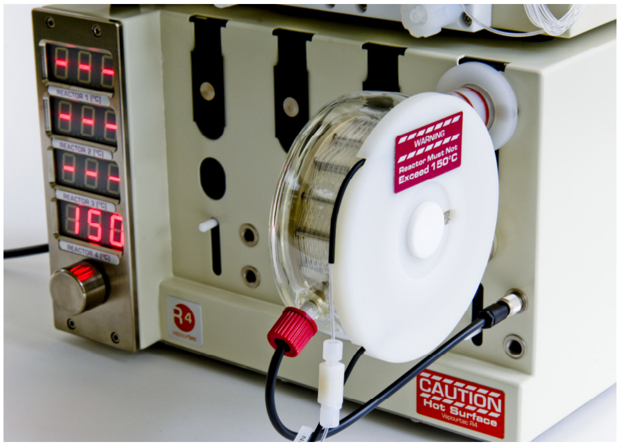
How to Safely Quantify a Reaction Exotherm



Vapourtec forced convection heated/cooled reactor manifold.

One of the well publicised benefits of Flow Chemistry is the high available surface area and the superior heat transfer.

This is particularly important with an exothermic reaction which might run away if not tightly controlled. Indeed much published work has demonstrated the utility of flow for reactions which would be unsafe at scale in batch. [1]

Here the process of safely exploring (and even *quantifying*) reaction exotherms in a Vapourtec system is explained.

Heating and Cooling – How the Vapourtec system works

Before explaining how to quantify an exotherm, it is worth a recap on how the system works.

The Vapourtec R Series controls reaction temperature using a unique “forced convection” principle. Air is continuously fed around the reactor, and in an “above ambient” reactor, this air is either heated or at ambient temperature as required to maintain target temperature.

The amount of heat supplied to the incoming air is digitally controlled and, with the FlowCommander software, an instantaneous power consumption figure can be observed (and charted and logged) for each of up to 4 reactors.

Unlike some other systems in use (which include a solid heated metal mandrel), the Vapourtec system has

- very low thermal inertia and
- the ability to remove heat at a high rate as well as being able to put heat in

Low thermal inertia is quite apparent when (for example) flow rate is changed. The power consumption of a heated reactor is made up of i) that required to rapidly heat incoming fluid to target temperature, and ii) that lost to the outside world. When the flow rate is increased, the first of these two components makes a step change upwards. So responsive is the Vapourtec control algorithm, that the power consumption can be seen to increase almost instantly, while the actual reactor temperature changes transiently by less than a degree.

The ability to remove heat at a high rate can be demonstrated by the rate at which a reactor cools. The Vapourtec high temperature reactor cools from 250°C to 60°C in 7 minutes, whereas in a comparative test a “heated mandrel” design took approx 50 minutes.

Why is low inertia and fast heat removal important ?

If a flow chemistry system has insufficient rate of heat removal to contain an exothermic reaction, but the reactor system has a very high thermal inertia, it may not be apparent immediately that the system is not “coping”. It may be left running unattended, and the reactor temperature will creep up (slowly, uncontrollably) as the excess heat is not removed and the thermal inertia of the reactor warms.
And this could lead to increased rate of reaction, and ultimately thermal runaway.

Hopefully the system would recognise this and shutdown†, and all that would be lost is some time and some reagents. Perhaps worse would be the situation where the system carried on running unnoticed at the wrong temperature, producing results for a setpoint other than the one intended.

† The Vapourtec system would certainly shutdown if the actual temperature rose above the target temperature, but not all systems work this way.

Because the Vapourtec system is so responsive, should there ever be an exotherm it could not control continuously, it would become apparent immediately.

Safely Exploring an Exotherm

It is a simple matter using the Vapourtec FlowCommander software to test whether a given exothermic reaction will be completely controllable by the R Series system.

(With known exothermic reactions, the **Internal Mixer**^{2} reactor manifold may be preferred. This includes a manifold which has the reagent mixing inside the temperature controlled zone, where it can be kept at target temperature even if heat is dissipated by the reaction the moment the reagents meet)

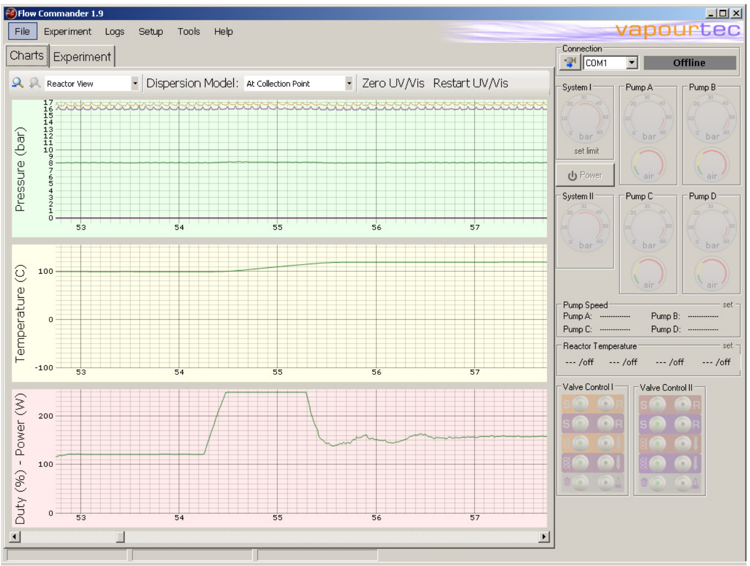
The steps are as follows:

- The reactor is equilibrated at target temperature with a representative flow of solvent.
- FlowCommander software is set to continuously display the reactor power consumption and temperature.
- The solvent/reagent selection valves are switched for a short period to allow in a small plug of reaction mixture which is much smaller than the reactor volume (ie 1ml in a 10ml reactor)
- The reactor temperature and heater power graphs in FlowCommander are watched carefully throughout the passage of the plug.
- Put simply, provided that the instantaneous heater power never drops to zero, there is still more cooling capacity available
- Repeat with a larger reagent plug.
- Moving in careful steps work up to a reaction mixture plug larger than the actual reactor volume. If the system still never drops to zero heater power then the reaction temperature can be controlled at steady state.

Quantifying the exotherm

Because the Vapourtec temperature control system is digital, a display of power consumption by the reactors is continuously available.

In this screen shot, (right) it is possible to see the power (bottom chart) vary as the temperature (centre chart) changes to a new setpoint.



So it is actually possible to quantify the extent of the steady state reaction exotherm as follows:

- run the system with pure solvent at the target rate and temperature for at least 20 minutes so that the outer surfaces of the manifold glassware stabilise at a set temperature †
- note the heater power displayed with FlowCommander (it is given in Watts)
- switch to reagents, and wait for reagents to completely fill the reactor
- wait for the heater power to stabilise at the new lower value
- again note the heater power

The power consumed by the reactor can be represented as

(Power to raise liquid temperature) + (power lost to surroundings) – (exotherm power)

The power used to raise incoming liquid from ambient to working temperature will be similar between solvent and reagent unless their specific heat capacities differ significantly (and any significant difference can be calculated from known data).

The only remaining term is the exotherm power. Given that the reagent concentration and flow rate are known, a value in joules per mole can be calculated.

†The power lost to surroundings will be the same with reagent or solvent provided that the glassware has reached a steady temperature. Hence this first step.

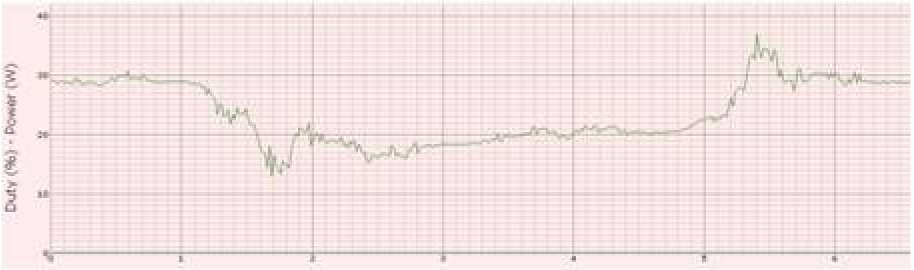
An Actual Example

During 2011 a customer's nitration reaction was carried out on a Vapourtec system using nitric acid and acetic acid. This was known to be exothermic so the reaction was initially tested by sending discrete plugs through the reactor to ensure that the heat was safely handled. When this was confirmed, a number of steady state runs were carried out to quantify the exotherm. The data below was gathered.

First the reaction was run at 1ml/min.
Power to keep the reactor at a steady temperature fell from 28 to 26W when the input stream switched from solvent to reagent, implying a 2 watt continuous exotherm.

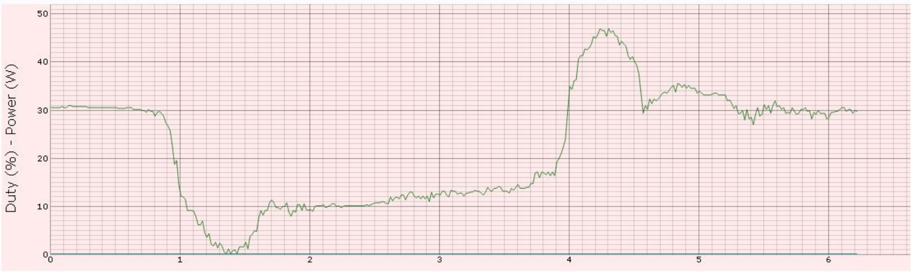
Then the reaction was run at 2ml/min.
Power to keep the reactor at a steady temperature fell from 28 to 24W when the input stream switched from solvent to reagent, implying a 4 watt continuous exotherm.

At 4ml per min, slightly more heat was being used just to heat up the solvent so the background power was 29/30W and this fell to 20W when the infeed was switched, implying 9/10W of continuous exotherm output.



The centre portion of the power plot shows the power drop when the reagent is flowing through the reactor and the exotherm is contributing to the reactor heating task

At 8ml/min, it dropped from a background of 31W with solvent to approx 10W with reagent, meaning 20W of exotherm power was being generated.



(Note that during every one of the transients shown above, the actual reactor temperature was controlled within a degree of target.)

In conclusion

It can be seen that this approach can give sufficient information for a rudimentary estimate of the magnitude of an exotherm, in a very short time and without the risk of a runaway event.

FAQ

Q When is this facility available ?

A Immediately. The display of reactor power is an existing feature of the FlowCommander software.

Q Can the same “exotherm quantification” approach be used with a cooled reactor ?

A No, although a duty cycle is displayed for the cooled reactor, it cannot be readily converted to a figure in Watts.

Q Can I use this approach to quantify the exotherm for a series of reactions carried out automatically using FlowCommander.

A Unfortunately not. To correctly contrast power consumption with solvent and power consumption with reagents, it is necessary to run for a stable period in each state. When running an automated queue of reactions, FlowCommander commences each reaction (i.e. starts feeding reagents into the reactor) as soon as stable conditions at each temperature setpoint are reached, (to maximise productivity) so hardly any data is gathered with just solvent running at exact reaction conditions.

References

1 A modular flow reactor for performing Curtius rearrangements as a continuous flow process
Marcus Baumann1, Ian R. Baxendale, Steven Ley, Nikzad Nikbin, Christopher D. Smith and Jason P. Tierney
http://dx.doi.org/10.1039/b801631n

2 The Vapourtec Internal Heated Mixer Reactor was launched in January 2011
http://www.vapourtec.co.uk/newsletter/archive/jan11