Case Study 5: Intensification of Chemical Processing Involving Solid Reagents

Case study host:

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Brief description of process unit(s) of interest for intensification and motivation:

Scale reduction is a key aspect of process intensification. The benefits can be related to enhanced performance of small equipment or more efficient use of space and is usually a combination of the two. The productive operating times of large batch reactors is generally less than 10%. A typical batch plant uses 10 to 20 batch reactors of different sizes to cope with variations in working volume requirements. A 10-litre flow reactor by comparison, can process 480 litres in a 24 hour cycle for a 30 minute reaction. The same reactor can also process from 1,000 or 100,000 litres in a single operating cycle depending on the number of reactors used in parallel. This efficiency means that 4 or 5 flow reactors of a single size can replace 10 or 20 large batch reactors of different sizes, which delivers substantial reductions in capital expenditure and operating costs. Given the significant advantages of flow reactors, there are strong drivers for industrial process intensification of flow systems. However, traditional (single-tube) plug-flow reactors have a critical downside, being the small residence time distributions for reactions requiring fast turbulent flows for good mixing. This limitation is particularly true for reactions involving solids, as plug flow reactors generally do not have the capacity to pump at speeds to keep solids suspended, leading to sedimentation and fouling at inlets/outlets.

Brief description of PI technology chosen:

The AMT *Coflore ATR* reactor (http://www.amtechuk.com/pilot-and-plant-scale-atr/), shown in Figure 1, is an agitated tubular reactor that provides a novel solution to the issue of mixing dynamics in plug-flow to enhance residence times. This solution decouples the plug flow and mixing from bulk flow, giving the ability to handle gases, liquids and solids: the *ATR* consists of a pneumatically driven main body that contains a number of reaction tubes into each of which a smaller, free-moving, perforated agitator tube (with plastic end-caps to minimise friction) is inserted. The lateral driving motion applied to the system results in efficient mechanical mixing, even in cases of slow bulk flow (leading to long resistance times and faster reaction kinetics). In this case study, the *ATR* is demonstrated as a novel intensified plug-flow reactor, suitable for a variety of solid-liquid chemical processing operations, with focus on intensification of solids catalysed chemical reactions. AMT's interest is strongly focussed towards more efficient use of equipment with improved performance as an added benefit.

In this case study, a 1 L pilot scale AMT *Coflore ATR* reactor is characterised, to better understand the mechanical motion and hydrodynamics, enabling optimisation of the reactor to conduct solids catalysed liquid chemical reactions. The associated Deliverable reports detail work that has been

undertaken to commission and demonstrate the ATR reactor at the University of Leeds. It includes analysis of the reactor movement frequency versus amplitude relationships for different pneumatic drive pressures, using a laser displacement device, as well as the characterisation of the relative movement of the inner agitator in relation to the outer reactor tube, using high-speed video-image analysis. An ultrasonic velocity profiler (UVP) is used to provide velocity profiles of the fluid across the diameter of the outer (*i.e.* driven) tube, which is, to the authors knowledge, the first time such as system has been used to measure the complex flow patterns of such a complex process-intensified tube reactor. Physical characterisation is coupled with computational fluid dynamics (CFD) simulations of the full-scale ATR system, to provide a more complete understanding of the mixing hydrodynamics and mixing energy for different oscillation frequencies. Additionally, the influence micro-mixing and turbulence regimes on particle suspension is modelled using direct numerical simulation (DNS).

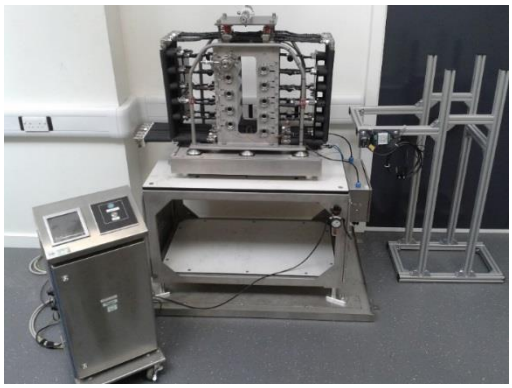
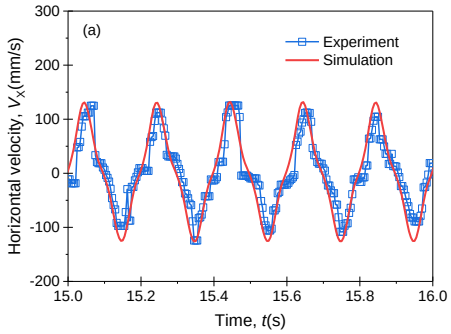
(a)  (b) 

Figure 1: (a) *ATR* in place at UNIVLEEDS, July 2017, without full diagnostic set-up. Laser displacement device shown on right of picture; (b) rendered image of the design of a perforated inner agitator tube used in experiments.

Brief summary of results:

A regime map of the motion of the agitator was derived using data from the laser displacement device in order to determine the optimal operating conditions. On the basis of the regime map, three test cases (in terms of applied pneumatic pressure, p, and therefore amplitude of motion, a, and agitation frequency, f) were chosen for more detailed experimental and computational investigation: (1, base) f = 5.00 Hz, a = 12.5; (2) f = 4.07 Hz, a 10.2 mm; and (3) f = 3.13 Hz, a = 11.2 mm. Selected results for one test case are shown in Figure 2 and Figure 3. Here, it is evident from Fig. 2, that CFD simulation and direct visualisation of the relative agitator motions are directly comparable, while measurements of the RMS of velocity (associated with turbulence modulation) with the UVP also correlated closely.

(a) 

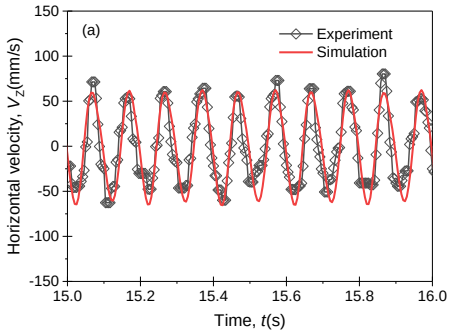
(b) 

Figure 2: Comparison between experimental video analysis and CFD simulation - relative velocity of ATR motion of internal agitator: (a) horizontal velocity, and (b) vertical velocity under shaking condition of Case 1 (*f* = 5 Hz, *A* = 12.5 mm).

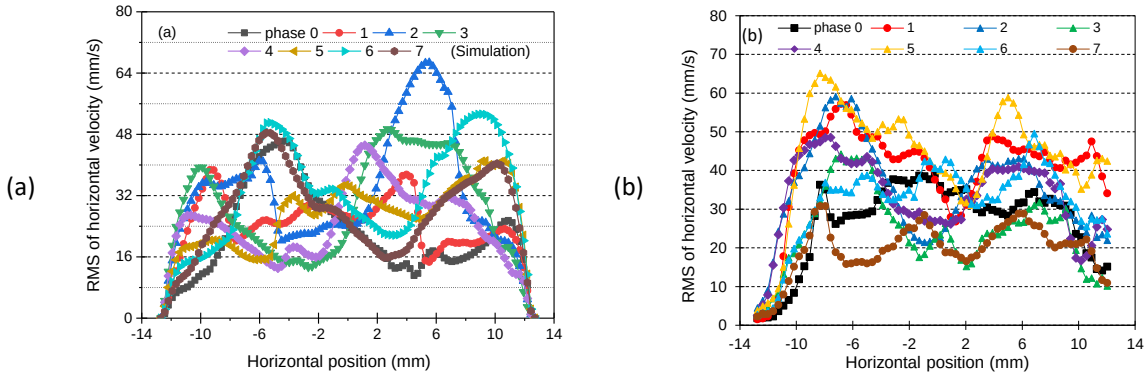


Figure 3: Phase-resolved RMS of horizontal (radial) fluid velocity under condition of Case 1 (*f* = 5 Hz). (a) CFD simulation, (b) experimental results via UVP.

Flow-field maps and power consumption calculations from the numerical model were also prepared for each of the three cases and are available in Deliverable report D6.3, but are not shown here for concision. The process-scale CFD predictions of particle mixing and sedimentation were also compared against direct numerical simulations of a simplified system with similar relative turbulence levels. Work additionally included understanding process chemistry kinetics and yield variation for a model solids catalysed reaction at various oscillation frequencies versus batch reactor results. Finally, a larger industrial scale unit (2x geometric size of the pilot-rig) was demonstrated at AMT (reported in D6.4) with process chemistry results compared to the pilot rig.

Final conclusions from case-study:

The motion of an agitated tube reactor (ATR) rig has undergone intensive experimental and numerical characterisation by varying its motion over a range of parameters. The goal was to characterise the basic dynamics of the internal agitator with and without solid particles, using a laser displacement device, high-speed video and an ultrasonic velocity profiler (UVP) for three test cases ($f \approx 3 - 5$ Hz). The experimental data was compared to computational fluids dynamics (CFD) simulations of the *ATR* motion under the same operating parameters (frequency and displacement). There was very good agreement between simulation and experiment, in terms of agitator dynamics and fluids velocity field, demonstrating the numerical model can accurately predict the system: the velocity profiles and associated RMS through the reactor were determined, highlighting the complex coupling of the agitator and fluid, indicating areas of relatively low mixing in the centre and upper segments of the reactor. The CFD simulation was then used to calculate the power dissipation per unit volume, suggesting the 5 Hz case was the most effective for particle dispersion. Initial testing of the ATR with catalyst loading between 0.1 – 1 wt%, showed the solids did not cause measureable changes in reactor movement or fluid velocities. A phenomenological model – to be confirmed with numerical and experimental results – suggests that there is a critical frequency below where the power input is negligible. Above the critical agitation frequency, the power per unit volume varies as f^3a^2. Finally, the influence of turbulence on particle dispersion was correlated to direct numerical simulations (DNS) of particles suspended in a turbulence 'bomb', wherein turbulence levels correlating to those in the

reactor are generated without any bulk fluid motion. In all simulations over a particle-size range of 5 – 500 µm, particles > 10 µm were observed to sediment to some degree, suggesting that there may be dispersion issues within the ATR for larger catalyst particles. However, there were also clear differences to particle transport in a DNS of a channel flow used for comparison, and as there was no direct experimental evidence for catalyst sedimentation, it may be inferred that the DNS did not fully capture the micro-scale hydrodynamics of the ATR's oscillatory motion

Yields and reaction kinetics of a model solids-catalysed reaction (oxidation of benzyl alcohol catalysed palladium-impregnated carbon particles) were determined in the batch-tests, and compared to results in the ATR from the same reaction. There was no evidence of catalyst particle hold-up in the reactor, when tested at the highest frequency test case (5 Hz). Both the 1 L and pilot-scale 10 L ATRs attained, at least, similar yields over time to the small batch tests, however with much lower power per unit volume consumption (see discussion below). However, when the relative flows of generated gas were taken into consideration in terms of average reactor residence times, ATR reactor performance was considerably greater than the corresponding batch results.

TRL of PI Technology:

Technology Readiness Level (TRL) of the pilot-scale Coflore reactor at beginning of the study was estimated at ~5. TRL at the completion of the study, including knowledge gained form the full hydrodynamic and chemical characterisation of the reactor for solids catalysed reactions, as well as the scale up studies, is estimated to be 7. We are confident that the reactor will reach production.

Using calculations established from the model solids catalysed reaction process, an estimation of the cost and environmental savings were completed, by comparing the ATR against regular batch mixers on a per volume basis. These estimates are based on calculations performed to generate energy savings case for a comparable Coflore® device. The table below lists the headline percentage saving in each category. For example, considering the mechanical power consumption from the batch reactor trials, in comparison to estimates from the ATR (using a combination of measured and simulated parameters) on a per volume basis, the ATR is estimated to achieve an 80% reduction in power. An independent calculation of the electrical power saving (based on estimated savings from stirrers and vacuum pumps) estimated a similar figure of a 64% reduction, with overall process energy savings of >90%. These figures are very impressive and highlight the potential of the ATR as an intensified chemical reactor system, within a wide variety of industries.

	Estimated % saving per unit production volume	Basis
Overall Energy Savings	91%	Estimated on a cost per tonne basis for a typically sized production plant.
Solvent Consumption	50%	3000 litres solvent per tonne of product is used in batch. In flow this is reduced to 1500 litres due to improved reaction control.
Excess Reactant Consumption	55%	Assumes a 90% yield in batch and a 95% yield in flow due to improved heat transfer, mixing, and residence time control.
Space Reduction	67%	Estimated 3 times more productive per unit volume.
Mechanical Power saving	80%	Based on scale-up estimates of p/v from completed batch versus ATR experiments.
Electrical Power Savings	64%	Based on estimated savings from stirrers, vacuum pumps and HVAC.
Heating and Cooling Power Savings (Brine and Steam)	75%	Large portion of heating and cooling load for batch equipment is negated by using continuous flow equipment.

Solvent Emissions	100%	At the end of a batch cycle, saturated vapour is typically purged to atmosphere. This is not necessary for flow equipment.

Estimates for energy consumption in a typical mid-size batch plant are taken from the following: Bieler, P.S., Fischer, U, & Hungerbuhler, K. 2003. Modelling the Energy Consumption of Chemical Batch Plants – Top Down Approach. *Industrial & Engineering Chemistry Research*. 42. 6135-6144; Bieler, P.S., Fischer, U, & Hungerbuhler, K. 2004. Modelling the Energy Consumption of Chemical Batch Plants: Bottom-Up Approach. *Industrial & Engineering Chemistry Research*. 43. 7785-7795