New Vapourtec Gas / Liquid Membrane Reactor

May 2011 - Vapourtec announce a new cost-effective reactor for gas/liquid reactions, offering the facility to control reaction temperature and feed in gas within the same coil tube reactor. The new reactor is fully compatible with existing Vapourtec R Series systems, and reactor heat exchangers.

Background

There has been a great deal of interest in gas/liquid reactions in flow chemistry Hazardous reactions such as carbonylations and hydrogenations are of particular interest.

Most commonly the implementation of these reactions falls into one of two categories:

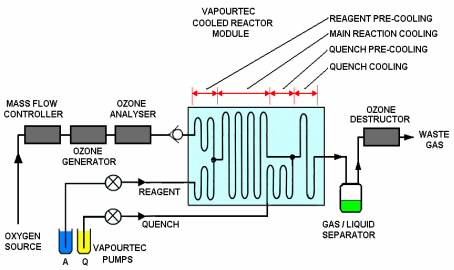
- Blending of a controlled flow rate of gas with the liquid flow
- Introduction of gas to the liquid via a membrane of some sort

Mixed Flow

The first of these can be seen in this example of Ozonolysis:

http://www.vapourtec.co.uk/datasheets/ozonolysis

In this example, *annular* flow is used (necessarily, as only 11% of the gas is actually useful ozone) but there has also been work with segmented *Taylor* flow (where alternate zones of gas and liquid are of the same order of size).



Taylor flow can be tricky to control (liquid surface tension varies significantly with temperature and the volume occupied by the gas varies with pressure) and not always easy to scale. It also requires certain auxiliary equipment (mass flow controller) and will often result in the need to dispose of a flow of gas at the end (which could be saturated with flammable solvent vapour). Automated optimisation of such reaction setups may require the integration of the auxiliary equipment with the flow system

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Membrane Reactors

Some membrane reactors involve very small machined or chemically etched holes in a metal membrane but these involve extremely precise management of the pressure difference between the gas and the liquid.

More recently, “tube within a tube” membrane reactors have become available, featuring a semi permeable tube that permits gas but not liquid to pass through. [1]

Compared with the mixed flow method, the gas management of a “tube within a tube” diffusion membrane reactor is less complex.

Instead of requiring a mass flow controller, the flow of gas can be controlled simply with pressure regulation. There is still some control involved to keep the pressure differential between the gas and liquid within a certain range, but this is fairly straightforward to manage (even manually) as a control range as broad as a few bar is all that is required.

The common way to use a membrane reactor up until now has been to use the membrane as a way of introducing dissolved gas into one reagent stream before carrying out the actual reaction. This saturated stream is then mixed with other reagents and fed into another reactor where temperature is then raised to the desirable reaction conditions and the reaction takes place.

This does, however, suffer from a significant drawback. The amount of gas that can be supplied to the reaction is limited by its solubility in the solvent, regardless of the effectiveness of the membrane. With some gases (for example H_2) the solubility in desirable solvents is low.

Carrying out the reaction within the membrane reactor addresses this but thus far control of temperature in the membrane reactor has not been available so reactions carried out within the membrane reactor have tended to be reactions that can be completed rapidly at room temperature.

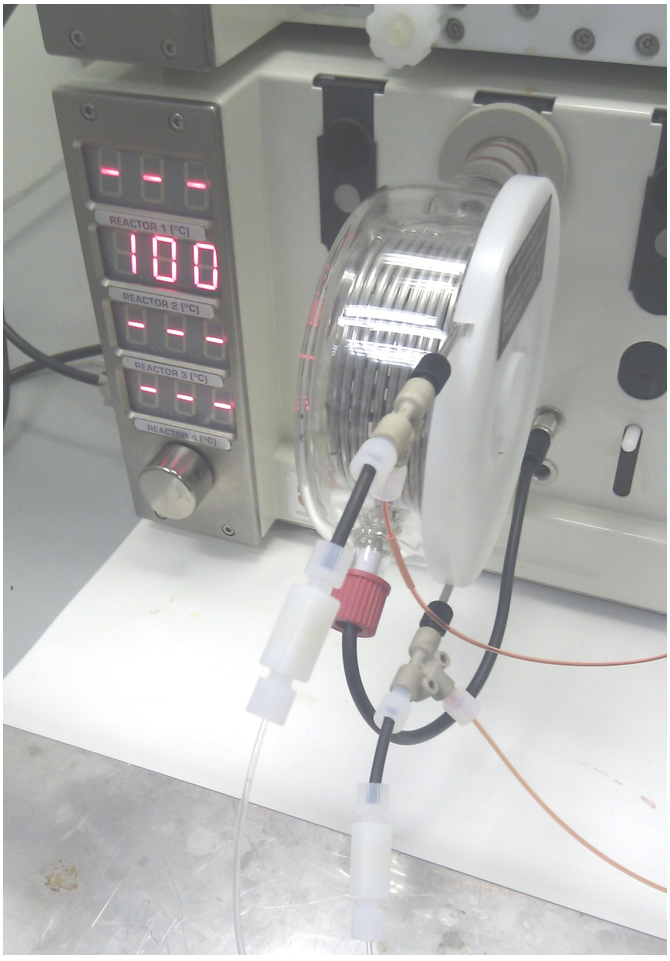
But there is now a solution.

The New Vapourtec Gas / Liquid Reactor

Vapourtec have developed a tube in tube reactor which is compatible with all existing R Series systems.

With the Vapourtec platform, all tube reactor coils are contained within an insulated glass manifold (shown, right) and the temperature is controlled by rapidly circulating gas. Coils can be changed in seconds, and up to 4 separate manifolds can be used for multiple reaction steps or increased scale.
Standard coils available include PFA (fully acid resistant) , Stainless steel (316L or Hastelloy®) for reactions up to 250°C, and copper for Cu catalysed reactions.

A standard manifold with PFA coil reactor



Vapourtec Tube in Tube Gas Reactor, shown running at 100°C

The new gas/liquid reactor fits into the standard glass manifold just like any other, so is compatible with all existing R Series systems immediately.

Liquid is fed through the coil just like any other reactor, but there is also a connection for gas which is fed at the desired pressure from a regulated supply.

The reactor can be used in two ways

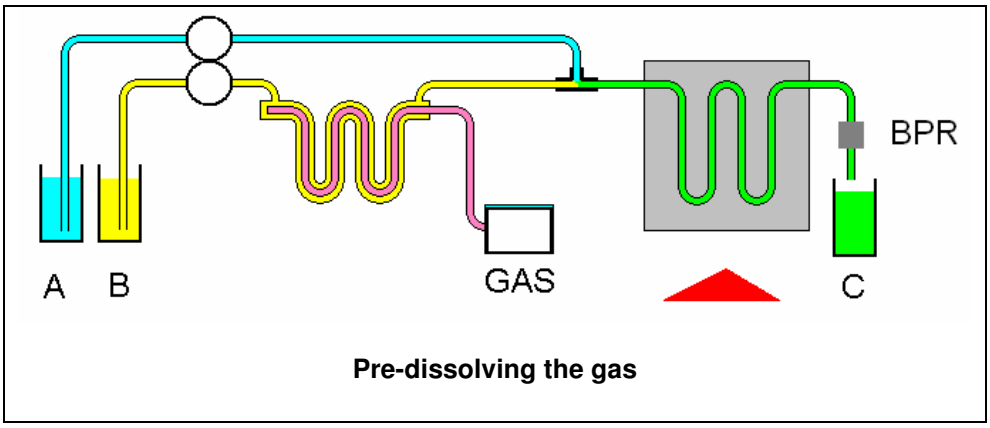
- pre-dissolving the gas into the liquid before the reaction
- performing the reaction in the new reactor, feeding gas as it is consumed by the reaction

These are explained overleaf.

Pre-dissolving the gas in the reagent stream

As mentioned above, this method involves saturating one reagent stream with gas before the reaction itself.

It is limited by the solubility of the gas in the reagent and solvent liquid stream, which for some gases will impose quite a significant limitation on the concentration at which the reaction can be run with useful conversion.



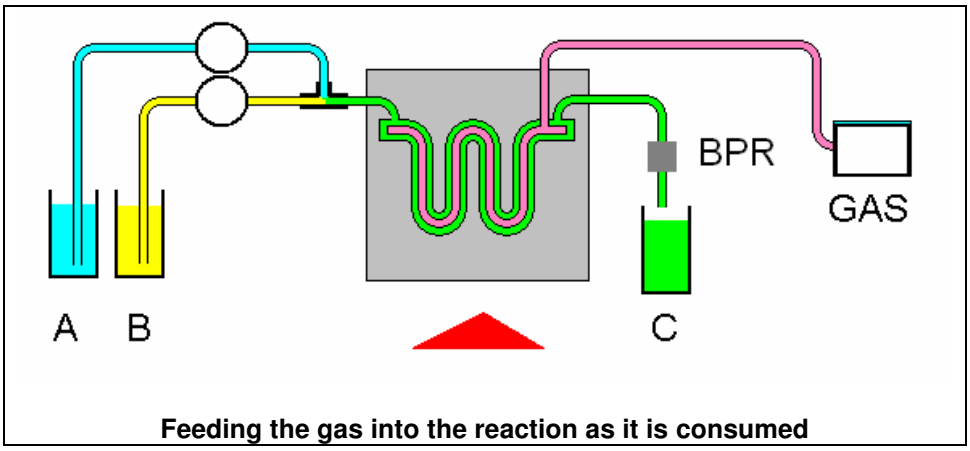
Pre-dissolving the gas

Feeding the gas into the reaction as it is consumed

Because the new Vapourtec reactor is compatible with the existing R4 reactor heater, it is possible to use it for the main reaction, controlling the reaction temperature as required while feeding in gas.

Therefore the solubility of the gas in the solvent/reagent is no longer the limiting factor. As gas is consumed by the reaction, more is fed into it.

The limiting factor may then become the rate at which gas can be fed through the membrane.
This is determined by a number of factors, including the gas pressure setting, the temperature of the membrane, and the gas molecule in question. (H_2, for example, is small and will diffuse at a greater rate than, say CO_2, all other things being equal).



Feeding the gas into the reaction as it is consumed

Considerations with Gas / Liquid Reactions using a Membrane

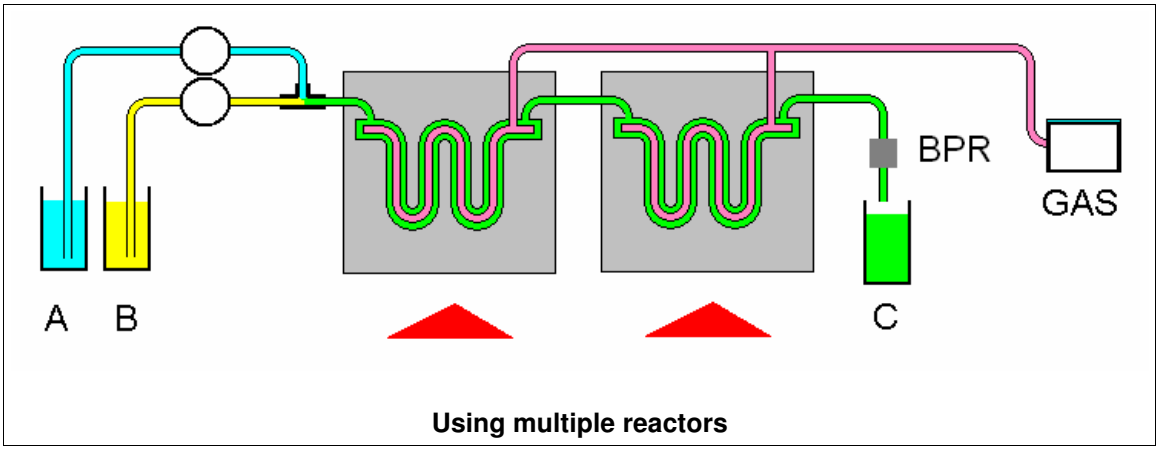
The rate of diffusion of gas through the membrane into the liquid is dependent on gas pressure (but not liquid pressure), the size of gas molecule and the temperature.

(The temperature which influences gas diffusion at the membrane is in effect the temperature of the liquid).

The gas pressure needs to be controlled within a certain range for effective use. If the gas pressure significantly exceeds the liquid pressure, bubbles may form in the liquid within the reactor, which is not desirable (it's not very reproducible and it makes residence time calculations inaccurate).

Increasing the gas flow

If required it is possible to increase the scale of the reaction and the gas flow by using more than one reactor in series. The Vapourtec system can heat up to four gas membrane reactors in series.



Using multiple reactors

References

1. Polyzos, M. O'Brien, T .P. Petersen, I. R. Baxendale and S. V. Ley, *Angew. Chem. Int. Ed.*, **2011**, *50*, 1190. **http://dx.doi.org/10.1002/anie.201006618**

FAQ

Q **Is this new reactor coil compatible with my existing Vapourtec glass manifolds ?**
A Yes.

Q **Is the reaction visible ?**
A No, stainless steel is used for the outer tube
.
Q **Is this compatible with my existing FlowCommander™ software ?**
A Yes, Flow Commander™ just needs to know the reactor volume and all collection timings will be correctly calculated

Q **What temperature range is this available for**
A Ambient to 150°C (in a standard glass manifold).

Q **Is there a high temperature version (up to 250 °C)**
A No

Q **Is there a strong acid resistant version ?**
A No, stainless steel.is used as part of the wetted path

Q **Is there a cooled (below ambient) version of the larger reactor ?**
A Not at this time. However, note that an exothermic reaction above ambient can be effectively controlled, as with all Vapourtec reactors.

Q **Is the reactor temperature under the control of FlowCommander software ?**
A Yes, it is controlled just like any other reactor in the Vapourtec system. So you can use FlowCommander to automate a series of gas reactions at different temperatures. Or if you do not use FlowCommander, the temperature is set using the R4 front panel.

Q **How quickly can the temperature be changed ?**
A As with all Vapourtec reactors, the thermal inertia is small, so temperature set point changes are rapid, whether the temperature is rising or falling.

Q **How accurate is the temperature measurement ?**
A The temperature probe measures the temperature at the steel wall of the reactor liquid tube, so is absolutely representative of the liquid temperature.

Q **How is the gas controlled**
A The user feeds gas via a pressure regulator into the gas ports on the reactor. Currently this is manually controlled. At a later date Vapourtec expect to announce an automated gas management accessory, which would maintain gas pressure at the optimum pressure at all times.

Q **How much does this reactor cost ?**
A Please contact Vapourtec.

Q **When is this item available for delivery ?**
A 1st July 2011

Q **Has this been used for actual work yet ?**
A At the time of writing, work has already been submitted for publication.

Q **What gases can this be used for**

A Testing so far has been done with H_2, CO, O_2 . It is less suitable for much larger molecules (e.g. ethene) because the rate of diffusion is lower.

Q **What about Ozone ?**

A Typically ozone is available as a perhaps 10% in oxygen. Using the reactor as shown above would result in a build up of (unconsumed) oxygen in the gas part of the reactor. Continuous flow of gas in and out of the membrane would be required (perhaps by a metered vent). While quite possible, this has not been the subject of any development work yet

Q **What is the concentration of reagents that can be used?**

A Testing so far has been completed with reagent concentration in the reactor of between 0.5M and 1.0M.

Q **Is it necessary to recycle the reagents through the reactor multiple times ?**

A No. All testing so far has involved a single pass through the reactor system to collection.

Q **I already have an R series system – what do I need to start using this ?**

A You will need the new reactor plus a regulated supply of the gas in question that can be connected to the reactor gas ports. A finely adjustable pressure regulator up to 20 bar with a calibrated gauge is recommended.

Q **Are there safety considerations**

A It is advisable that your gas supply includes a flow restriction so that in the worst case event of a leak the flow rate of gas that could actually be emitted from the system would be small, and easily extracted by the fume cabinet. The pressurised gas volume of the Vapourtec reactor is small (< 10ml) so represents very little stored energy.

About Gas Reactions

Q **How can I tell if my reaction is gas limited ?**

A If there is an excess of dissolved gas at the end of the reaction, then you will probably see bubbles of gas in the output stream after the Back Pressure Regulator (BPR) when the pressure is released. If there are no bubbles, all the gas has been consumed by the reaction, and it may be gas limited.

Q **What if I don't get enough gas flow for full conversion**

A It is possible to extend the residence time by lowering the flow rate or by using multiple consecutive gas reactors. The R Series system permits the use of up to 4 reactors in series.