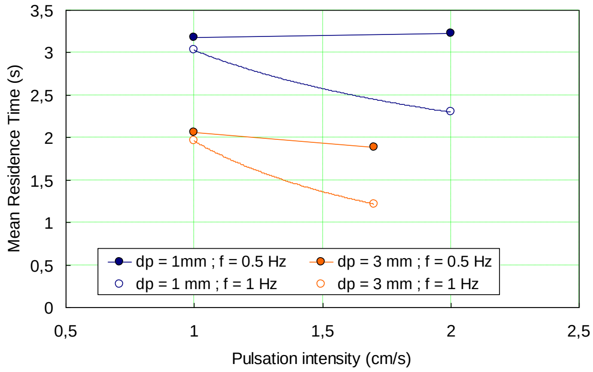

Figure 5 Mean residence time evolution with the drop diameter (1 - 3 mm) and the pulse frequency (0.5 - 1 Hz).

Modeling: Lagrangian approach

This experimental study was completed by a Lagrangian simulation approach using the Discret Phase Model of the commercial CFD software ANSYS-Fluent® (Fluent Inc). The model consists in the simultaneous resolution of the Navier-Stokes and continuity equations for the continuous phase, together with the force balance on the dispersed phase. The drag force, calculated in our case by the Morsi and Alexander (1972) correlation, the virtual mass force and the pressure gradient force (Fluent user's guide, 2006) were taken into account in the present study. Several turbulence models, and their influence on turbulent dispersion, were investigated: the standard k-ε model (like previous studies), the realizable k-ε model, the RNG k-ε model and the Reynolds Stress Model (RSM), provided with a more physical approach of the stress tensor.
Experimental and simulated results are compared (see Appendix A). The models yield generally good results compared with the experiments. A good qualitative agreement was achieved regarding the residence time calculation (decrease of the residence time with the pulsation intensity and the droplet diameter, separate effect of frequency and amplitude). The discrepancy from experimental results is in most cases lower than 30%, which is acceptable given the model advantages and its ease of use. The best quantitative agreement was achieved by the Reynolds Stress Model. This result can be explained by the flow anisotropy in the pulsed column (figure 6), as highlighted by our PIV measurements (*to be published*). It is known that the investigated turbulent models are based on the assumption that the flow is isotropic, except the RSM, hence its better behavior. This assumption is not satisfied every time in our case especially near the walls.

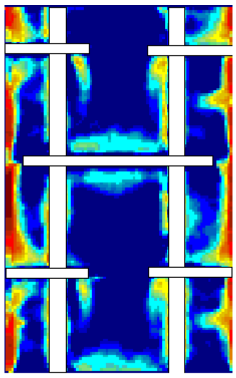

Figure 6 Flow anisotropy illustrated by the ratio of the RSM of the velocity in the two directions (from PIV measurement at A = 2cm, f = 1 Hz ; the ratio is normalized by the maximum value)

Modeling: Eulerian approach coupling CFD and PBE

Next, an Eulerian modeling approach is currently developed to investigate the behavior of the dispersed liquid phase. This study is mainly based on the experimental results published by Jahya *et al (*2009). The problem is treated in an axisymmetric way, the flow of the continuous phase was calculated first until convergence, and the dispersed phase was then injected as a source term (figure 7). The mean diameter was assessed and compared with experimental results after convergence.

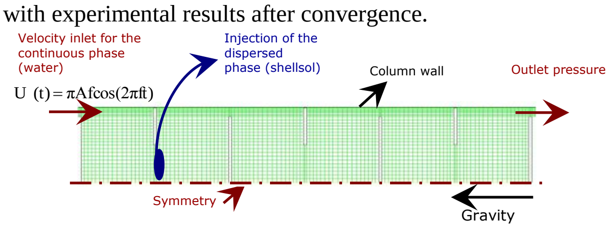

Figure 7 Mesh for the Jahya et al (2009) test case. The mesh is 2000 nodes, treated as axisymmetric flow

Two methods, both available in the software, were used to model the PBE: the Discret Method (or Classes Method, CM) proposed by Ramkrishna (2000) and the Quadrature

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Method of Moments (QMOM). Different models of breakage and coalescence kernels were implemented as User Defined Functions in the code.

Mesh convergence was examined first for the Classes Method; a number of at least 22 classes appeared to be necessary to achieve independence. For the QMOM model, 6 moments were chosen, in agreement with Marchisio et al. (2003) recommendations.

Unfortunately, regarding the mean drop diameter in the column, both methods gave results far from the experimental ones, as illustrated in figure 8. The observed discrepancy from the experimental results is probably due to the uncertainty on the breakage and coalescence kernels, whose constants need to be fitted to the considered phase system. Moreover, the calculation of the turbulent dissipation, which is a key parameter in the PBE, may be poor due to the turbulence model used in this case (the *k-ε* standard model). The dispersed phase influence on the flow, which has been neglected in the simulation, might also contribute to the error.

Further work on the model is currently conducted, decomposing the problem to have a separate description of the turbulence and the PBE. The QMOM method, which is less CPU consuming, has been retained for the rest of the study since the discrepancy between the two methods is not significant. Our relevant phase system, described in table 1, is considered in this aim, for which a set of experiments carried on in a stirred-tank reactor is in progress in order to identify the coalescence and breakup kernels. Details of the techniques and experimental setup can be found in Becker *et al* (2011).

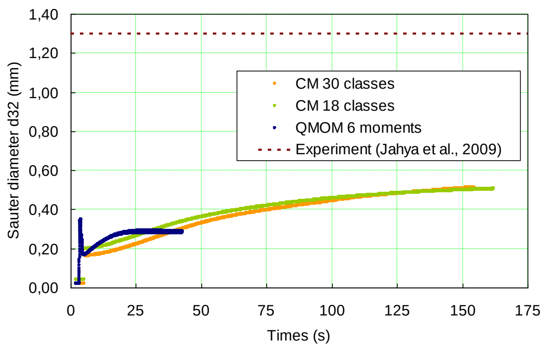

Figure 8 Sauter diameter prediction: comparison of the CM and DQMOM method.

Future work will include PBE simulations validated on experimental droplets size distribution and Sauter diameter measurements.

Discussion on the continuous phase flow

The continuous phase flow-field was validated by PIV experiments. These experiments were focused on the validation of turbulence dissipation for accurate modeling purpose. The experimental setup is the same as in figure 1 except that a Lavision® PIV system is used. It includes a pair of Nd:YAG lasers, an sCMOS camera and a synchronizer (Programmable Time Unit, PTU).

For the single phase system, the TPH was seeded with hollow glass spheres of 10µm diameter and 1100kg/m^3 density. In two-phase flow experiments, TPH is still used as the continuous phase and a water/glycerin mixture is used as the dispersed phase for refractive index matching (Augier *et al*, 2003).

Because the flow is transient (although periodic), phase averaged velocity field were derived, for each experiment from at least 300 pairs of frames taken at the same instant of the pulsation.

The PIV results will be presented in a shortcoming paper. An example of monophasic result is given in figure 6.

CONCLUSION

One of the challenges of the optimization of the precipitation process in emulsion in a pulsed column is to understand the behavior of the dispersed phase inside the column. Different approaches were undertaken in this aim. The Lagrangian approach gives us useful information about the trajectories of the droplets and their residence time. The Eulerian approach helps us to discuss the validity of the *k-ε* turbulence model to model the continuous phase behavior, and to adjust different breakup and coalescence kernels on our system. The CFD-PBE coupling allows us to have a better knowledge of the droplet size distribution inside the column. All this information is essential as the precipitation reaction takes place inside the droplets. These data are indeed used in the droplets scale simulations (Charton et al., 2012), where chemistry (precipitation reaction) is considered together with hydrodynamics.

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APPENDIX A

dp	*f* (Hz)	A (cm)	Mean Residence Time (Measure)	Relative deviation between measured and calculated value			
				k-ε	k-ε RNG	k-ε Real.	RSM
3 mm	1	1	1.96	+ 30 %	+ 32 %	-	+ 4 %
		1.7	1.22	+ 4 %	-	-	- 8 %
	0.5	2	2.06	+ 42 %	+ 19 %	-	+ 8 %
		3	1.89	- 8 %	-	-	- 17 %
2 mm	1	1	3.25	- 10 %	- 14 %	- 19 %	- 14 %
		2	1.02	+ 34 %	+ 31 %	+ 26 %	+ 17 %
	0.5	2	2.97	+ 5 %	+11 %	+ 2 %	+5 %
		4	1.49	- 13 %	- 8 %	- 23 %	-
1	1	1	3.03	- 2 %	- 3 %	-	- 6 %
	0.5	2	3.18	+ 23 %	+ 10 %	-	+ 8 %

Table 2: Comparison of measured (at least 300 drops per case) and calculated (at least 3000 drops per case) mean drop residence time for various drop diameter (1-3mm), pulsation amplitude (1-4cm) and frequency (0.1-1Hz).

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