Reaction inhibition in the control of exothermic runaway

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Abstract

A research programme has been undertaken into the use of chemical inhibition techniques as a basis of safety for the control of exothermic runaway reaction hazards. The principal element of the research has been the design and running of a series of pilot scale trials at the Health and Safety Laboratories into the inhibition of an uncontrolled styrene monomer polymerisation with associated laboratory and analytical work to plan the tests safely. Pilot scale experiments on the uncontrolled polymerisation of styrene have demonstrated the effectiveness of the injection of the inhibitor para tertiary butyl catechol at two different agitation speeds and under conditions immediately following agitation failure. Modelling of the experiments using a network-of-zones approach has shown some inadequacies with the reproduction of the pilot scale data, notably in the inability to simulate the jet mixing effects that dominate in small scale plant with the conditions employed. The present modelling results do, however, underpredict the mixing efficiency, thereby leading to a more conservative design for the cases studied.
Keywords: reaction, inhibition, runaway, polymerization.

1 Introduction

Many chemical reactions within the process industries are exothermic in nature. Under normal operating conditions the release of this heat from the reactor is controlled by the use of internal cooling coils and/or jackets. If the rate of heat

generation exceeds the rate of heat removal a self-sustaining uncontrolled runaway reaction may occur.

Processes in which heat is absorbed (endothermic processes) are generally easier to control than processes which generate heat (exothermic processes). This is due to the fact that, as the exothermic reaction causes an increase in temperature, the rate of reaction is also increased. Polymerization reactions also add a problem with the increased viscosity which reduces thermal exchange and inhibitor spread. Most mitigation and control methods act to remove the heat that is being, or has been, generated. Inhibition differs in that it interferes with the chemistry itself retarding the mechanism that generates the heat.

A number of techniques are available to ensure safety in the event of runaway reactions. The use of small quantities of active quenching agents that are capable of halting a runaway reaction is one such technique.

In order to assess the effectiveness of inhibition as a technique for mitigating the effects of runaway reactions, a number of lab scale trials and pilot plant tests were conducted on the polymerisation of styrene catalysed by benzoyl peroxide [1].

2 Experimental

Laboratory scale tests were performed in an RC1 reaction calorimeter, an ADC II adiabatic pressure Dewar calorimeter and a Phi-Tec II adiabatic calorimeter with the aim of deriving kinetic information. The results of these experiments were analysed to yield a complex empirical expression to describe the kinetics throughout the runaway. Data were analysed to provide a pseudo-first order kinetic expression suitable for the initial stage of the runaway. The results of these kinetic studies were used in a pilot plant simulation program (Chem Model) to help in the design of the pilot scale experiments.

Para tertiary butyl catechol (ptbc) was used as inhibitor, being known that, among the inhibitors of styrene polymerization, it is effectively used during monomer storage.

2.1 Results and discussion

2.1.1 Laboratory investigation
An assessment of the styrene polymerisation under normal operating conditions was conducted using a heat flow calorimeter. A heat flow calorimeter simulates conditions at plant scale by maintaining the reaction mass temperature at a previously set temperature. Two experimental runs were conducted, the first at a temperature of 80°C and the second at a temperature of 90°C.

Styrene monomer was charged to the vessel at room temperature. Agitation was initiated followed by a number of temperature ramps and calibrations until the desired reaction temperature had been achieved. Once equilibration had been achieved the benzoyl peroxide initiator, dissolved in styrene to aid dispersion, was added. After a period of time, approximately equivalent to a conversion of 10%, ptbc inhibitor, also dissolved in styrene, was injected. Experimental data is summarised in Table 1.

Table 1:   Parameters for heat flow calorimetry study.

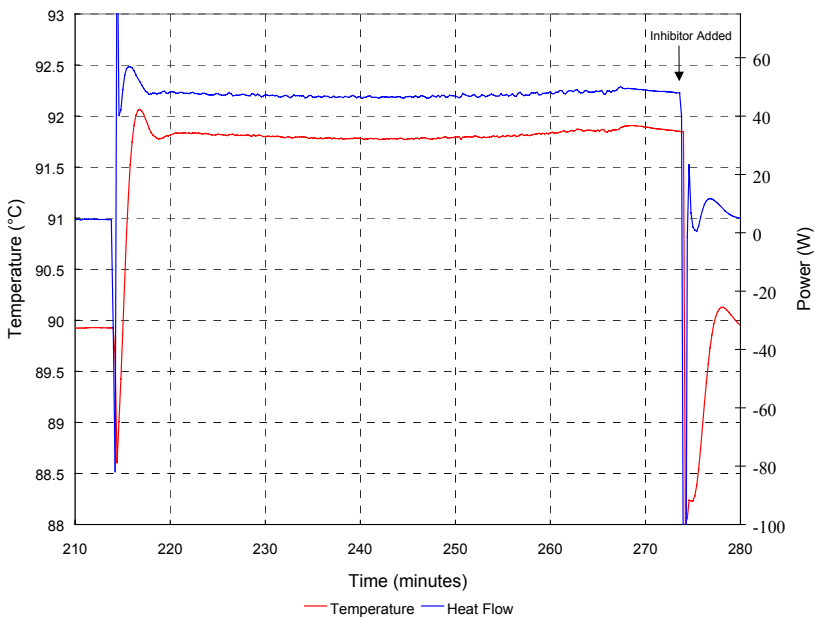|	Experiment 1	Experiment 2
Reaction temperature (°C)	80	90
Mass of styrene (kg)	0.7212	0.7212
Mass of benzoyl peroxide (kg)	0.00533	0.00533
Mass of inhibitor/styrene (kg)	0.0119/0.025	0.0119/0.025
Agitation speed (rpm)	100	100
Overall heat transfer coefficient (W m^{-2} K^{-1})	95.8	136.6
Rate of heat output (W)	12 ÷ 14	~ 45

Figure 1:   Temperature/power profile for heat flow calorimetry experiment 2 at 90°C.

Upon injection of the initiator an immediate increase in the rate of reaction occurred in both experiments as seen in the heat flow curves for experiment 2 (Fig.1). It is known that styrene will thermally polymerise at a temperature of 90°C, however, at this temperature the rate of thermal polymerisation is low and the observed reaction in experiment 2 may be considered chemically initiated only.

Another test was conducted in an ADC II adiabatic pressure Dewar calorimeter. Benzoyl peroxide (0.5 % wt/wt) in styrene was charged to the Dewar vessel. After sealing and connecting to all relevant logging and control systems, the sample (750 g) was heated to 343 K (70°C) and maintained under

adiabatic conditions. The inhibitor was injected at 110°C and the test was left under adiabatic conditions. Upon injection of the inhibitor there was an immediate fall in the rate of temperature rise, thus confirming that there is cessation of the reaction at this stage. However, it was noticed that the temperature began to rise again, after approximately 1 hour. After approximately 3 hours the runaway reaction has resumed although slightly less vigorously than for the uninhibited case.

In response to the discovery that the runaway reaction was able to recover, further laboratory trials were conducted in an adiabatic pressure Dewar calorimeter to assess the effect of inhibitor concentration. Figure 2 illustrates the recovery time for a number of different ptbc concentrations, all injected at 110°C.
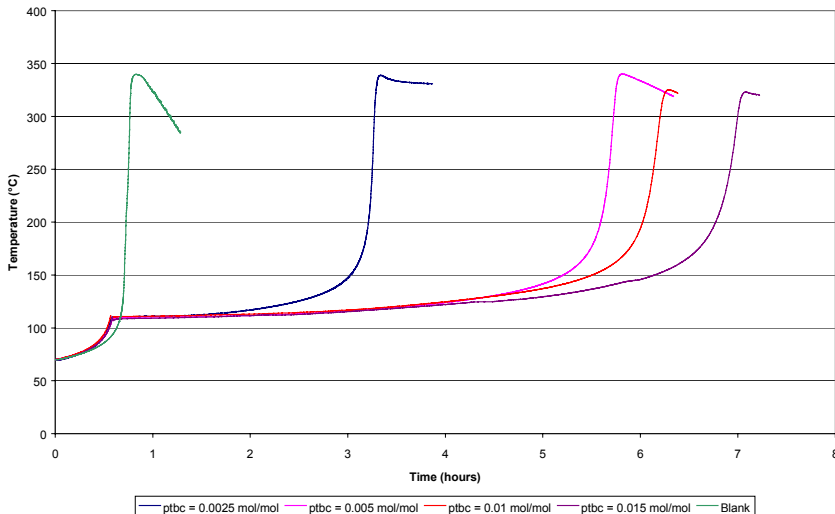

Figure 2: Effect of inhibitor concentration upon runaway reaction recovery.

Clearly there is a correlation between the inhibitor concentration and recovery time for the runaway. There also appears to be little effect upon the overall maximum temperature under adiabatic conditions from the inhibitor concentration, suggesting that the inhibitor only affects the radicals already formed, although it retains a reduced retarding effect. It was decided that for the pilot scale trials an inhibitor concentration of 0.01 mol/mol would be used.

It is thought that the mode of action of the ptbc is to prematurely terminate growing polymer chains, thereby yielding significantly shorter chains and causing the observed retardation.

2.2 Analysis of kinetics

Although the complete polymerisation kinetics are complex, for the early stage of polymerisation, over the temperature range of interest for the pilot plant tests,

a first order kinetic expression may be an adequate approximation. The more complex kinetics identified for higher temperatures should not be encountered if the inhibitor is successful. From the slope and intercept of the plot shown in Figure 3 the following pseudo first order kinetic parameters for temperatures between 77°C and 150°C were derived:

pre-exponential factor $\quad\quad\quad$ A = 6.405×10^{11}
activation energy (J.mol^{-1}) $\quad$ Ea = 105992

$$\frac{dXc}{dt} = A\exp\left(\frac{Ea}{RT}\right)(1-Xc) \tag{1}$$

This pseudo first order kinetic expression, combined with estimates of the heat transfer characteristics of the pilot reactor, provided the input parameters into a computer simulation model of the runaway scenarios using the following expression:

$$\frac{dT}{dt} = A\exp\left(\frac{Ea}{RT}\right)(1-Xc)\left(\frac{HoR}{Cp}\right)-\left(\frac{UA}{mCp}\right) \tag{2}$$

With: Xc= conversion, T = temperature, H_0R = heat of reaction (J mol^{-1}), Cp = specific heat (J kg^{-1} K^{-1}), U = overall heat transfer coefficient (W m^{-2} K^{-1}).
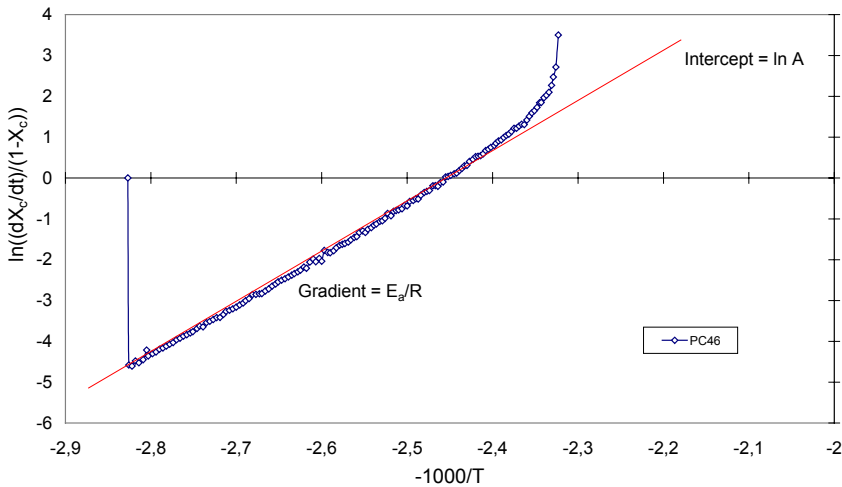

Figure 3: $\quad$ Activation energy and pre-exponential factor from Phi Tec adiabatic calorimetry.

2.3 Laboratory trials

Prior to designing the pilot scale experiments, qualitative tests were carried out in a 1.4 litre laboratory reactor to investigate the feasibility of the pilot scale

tests. The aim of the experiments was to determine whether *tert*. butylcatechol can successfully inhibit the runaway polymerisation of styrene under various conditions. The effect of the degree of mixing on inhibitor effectiveness was also studied in brief.

Experiments were performed either with an open, or an initially closed, system. In open tests the reactor vent is left open throughout the test. In the latter case, the reactor vent valve is closed and switched to automatic control after charging of the reactor is complete. Both open and closed tests were investigated on the laboratory scale to study possible effects of reactor pressure on the efficacy of the injector. The pressure vent controller is set to open the reactor vent valve at the desired set pressure.

When inhibitor solution was injected into a 1 litre batch of styrene undergoing an accelerating polymerisation reaction, the runaway reaction was successfully stopped when the reactor contents were subject to strong agitation of 300 rpm. These experiments tested injection at 110°C, 120°C and 130°C in separate experiments in both open and closed tests. However, when there was no agitation or only slow agitation of 30 rpm, the mixing of the inhibitor seemed insufficient to retard the polymerisation throughout the entire laboratory reactor vessel. Also a number of tests were undertaken with a 23 litre transparent reactor in order to investigate the effectiveness of the mixing through the injection of a dye into the liquid the parameters of mixing were optimized in this way.

2.4 Pilot plant trials

The objective of the pilot scale trials was to examine the influence of the vessel agitator on the incorporation of the injected inhibitor. A runaway reaction was initiated at approximately 82°C. Once the reaction temperature reached 120°C, inhibitor solution was injected from a pressurised bomb. The conditions of the tests were held identical, except for the vessel's agitation behaviour. Across the three tests, this was varied:

Experiment 1: Vessel agitator speed held at 103 rpm
Experiment 2: Vessel agitator speed held at 51.5 rpm
Experiment 3: Vessel agitator halted (from 103 rpm), 0.5 K before the inhibitor injection.

The data for the experiments are presented in Figures 5 - 7. The figures present the variation with time of the measured temperatures The labelling of the thermocouples (TC) and resistance thermometers (RTD) allow their identification on the schematic Figure 4. The monitoring of several temperature signals from differing locations permits the spread of the injected inhibitor to be followed.
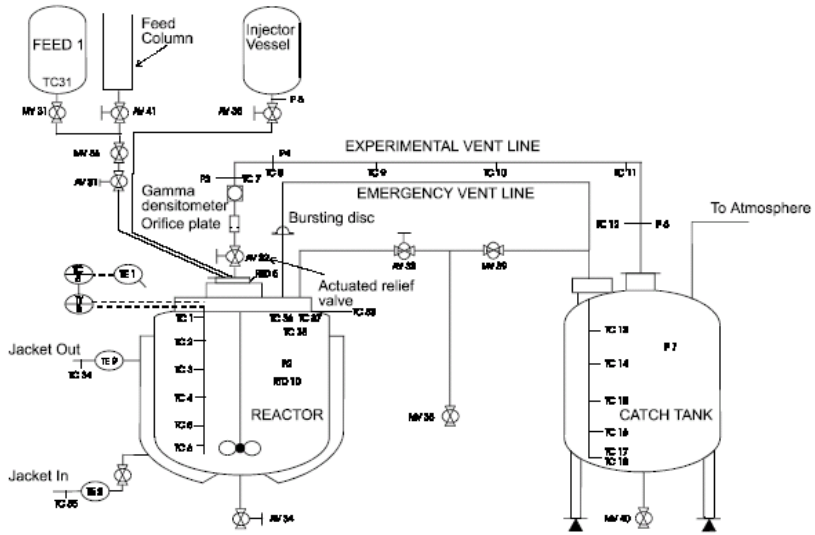
Figure 4:   Pilot plant instrumentation diagram.
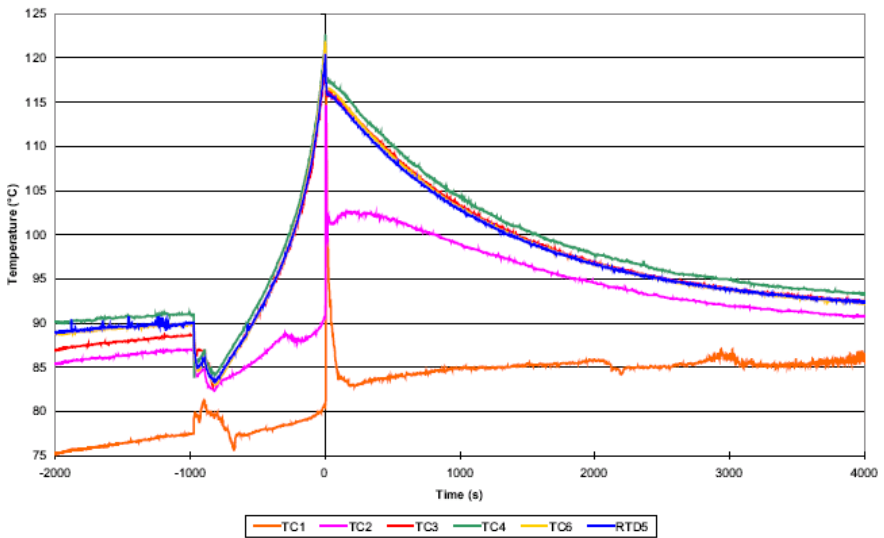

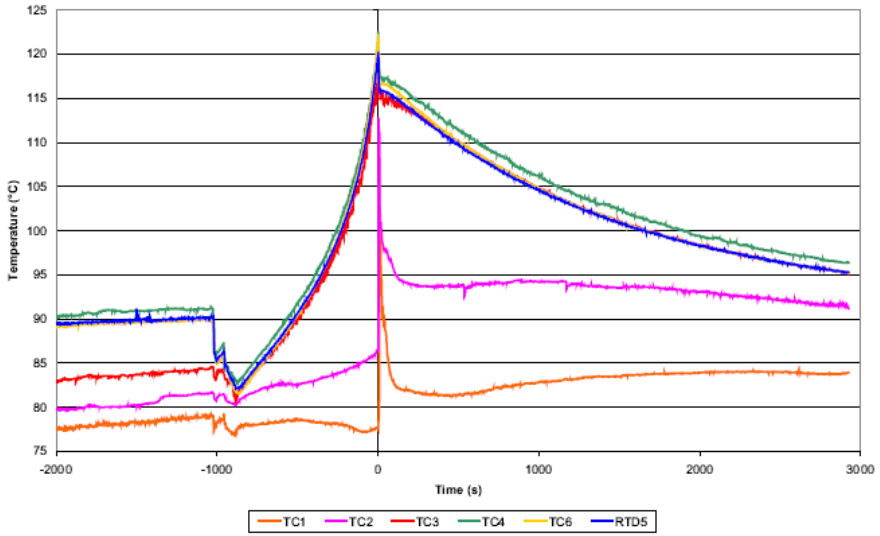Figure 5:   Runaway reaction data for pilot scale Experiment 1.

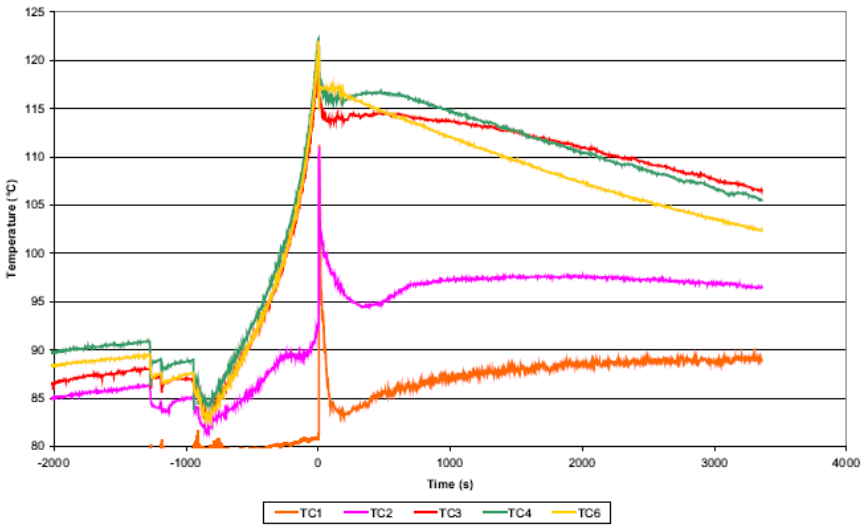Figure 6:   Runaway reaction data for pilot scale Experiment 2.

Figure 7:   Runaway reaction data for pilot scale Experiment 3.

2.5 Application of kinetics

From the rate expression derived in eqn. (2) a theoretical heat output rate may be obtained, in order to simulate the pilot scale experiments. The heat balance must

account for heat generated by the polymerisation reaction as well as the heat transfer to the vessel jacket and the surroundings.

Further analysis reveals that the kinetic fit falls within 1% of the experimental data, and therefore, may be considered adequate for the purposes of modelling.

2.6 Heat transfer analysis

Pilot plant was also used for performing an analysis of the cool down data using dimensionless numbers. This allows the extraction of appropriate coefficients for further modeling. The use of empirical dimensionless group correlations to design large scale plant based upon small scale experimental measurements is well documented, Wilson [2]. In particular the correlation for the inside film heat transfer coefficient for agitated, jacketed vessels has been employed.

The overall heat transfer coefficient (U) is defined as, Perry [3]:

$$U = \frac{1}{\dfrac{1}{h_0} + \dfrac{x}{\lambda_w} + \dfrac{1}{h_i} + ff} \tag{3}$$

Where: (hi) is the inside film heat transfer coefficient; (ho) is the external film heat transfer coefficient; (x/λ_w) is the heat transfer due to conduction across the reactor wall; and (ff) is the fouling factor

Table 2 illustrates the dependence of heat transfer upon stirrer speed.

Table 2:   Internal film heat transfer coefficients.

Experiment	U (W m⁻² K⁻¹)	Φ (W m⁻² K⁻¹)	hi (W m⁻² K⁻¹)
Experiment 1	190	239	915
Experiment 2	155	239	441
Experiment 3	60	239	80

2.7 Comparison between mathematical modeling simulations and runaway reaction trial results

Simulations using the network-of-zones model, Mann et al. [4], were conducted, incorporating the reaction behavior and using the parameters of each of the 210 l pilot plant reactor tests. The injection of a cold fluid results in an initial temperature oscillation, which resolves into a steady value. At the point of successful reaction inhibition, this steady value will follow a decreasing trend, caused by the jacket cooling.

The variation between the different thermocouple probes at different levels revealed how the simulation is predicting the mixing of the incoming inhibitor solution. It was seen that the two central thermocouples were first to be affected by the cool stream, which then spreads out to the upper and lower devices.

As regards the experiment 3, halting of the agitator results in a reduction of fluid motion, which results in a predicted cessation of mixing. At this point, the runaway is predicted to continue, having not been halted. The simulation does not contain any diffusion mechanism to allow mixing to continue.

It was seen that there was some discrepancy between the simulation trends and the experimental results. The magnitude of the initial temperature drop observed in the experiments is less than predicted, the two central probes do not preferentially see the "ribbon" of inhibitor, and the mixing/reaction cessation in experiment 3 is considerably better than predicted.

The principal reason for these differences is considered to be due to inadequacies in the modelling of the incoming jet, the considerable momentum of the actual jet not being reproduced in the simulation. The mathematical description of the introduction of the inhibitor jet, with its associated momentum was considered a primary cause of the differences noted between the simulated and experimental results. Equally, the supplementary mixing due to the gas bubbles has not presently been modelled.

3   Conclusions

The principal conclusion from the three pilot plant trials conducted was that the inhibitor injection system successfully halted the advancing runaway reaction in all cases. Thus the conditions employed for the injection operation were well chosen.

The study considered inhibition during consistent agitation at two different speeds, and agitation failure leading to the rapid decay of liquid swirl.

An analysis of the agitation based solely upon the behaviour of the mechanical stirrer, using both a classical dimensionless number approach and the network-of-zones modelling suggested that the initial mixing (and consequent chemical inhibition performance) should deteriorate as the agitator speed was reduced. The results from the trials do not, however, support this analysis. It is therefore clear that the mixing and turbulence invoked by the injection system dominates that of the mechanical agitator in the pilot scale equipment.

The modelling studies employed so far to analyse the pilot scale results do not provide a detailed analysis of the fluid dynamics of the incoming jet, the momentum of the injection stream being underestimated. Thus the use of the network-of-zones model alone to simulate the system behaviour has presently not been demonstrated.

References

[1] HSE Research Report 145, "Reaction Inhibition in the Control of Exothermic Runaway", Middle KV, Bussey R, Cusco L, Kerr D, Snee TJ, 2003, ISBN 0 7116 2730 6.
[2] Wilson, E.E.. A basis for the rational design of heat transfer apparatus. Am. Soc. Mech. Eng., 1915, 47-83.
[3] Perry's Chemical Engineers handbook, 7th Edition.
[4] Mann, R. et al. Application of a 3-D Networks-of-Zones Mixing Model to a Stirred Vessel. IChemE Symp Series 136, 1994, pp317-32.