

INHERENTLY SAFER PROCESSING: BATCH AND SEMI BATCH REACTORS FOR EXOTHERMIC PROCESSES. IMPACT ON RELIEF SIZING

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Semi-batch processes for strongly exothermic chemical reactions are, in principle, inherently safer than batch processes. This is most evident if they are operated under feed rate limited conditions. This paper shows how a combination of isothermal and adiabatic calorimetry can be used to extend the DIERS vent sizing methodology to apply to semi-batch operations. "Vapour pressure" and "gassy" systems are considered when the reaction rate is either kinetically controlled or feed-rate controlled.

Keywords: Semi-batch, batch, DIERS, relief sizing, feed-rate control, kinetic control

1. INTRODUCTION

Chemical reactions carried out in the fine chemicals industries are typically exothermic with temperature control achieved by heat removal through a jacket or cooling coils. A commonly recognized problem is the inability to remove sufficient heat (due for example to loss of cooling capacity) resulting in the reaction running out of control and leading to elevated pressures and temperatures. The size of a vent which may be installed on the vessel to protect against the consequences of such an event depends on the contents at the time of the event. Conventionally it has been assumed that the full reactor charge will take part in the runaway. This is often the "worst case assumption" and the choice can be defended in many situations.

While this approach can adequately protect the reactor vessel, it often leads to impractically large vents which in many cases cannot even be installed in the available space on the vessel. This is particularly true since the widespread use of the DIERS methodology (1) in most cases requires the consideration of two-phase (gas-liquid) flow through the vent. Another undesirable aspect of large vents (combined with gas-liquid flow) is that excessive amounts of flammable and/or toxic chemicals may be released into the atmosphere unless containment of relieved fluids is present. If an external dump or quench tank is used to minimise such release then the danger is that the runaway can simply be transferred to the new location. The reactor is satisfactorily relieved but in the dump tank itself a new exothermic runaway develops.

The problem is that while vent sizing methodology has improved as a result of DIERS, it has failed to take realistic account of the fact that most chemical processes are operated in a semi-batch manner and therefore the assumption of a "full-charge" runaway is frequently unrealistic. This paper will show how industry's move towards inherently safer (semi-batch)

operations, combined with proper controls, can frequently lead to acceptably sized vents which are still fully consistent with the DIERS methodology.

2. SEMI-BATCH CHEMISTRY

Controlled dosing of a key chemical into a stirred vessel has the widely recognized advantage of minimizing the amount of energy available for a potential exothermic runaway. The extent of safety improvement resulting from semi-batch operation depends on the relative rates of reactant addition on the one hand and consumption by chemical reaction on the other. It is important to understand how these two rates compare and therefore how much (if any) unreacted dosed material is accumulating in the reactor vessel.

Consider for example the esterification reaction between methanol and acetic anhydride. This has been studied extensively over the years and is known to occur relatively slowly at modest temperatures but can accelerate rapidly if the temperature is allowed to increase. At 40°C for example, if anhydride is dosed into methanol considerable accumulation can occur. The results from an isothermal calorimetry experiment for this system are shown in figure 1, note that most of the heat is released after dosing is completed.

At higher temperatures the reaction rate of anhydride consumption is much greater and therefore the accumulation much reduced. Another way of reducing the accumulation is to catalyze the synthesis; for this reaction it is easily achieved with a few drops of sulphuric acid. The results of a catalyzed reaction are shown in figure 2. This is also at 40°C and it is clear that the "accumulation" is small (~ 30%) compared with the uncatalysed data (over 70% accumulation). The results are compared in Figure 3.

It is not always appropriate or necessary to use a catalyst in order to obtain the type of power output curve illustrated in Figure 2. An example of an industrial synthesis reaction where this occurs naturally is shown in Figure 4. The power outputs at 75°C and 90°C are plotted while one of the components is dosed over 160 minutes. The "square-shaped" heat output trace is characteristic of fast kinetic reactions operated under feed rate limited conditions and confirms that accumulation is essentially negligible.

The chemical power output data presented in figures 1 to 4 were obtained using the SIMULAR reaction calorimeter. This is essentially a 1 liter bench-scale computer controlled reactor with special facilities to monitor power output at the same time. The basic instrument lay-out is shown in Figure 5, see Singh (2). It is commonly used to mimic real, or proposed, industrial operations but on the small scale.

The power-output from semi-batch reactions can conveniently be described as being either kinetically controlled or dose controlled. The uncatalyzed esterification reaction is an example of the former: power output is limited by the rate of reaction (ie kinetics) and not by the rate at which the dosed component is being added. If the same reaction is performed at a higher temperature the power output is increased. If the temperature is held constant and the feed rate significantly altered, the power output will also be influenced.

The synthesis reaction (Figure 4) is dose controlled; if the feed rate is altered, the power output will change in proportion (provided the reaction is not moved from feed rate

limited conditions to kinetic limitations). Changing the operating temperature by moderate amounts however (thus altering the kinetic rate) will have little effect on the heat output rate - this is clear from the synthesis reaction data in Figure 4 where a change of 15°C in operating temperature is shown to have little effect on the reaction rate. The catalysed esterification reaction is an intermediate case and could be moved towards true feed rate limited conditions by speeding up the reaction (higher temperature, more catalyst) or reducing the acetic anhydride feed rate.

3. DEFINITION OF RELIEF SIZING CASE

The three examples presented above represent a reasonable cross-section of the semi-batch reaction types. Depending on the degree of automation, reliability of equipment (including maintenance standards) and the expertise of operators, it is possible to define the worst "credible" basis for relief sizing, for each reaction type.

For a kinetically controlled reaction, where accumulation of reactant cannot be avoided, the most reasonable assumption is to size the vent at least to cope with the runaway that would occur from the worst amount of accumulated reactant. Thus for the uncatalyzed esterification example, this would imply that ~ 75% of the batch anhydride is mixed with methanol and reaction products and that this mixture runs away exothermically.

In the case of the dose controlled reactions, a case can be made for total exclusion of a true runaway by arguing that reactant accumulation is prevented by instrumentation and control. This would leave only the "steady-state" power output from constant dosing to be accommodated by the vent. This will normally be much less onerous (by an order of magnitude or more) than even a moderate exothermic runaway.

It should be recognized that the basis for relief sizing described above does not represent the absolute worst case. Consider for example the following scenarios:

- Agitation is temporarily ineffective or deliberately turned off, while dosing is maintained resulting in negligible or no reaction. Then, at a later stage, mixing is resumed (or the accumulation of reactant produces sufficient reaction and then mixing) causing a sudden batch-type runaway.
- Dosing is started when the reactor is at a substantially lower temperature than normal (for example because the temperature sensor is faulty), leading to negligible or no reaction. After some considerable delay, either the reactor is warmed up to the correct temperature or the reactant concentration builds up to a point where significant reaction occurs even at the low temperature; in either case, accumulation followed by a runaway can result.
- other scenarios such as an external fire can mean that adiabatic conditions are not a "worst case".

The above possibilities (and others) have led to industrial accidents and are therefore quite credible. However, in a modern well-instrumented plant with proper interlocks and good operator training, these may be rendered "unlikely" and justifiably eliminated as a basis for vent sizing.

Note that the acid catalyzed esterification and the synthesis reaction are both close to being "dose controlled" types and vent sizing could be based on steady-state power output alone resulting from continuous feed remaining uninterrupted for a period of time. (Strictly speaking, the catalyzed example in Figure 2 does show a small accumulation). It should be noted however, that this basis for relief sizing is more easily justified for the organic synthesis system than the catalyzed reaction. This is because in the case of the catalyzed reaction it requires an important additional step in order to realize the dose-controlled chemistry, namely the addition of a catalyst. If the catalyst were inadvertently not added and then dosing commenced, it would behave just like a kinetically controlled reaction with reactant accumulation. Worst still, imagine the consequences if the operator now remembers that the catalyst has been omitted and adds it at this later point!

4. VENT SIZING FOR A FEED RATE LIMITED REACTION

The relief scenario described for this type of situation implies that cooling is somehow lost and dosing continued. Under these conditions, the temperature would rise essentially linearly at a rate governed by the steady-state heat output rate. As the temperature rises the heat output would remain constant since (by definition) it is only influenced by the feed rate. Eventually the pressure will rise to the point where the vent will open and this must be sized to prevent further increase in pressure.

4.1 Vapour Pressure Type System

Consider first a reactor with contents that are sufficiently volatile to produce "tempering" under relief conditions. This implies that when the relief pressure is reached, heat from the reaction will be used to produce an equivalent amount of vapour and that the contents will be boiling at the relief pressure. Provided the vapour can be removed, the pressure rise will be arrested.

If the instantaneous steady-state power output due to chemical reaction is Q_r (W), then the additional volume M_v (m^3s^{-1}) generated as liquid is converted to vapour is given by

$$M_v = \left(\frac{Q_r}{h_{fg}} \right) v_{fg} \quad (1)$$

where h_{fg} is the latent heat of vaporization and v_{fg} the difference in specific volume between vapour and liquid.

If the venting occurs as an essentially homogeneous two-phase vapour-liquid froth, then the relief rate needed must satisfy the following volumetric balance:

$$W v_{fp} = M_v \quad (2)$$

where W is the necessary venting rate (kgs^{-1}) and v_{fp} is the two-phase specific volume $\sim (V/M_o)$, where V is the reactor volume (m^3) and M_o the total liquid charge (kg). The relief area A (m^2) which is needed is therefore given by equation (3a).

$$A = W/G \quad (3a)$$

$$= \frac{Q_r}{G v_{tp}} \left(\frac{v_{fg}}{h_{fg}} \right) \quad (3b)$$

where G is the flashing two-phase mass flux ($\text{kgm}^{-2}\text{s}^{-1}$) through a nozzle and may be approximated by:

$$G \approx \frac{h_{fg}}{v_{fg}} (C_p T_s)^{-0.5} \quad (4)$$

where C_p ($\text{Jkg}^{-1}\text{K}^{-1}$) is the liquid specific heat and T_s (K) the absolute temperature at the relief pressure (ie the liquid boiling point at the relief pressure).

Combining equations (3) and (4) leads to

$$A = \frac{Q_r}{V} M_o \left(\frac{v_{fg}}{h_{fg}} \right)^2 (C_p T_s)^{0.5} \quad (5)$$

If the Clapeyron approximation is used the above equation reduces to

$$A = \frac{Q_r}{V} M_o \left(\frac{dP}{dT} T_s \right)^{-2} (C_p T_s)^{0.5} \quad (6)$$

where (dP/dT) is the slope of the vapour pressure-temperature curve (PaK^{-1}) for the boiling liquid in the reactor, at the relief conditions. Apart from C_p , the only additional information required is Q_r . This may be obtained experimentally from a reaction calorimeter and can then be scaled up in proportion to the addition rate of the dosed liquid. For the organic synthesis reaction in Figure 4, where the steady state experimental heat output rate was $\sim 17\text{W}$, Q_r would be $(17 F_p/F_e)$, where the F_p is the feed rate to be adopted on the plant and F_e is the value used experimentally, corresponding to 17W .

4.2 Gas Generating Reaction

Many semi-batch reactions are carried out in the presence of a volatile solvent which produces the "tempering" effect discussed above. Another important category is reactions that produce non-condensable gas (for example due to decomposition) and this has to be vented rather than vapour. In principle the approach remains unchanged since the gas generation rate will be in proportion to the feed rate of the dosed material. Therefore, it is now necessary to know

the steady-state gas generation rate in place of the heat generation rate. The necessary relief rate is now given by

$$W v_{sp} = M_g \quad (7)$$

in place of equation (2), where M_g is the gas generation rate (m^3/s). The vent area then follows from equation (3a) but G is now given by an equation for two-phase "frozen" rather than "flashing" flow, see Tangaren (3).

A key assumption in the above analysis for both types of reaction is that no complications are observed as the temperature rises from normal operation to the relief point. One possibility is that side reactions, or decomposition of products and intermediates, takes place which will contribute to the relief load. It is important to check for this possibility and if it is found to be true, the methodology needs to be reviewed substantially.

5. VENT SIZING FOR KINETICALLY CONTROLLED REACTIONS

Kinetically controlled systems are evaluated in a manner very similar to the traditional approach to reactive system relief sizing where the relevant reactants are combined in a batch manner and allowed to runaway adiabatically. The difference being proposed here is that the relative amounts of reactants which constitute the initial mixture are determined from the worst accumulation measured under appropriate isothermal conditions. Hence, for the methanol-acetic anhydride reaction (uncatalysed), the traditional approach would be to mix stoichiometric amounts of the two reactants and size the vent for the resulting exotherm. If the actual process is semi-batch however, it is possible to mix only a fraction of the stoichiometric acetic anhydride amount and thus considerably reduce the severity of the exotherm, the justification being that for a well instrumented plant, a worse case is not credible.

The vent sizing methodology for this situation follows the more familiar DIERS methodology (1). The isothermal data for the normal reaction under controlled conditions must now be supplemented by adiabatic data under runaway conditions, using the starting mixture defined above. For the methanol-acetic anhydride system, data for two different runaway conditions are given in Figure 6 in terms of the rise in temperature with time. The two conditions are the following:

- Stoichiometric amounts of reactants and so a full batch runaway from 25°C
- The anhydride amount is reduced to 40% of stoichiometric; this is the accumulation that was determined isothermally in a semi-batch run at 50°C. This runaway, though with reduced amount of reactant, is initiated at ~ 50°C since it would in reality start at this temperature

The data in Figure 6 were obtained in the PHI TEC adiabatic calorimeter using a magnetically agitated test cell of ~ 110 ml with a very low thermal mass (see Figure 7 and Singh (4)). The important point is that the information from the experiment is directly applicable to large scale plant with little or no modification.

The data from Figure 6 is re-plotted in Figure 8 in the form of rate of temperature rise (dT/dt) against temperature; this shows more clearly the marked improvement in safety due to semi-batch operation. The vent size for the two cases will be in proportion to the value of (dT/dt) at the chosen relief point. As the relief set-pressure is raised, the difference becomes greater, until eventually the semi-batch case does not need to be relieved. This relationship is plotted in Figure 9.

As stated for the dose controlled reaction, justification of the semi-batch relief size requires careful consideration so that scenarios more severe than the one selected are methodically eliminated rather than assumed to be improbable. In some cases, a quantitative risk assessment might be required in order to decide whether the level of risk being taken by using a reduced vent size is acceptable.

6. CONCLUSION

Improvements in the technology relating to relief sizing calculations for reactive chemicals has in most cases resulted in an increase in the relief area needed. The main reason for this is the widespread acceptance of the fact that two-phase flow through the vent should be assumed rather than the former practice of sizing for gas or vapour flow alone.

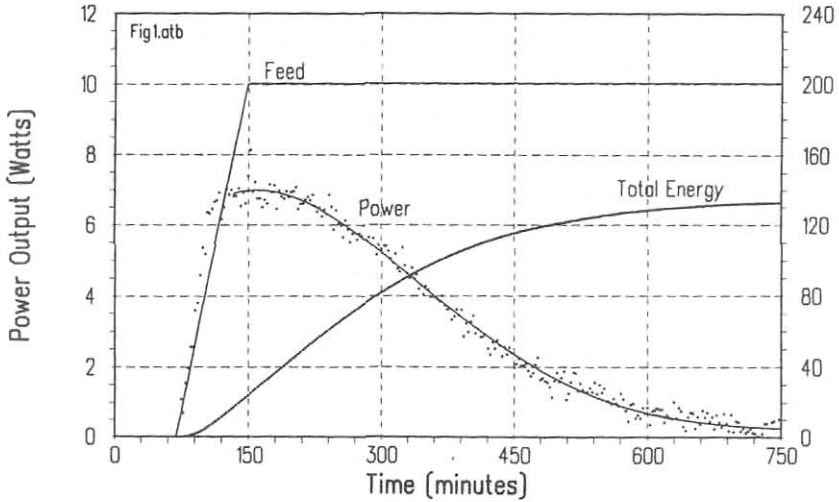
At the same time, there has been a widespread move towards inherently safer chemistry, plant design and operations, particularly the replacement of batch operations by semi-batch types. These improvements have often been ignored in relation to relief sizing and the definition of "worst credible maloperations".

By careful evaluation of each process operation and the underlying chemistry, it is possible to size vents for two-phase flow, fully consistent with DIERS practice but with much smaller vent diameters. In order to do this, it is necessary to study each chemical reaction under controlled (usually isothermal) conditions before developing a case for relief sizing scenarios. Adiabatic calorimetry to study the runaway reaction potential will still play an important role, but in general it should not be the only experimental technique considered.

7. REFERENCES

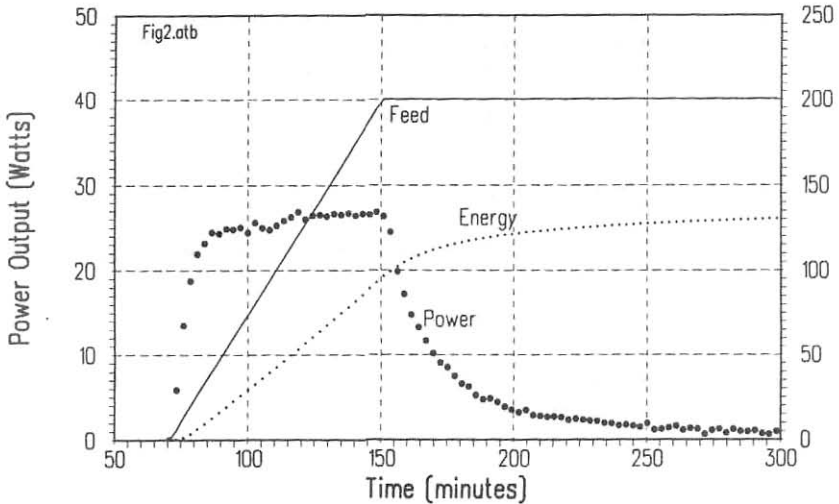
1. Fisher, H. G. et. al., 1992 Emergency Relief System Design Using DIERS Methodology, AIChE, New York.
2. Singh, J., 1993 Assessing Semi-Batch Reaction Hazards, The Chemical Engineer, 25 February.
3. Tangaren, et. al, 1949 J. Applied Physics, 20 (7), 637 - 645.
4. Singh, J. 1993 Reliable Scale-Up of Thermal Hazards Data Using the PHI-TEC II Calorimeter, Thermochimica Acta, 226, 211-220.

**Figure 1 : Uncatalysed Semi-batch Esterification
Power Output, Total Energy and Feed versus Time**



Feed (grammes) & Integrated Power Output (Joules)

**Figure 2: Catalysed Semi-Batch Esterification
Power Output, Total Energy and Feed versus Time**



Feed (grammes) & Integrated Power Output (Joules)

**Figure 3: Catalyst Effect on Esterification Rate
Total Energy and Feed versus Time**

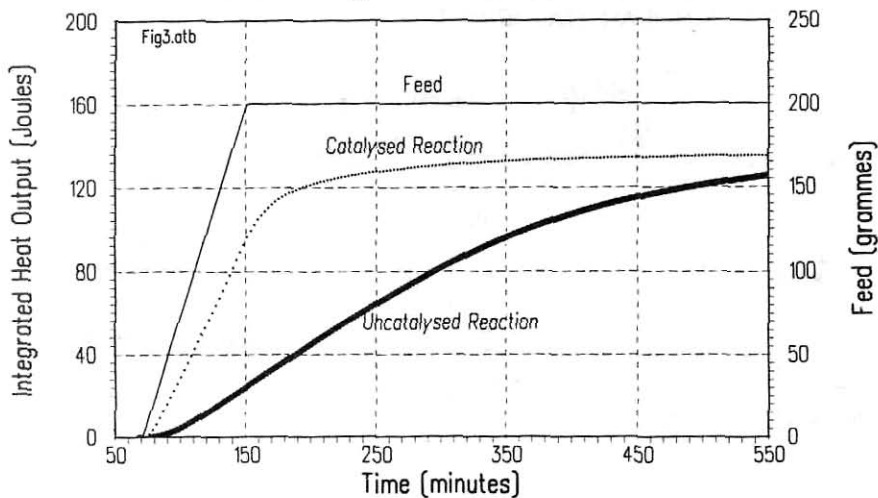


Figure 4: Comparison of Power Output at 75 and 90 deg. Celsius. Isothermal Organic Synthesis.

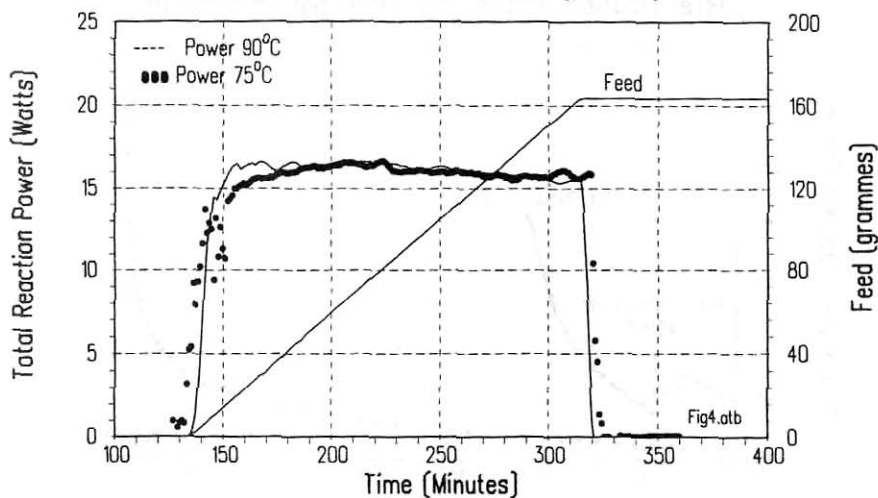


FIGURE 5
SCHEMATIC DIAGRAM OF
THE SIMULAR CALORIMETER

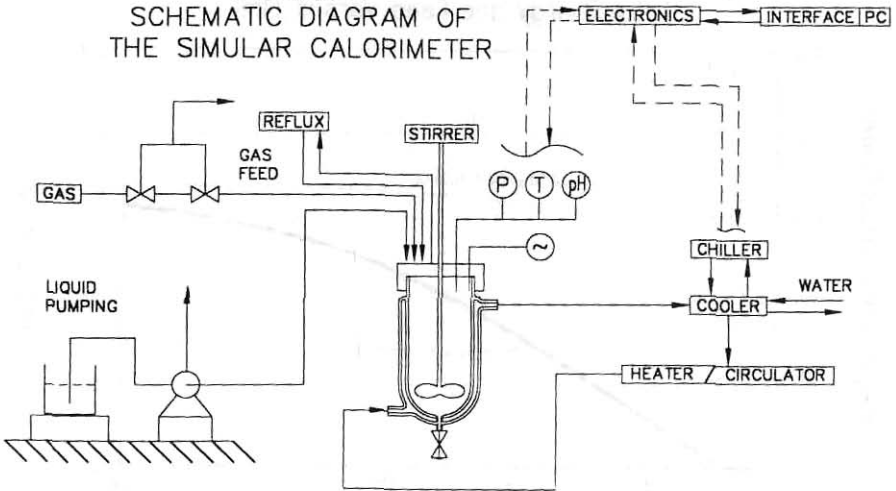


Figure 6 : Adiabatic runaway of the uncatalysed esterification. Batch and semi-batch at 50 deg.C

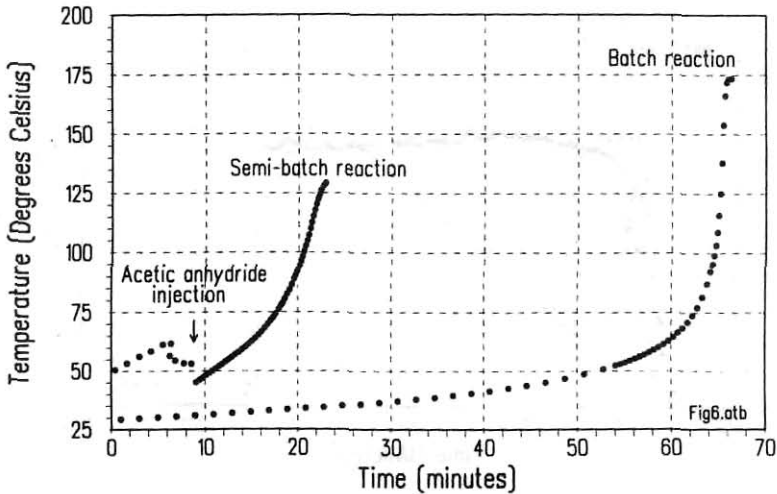


FIGURE 7: THE PHI-TEC ADIABATIC CALORIMETER FOR THE ASSESSMENT OF EXOTHERMIC RUNAWAYS

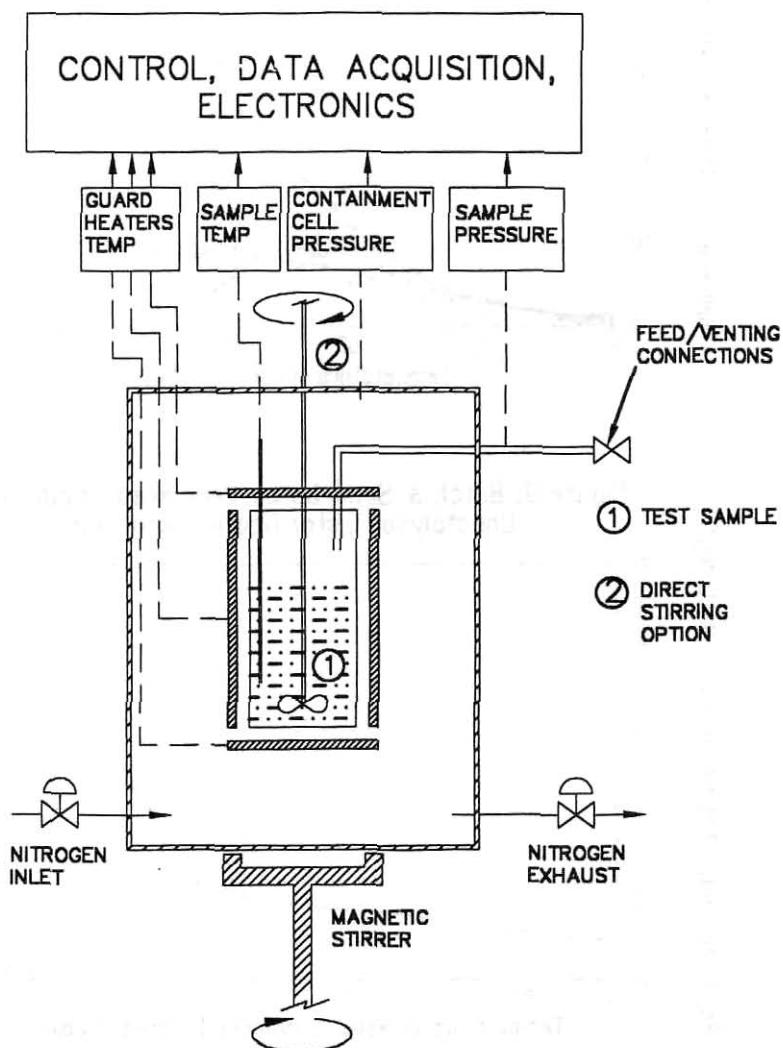


Figure 8: Self-heat rates for the uncatalysed esterification. Batch and semi-batch

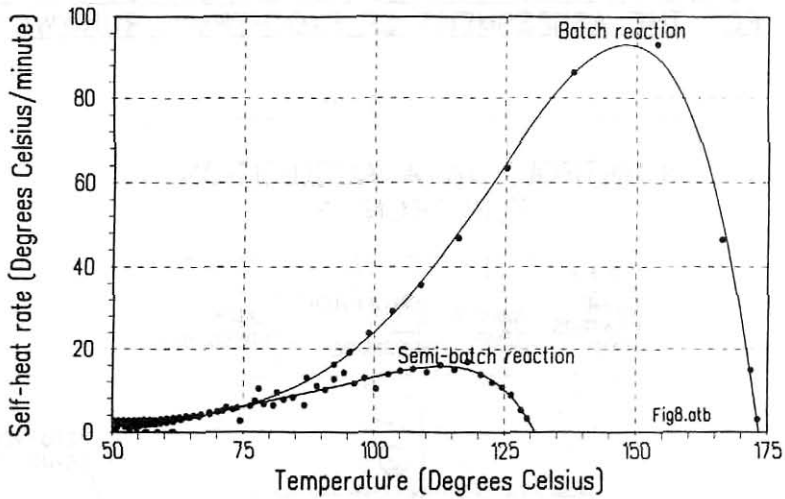


Figure 9: Batch & Semi-batch Vent Area Comparison Uncatalysed Esterification Reaction

