

Dispersion in Flow Reactors

This article explores the issue of axial dispersion in homogeneous flow reactors.

The Simple Tube Reactor

There are many different kinds of flow reactors but one of the simplest is the tube reactor. This usually consists of a long length of small bore tubing, often coiled to save space and to facilitate heat exchange. It can be made of a range of materials including fluoropolymers (which may offer transparency as well as wide solvent resistance), stainless steel (for higher temperatures) or other metals (e.g. copper) for catalysing reactions.

Tube reactors are relatively inexpensive and have a high surface area to volume ratio giving excellent heat transfer provided that the tube is suitably coupled to the heat source/sink. A long tube enables a reaction with a long residence time to be cost effectively handled in flow.

Dispersion

There is, however, the issue of axial dispersion. This is caused by the tendency of long smooth lengths of tubing to develop laminar flow.

This causes a issue because it means that some of the fluid takes longer to travel through the reactor than the rest.

There are two implications of this:

End Effects

When a flow reactor is used to process a finite "slug" of reagents, the leading and trailing ends of the slug of product emerging from the end of the reactor will have mixed to some extent with the fluid (usually system solvent) that preceded or followed it. This means that there is a zone at the leading and trailing ends of the emerging slug of reaction products in which the concentration of products is variable, and a steady state portion between these zones in which the concentration is as required. Users will normally prefer to capture this "steady state" portion of the output separately.

Figuring out exactly where the steady state region of the slug can be found is not a trivial exercise.





For one thing, two reactions in the same reactor setup will exhibit different amounts of dispersion if the reactor residence time (and hence flow rate) is different. (higher flow velocity = more dispersion).

So an unsuspecting user might incorrectly conclude that a reaction performed at the higher flow (i.e. lower residence time) gave worse results because he/she unwittingly collected some of the variable concentration end zones in the higher flow rate scenario, (simply by not realising these zones would be bigger at higher flow rates).

Fortunately, Vapourtec's Flow Commander[™] software features a tool for predicting in a given flow situation what the dispersion will be, allowing the user to automatically collect the steady state portion of the output. The algorithm calculates this for each and every reaction separately, taking into account all the tubing that makes up the system flow path, and factoring in the flow velocity.



(Interestingly, although dispersion increases with velocity and hence flow rate, **very** high flow rates cause a shift from laminar to turbulent flow at which point dispersion decreases significantly. Unfortunately the flow rates required for this transition in a typical straight tube reactor are significantly above the likely operating values.)

Residence Time Distribution (RTD)

The second implication of the dispersion effect is that even within the steady state zone of emerging reaction products, there will be some distribution of residence times. That is, a proportion of the reaction products emerging will have moved more slowly and hence experienced a longer residence time than the rest.

The same is of course true at larger scale (in continuous flow manufacturing, for example).



Minimising Dispersion

The first thing to note is that there is a trade-off between flow rate and dispersion.

So if a user is faced with two scenarios for testing a 5 minute residence time reaction:

- flow at 2mls / minute through a 10ml reactor

- flow at 0.2mls / minute through a 1ml reactor of the same cross section then the latter scenario has a much lower flow velocity and so produces less dispersion, but takes longer to achieve the same amount of output. A choice can therefore be made depending on overall requirements.

Secondly, there are certain things which can be done to address dispersion. There has been much research over the last decade, for example, on the subject of disrupting laminar flow in tube reactors, both for reducing dispersion and improving mixing and/or heat transfer.¹

Though some of this work focuses on ensuring all fluids make regular contact with the reactor wall (important for heat transfer in larger bore tubes) much of it is of potentially interest to the meso-scale flow chemistry user.

One simple, yet promising, technology is the "knitted tube" reactor.

This consists of a tube with almost continuous small radius bends, yet a compact overall structure. By forcing the flow to negotiate these bends, turbulent flow can be created at far lower flow rates than in a smooth straight tube, (flow rates that lie well within the working range of a meso scale flow chemistry system).

A knitted tube reactor

As the flow rate increases, turbulent flow becomes more dominant and dispersion (measured online by UV)

can be shown to be markedly reduced, resulting in more efficient use of reagents and smaller minimum reaction volumes.

The data shown overleaf illustrates this.



Analysis of "Knitted" reactor tubing

In this fairly straightforward analysis, a 0.75ml sample injection loop made of knitted tubing has been compared with an otherwise identical sample loop made of conventional plain tubing. Each sample loop is preloaded with reagent, which is then driven out by a flow of solvent.

A UV sensor is located immediately on exit from the sample loop.

Each of the three graphs shown (right) show UV reading plotted against amount flowed. Three different flow rates are shown. In each case the knitted tube result is shown in red.

Note that at the left hand side of each of the graphs, no dispersion is shown, as the leading edge of the slug has travelled no distance through the tubing when it passes the UV sensor. At the tail end of the slug, however, the full effect of the axial dispersion can be seen, as the reagent/solvent interface has travelled all the way through the loop. If the tubing had been used as an actual tube reactor in this analysis, similar dispersion would be present at both ends of each graph.

It can be seen that as flow rate increases, the effect of dispersion in the plain tubing increases, but that the knitted tube reactor (which at this range of flow rates exhibits turbulent flow) shows significantly less dispersion.

Note also that what little dispersion there is in the knitted reactor is almost flow independent.







Practicalities

Conducting heat in and out of such an intricate "three dimensional" reactor is easier on the Vapourtec system than some, due to the unique gas heating & cooling system used by the R Series.

Work on the knitted reactors is still ongoing, but these preliminary results show that there is plenty of potential for reducing dispersion and hence the minimum size of sample that can be realistically processed.

Avoiding Dispersion Completely

There are situations where such dispersion does not pose a problem. One is with **biphasic** reactions, where immiscible slugs of fluid alternate along the reactor tube. 2

Another is **plug flow**. With plug flow, the "slug" of reaction mixture is trapped between leading and trailing slugs of some immiscible substance. The slug stays self contained for its entire journey through the reactor.

When the slug exits the reactor, only a very small amount of reaction mixture needs to be discarded (based on the accuracy with which the system can determine the location of the "good" slug, and potentially independent of the distance travelled through the reactor), to ensure none of the immiscible phase is captured in error.

Plug flow can reduce the smallest viable reaction volume in a given system to very small amounts but requires a certain amount of system complexity to first encapsulate the plug at the start and then to accurately "extract" it.

Of course, there will still potentially be RTD within the plug, but this is limited by to the size of the plug. The fractional variation in residence time cannot exceed (plug volume / reactor volume), so if the plug is small compared with the length of the reactor, the RTD will be small.

It is worth bearing in mind that the phenomenon of dispersion (and RTD) is well known in modern continuous flow manufacturing. This means that an application developed at small scale with plug flow (and hence almost no dispersion) might be difficult to faithfully duplicate in truly continuous equipment when scaleup is required.

References

- 1. Cambridge University Chemical Engineering Department http://www.ceb.cam.ac.uk/pages/oscillatory-flow-mixing.html
- 2. July Vapourtec Newsletter http://www.vapourtec.co.uk/newsletter/archive/jul09