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## Safety and Other Aspects of Batch to Continuous Operation

Prof. Allan Wright,  
University Newcastle, UK



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### Abstract:

There is a current vogue in chemical manufacturing to consider moving batch processes to continuous reactors. Continuous operation offers some advantages, in particular reduced capital costs, operating costs and plant footprint. Despite claims that most molecules can be produced continuously, there are a number of technical problems which significantly disadvantage change from batch to continuous for many processes. This presentation will both outline the underlying chemistry and chemical engineering background to these operating considerations, and use a number of case studies as illustrative examples.

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# Safety and Other Aspects of Batch to Continuous Operation

Prof. Allan Wright,  
School of Chemical Engineering and Advanced Materials, University Newcastle, UK

"It is easier to do many things than to do one thing continuously for a long time."  
Marcus Fabius Quintilian (35 - 90) Roman orator

## Introduction

There is a growing interest in chemical manufacturing to consider using continuous reactors for processes previously operated in batch reactors. This interest has come from chemical engineers through Process Intensification and chemists through flow reactors. Continuous operation is attractive offering reduced capital costs, operating costs and plant footprint. Many general and optimistic claims are made for continuous reactors. Some of these are not supported by chemical engineering analysis.

For example

"It is believed that the reactors of the future will operate under continuous as opposed to the traditional batch mode and will be capable of achieving heat and mass transfer rates higher by orders of magnitude than the conventional batch reactors. More importantly the reactors will provide the ideal fluid dynamics environment for optimising product quality, reducing reaction times and enhancing selectivity."

"Most molecules can be produced continuously."

"The key advantage to performing reactions in a flow reactor lies in the enhanced process controls when compared to batch synthesis."

"Low holdup therefore must be safer."

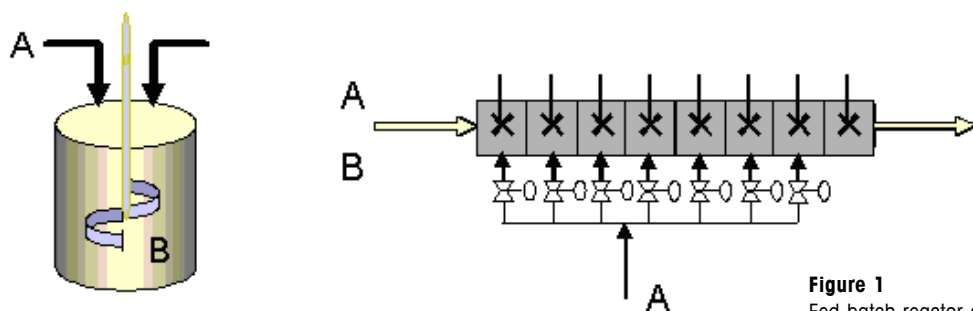
These and other claims made about the application of continuous flow reactors to the batch chemical processing industry will be assessed critically in this paper from the perspective of reaction engineering, thermochemistry, dynamic operability and control and safety. Case studies are used as illustrations. The studies will also demonstrate the use of conventional automated laboratory reactors, reaction calorimetry, and kinetics in screening processes for conversion from batch to continuous operation, and in design of the continuous process when a change of operating regime can be made safely, efficiently and economically. It is important to note that the analyses and conclusions in this paper apply to all PFRs, irrespective of scale.

## Reaction engineering principles and mathematical equivalence

"Most molecules can be produced continuously"

In an ideal tubular plug flow reactor (PFR) where reagents are fed at one end, the residence time is the length / flow velocity. This is mathematically equivalent to the residence time in a simple batch reactor. In a semi-batch reactor (fed batch), reagent can be added over time, however in a PFR, the mathematical equivalent is the addition of reagent at different distances down the tube. Semi batch operation enables variable backmixing which gives an important additional degree of freedom for optimising chemical yields.

This means of optimisation is lost to continuous plug flow operation (tubes and oscillatory flow reactors) unless provision is made to add reagent along the length of the reactor.



**Figure 1**  
Fed batch reactor and the PFR equivalent.

A survey in a recent paper identified selectivity and conversion as the most important requirements for continuous processing in microreactors<sup>1</sup>. The authors studied a Grignard reaction in a microreactor, and found experimentally that multiple injection points and mixing zones were needed to increase selectivity.

### Case study 1.

This example will be presented in detail. A company were interested in developing a continuous reaction system for a quaternary ammonium monomer. A combination of reaction calorimetry and process simulation was used to evaluate the idea. The first reaction step in the process was fast and exothermic. This was followed by a slow addition reaction requiring precise pH control. The exotherm would have required multiple addition points and individually controlled cooling zones. The requirement to regulate pH would need a second set of addition points. The process was found to be unsuitable for continuous operation.

### Thermochemistry

“Reactors ... will be capable of achieving heat and mass transfer rates higher by orders of magnitude than the conventional batch reactors”.

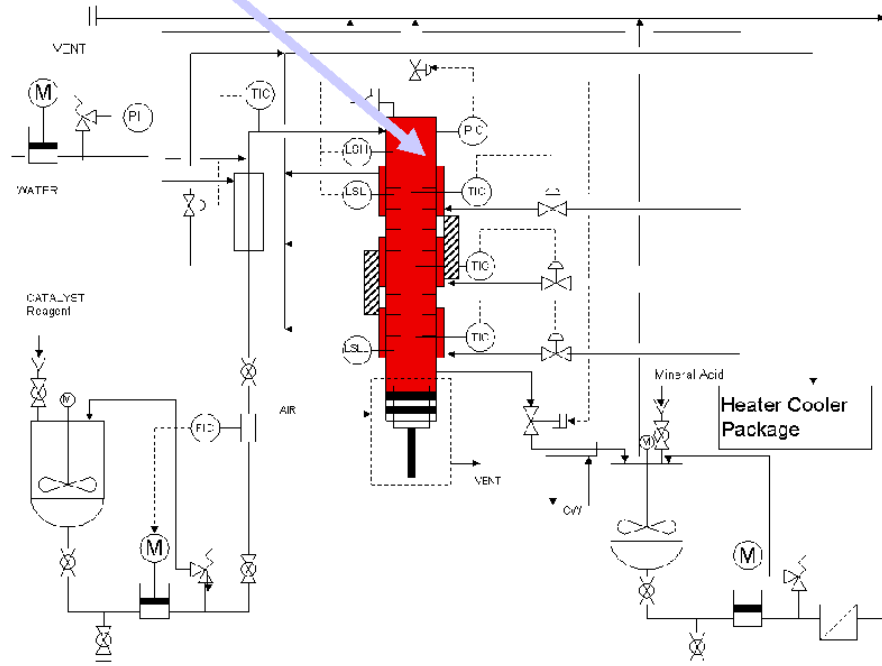
The Grignard reaction studied by Barthe et al was both fast and highly exothermic.<sup>i</sup> Even in a microreactor, the exotherm was sufficient to demand additional channels for chemical reaction heat management. The reaction stream passed through cooling loops between each injection point.

In a fed batch reactor temperature regulation is temporal rather than zonal and may be achieved by a single jacket and control valve. Zonal heating design is a non trivial problem.

### Case study 2.

A large scale batch process (>80 tonnes per batch, 8 hour batch time) was piloted using a 30 kg/day pressurised oscillatory flow baffled reactor with a 15 minute residence time. The residence time was calculated from the reaction kinetics to give the required conversion. The conversion attained in experimental trials agreed closely with the process model. The reaction was known to be mildly exothermic. With the reduced residence time this caused a localised 30-40 °C temperature rise along the single jacketed reactor. As a consequence the product quality did not meet the commercial standard and major resign became necessary.

## Oscillatory Baffled Reactor



**Figure 2**  
Pilot scale OFR reactor system

### Dynamic operability and control

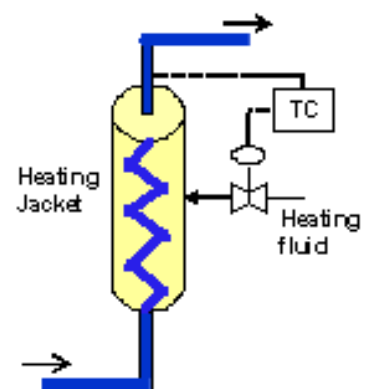
“The key advantage to performing reactions in a flow reactor lies in the enhanced process controls when compared to batch synthesis”

It is uncommon to measure the temperature inside a PFR, usually only the outlet temperature is measured and isothermal conditions are “hoped for” often without justification. As a result local temperature control is not effected and occasionally inverse response behaviour may be exhibited, resulting in loss of temperature control.

### Case study 3.

This case study presents an example of temperature inversion which occurred during the commissioning of a PFR for manufacturing a synthetic stage of a new blockbuster pharmaceutical. The incident happened after clinical trials when pressure for success was utmost.

When the steam valve was opened to raise the temperature of the process stream, cooling resulted. When the valve was closed to reduce the steam flow, the process temperature increased to a level where an off spec product was produced. The cause was eventually identified through a simulation study. The reason was complex and involved a moving reaction zone caused by the effect of steam flow on the tube heat transfer.



**Figure 3**  
Schematic of PFR system with steam jacket

## Safety

“Low holdup therefore must be safer”

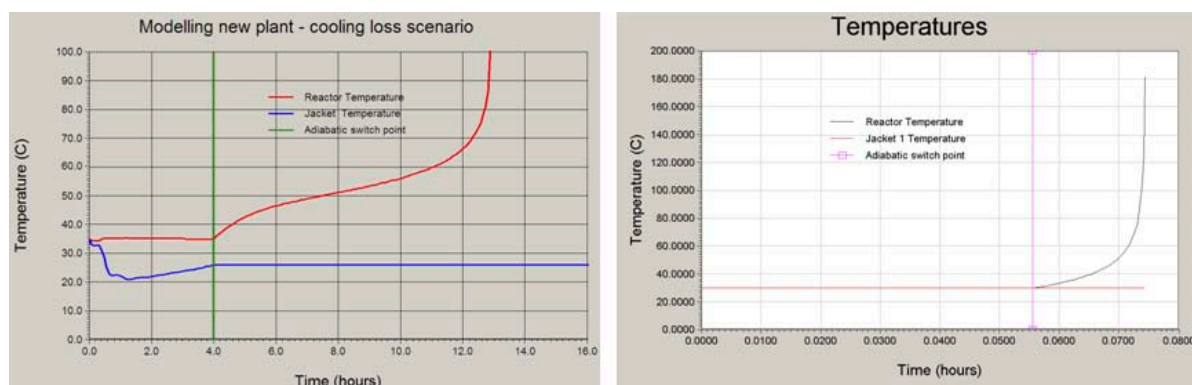
Case study 3 is an example of a controlled thermal runaway in a PFR. Another successful application of PFR under thermal runaway was developed by Agfa Gevaert <sup>ii</sup>. This process involved the oxidation of a sulfone using hydrogen peroxide. The original and problematic process was described at the RC1 user forum in 1995. Following successful batch scale up Agfa explored the use of a PFR. A pilot scale system was constructed which despite cooling resulted in a rise in reactor temperature to about 120 °C. The residence time became very short and the oxidation superfast, complete and clean. Although there was a thermal runaway in both of these examples, the temperature reached was not sufficient to initiate a secondary decomposition reaction. The final case study in this paper explores the consequence of such a reaction on TMR@MTR in a PFR.

It is generally assumed that PFRs are small with low hold up, and therefore intrinsically safe. In the author's experience of modelling reacting systems, including reaction kinetics, most rate constants fall in the range of  $10^{-3}$  to  $10^{-4}\text{s}^{-1}$ . By-products tend to be slower ( $10^{-5}$ ) and there are a minority of faster reactions  $>10^{-2}$  and faster. The residence time to achieve high conversion for a reaction can be roughly estimated as three times the inverse of the rate constant. To process say 100 tonnes of reaction mixture per year, a holdup of 10kg would be required and for a rate constant of  $10^{-3}\text{s}^{-1}$  and 100kg for a rate constant of  $10^{-4}\text{s}^{-1}$ , and far from a low hold up.

## Case study 4.

In June 1996 at Holliday Chemicals, Huddersfield UK, a violent runaway reaction occurred in a 2.3 m<sup>3</sup> Pfaudler reactor creating a high pressure that led to rupture of the vessel: consequential damage to equipment and buildings was very significant <sup>iii</sup>. At the time of the incident a diazonium ion was being produced for subsequent decomposition to form a phenol. A combination of isothermal and adiabatic calorimetry was subsequently used to investigate the incident. Simulation studies were used as an aid to analysing and understanding the events leading up to the accident. The model was tested extensively and found to be very accurate, identifying the true cause of the incident. As part of the re design, “what if” scenarios were tested, including the effect of cooling failure. The new process was designed to have a Time to Maximum Rate (TMR) of >8 hours before runaway.

The simulation model has been used to predict the behaviour of this process in a PFR. This showed that if the PFR becomes adiabatic, for instance feed flow to the reactor stops, TMR could be reached in less than 2 minutes.



**Figure 4**  
Simulation of TMR@MTR for fed batch and PFR

This simulation study illustrates that a reactor that is inherently safer with respect to one hazard (low hold up) may not be inherently safer with respect to another (TMR may approach zero). Similar conclusions were reached by Luyben and Hendershot in 2004 <sup>iv</sup>, this time using a nitration process as an example.

### **Conclusion**

Batch to continuous may be attractive but also problematic. Reaction engineering design methods coupled with experimental techniques such as reaction calorimetry and other high quality analysis and reaction engineering equipment can provide highly effective low cost screening and safe scale up.

- <sup>i</sup> P. Barthe , C. Guerneur , O. Lobet , M. Moreno , P. Woehl , D. M. Roberge , N. Bieler , B. Zimmermann Continuous Multi-Injection Reactor for Multipurpose Production - Part I Chemical Engineering & Technology Volume 31 Issue 8, Pages 1146 – 1154, doi:10.1002/ceat.200800132
- <sup>ii</sup> Bollyn, M, van den Bergh, A., Wright, A R Reaction calorimetry and reactor simulation – combined techniques accelerate scale up for toll manufacture of a highly exothermic oxidation reaction, Mettler RC User Forum, Interlaken, October 1995
- <sup>iii</sup> S. Partington and S.P. Waldram Runaway Reaction During Production of an Azo Dye Intermediate Process Safety and Environmental Protection Volume 80, Issue 1, January 2002, Pages 33-39 Incident Investigation, doi:10.1205/095758202753502398
- <sup>iv</sup> Luyben, W. L., and D. C. Hendershot. Dynamic Disadvantages of Intensification in Inherently Safer Process Design. Ind. Eng. Chem. Res. 2004 43, 384-396.