DEVELOPMENT OF A DYNAMIC MODEL FOR PRESSURE RELIEF OF GAS GENERATING CHEMICAL REACTIONS

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For untempered gassy systems, controlling the pressure by means of relief does not control the temperature increase due to the runaway reaction. Modelling of the entire course of the runaway reaction is therefore necessary to obtain a safe relief system size. The worst case model assumptions will be those which give rise to the least early mass loss by two-phase venting, since this leaves more reactants in the reactor at the higher temperatures later during the runaway. A dynamic model of a vented gassy runaway reaction has been developed (NIRVANA - new improved relief venting analysis).

INTRODUCTION

The sizing of pressure relief systems for liquid-phase runaway chemical reactions was looked at by DIERS (AIChE Design Institute for Emergency Relief Systems) in the 1980's. An understanding was gained of the level swell mechanism by which a two-phase mixture is vented. Useful short-cut sizing methods were also developed for vapour pressure systems, where the pressure in the reactor is due to vapour only. The main emphasis of the DIERS programme was on vapour pressure systems. Many runaway chemical reactions and decompositions generate non-condensable gas. A short-cut sizing method was proposed for such systems, but the method is usually very conservative and often yields impractically large vent sizes.

A runaway chemical reaction, may be defined as a thermally unstable reaction system which shows an accelerating increase of pressure, temperature and reaction rate, which may eventually result in an explosion. The most common method used to protect process vessels from the catastrophic consequences of a runaway chemical reaction is an emergency relief system, ERS, based upon pressure relief via a bursting disc or safety valve. This paper concerns work being carried out in a project sponsored by EPSRC, HSE and Zeneca. The objective of the project is to develop improved ERS sizing methods for runaway reactions which generate permanent gas, because pre-existing methods usually oversize.

ASSUMPTIONS IN ERS SIZING METHODS

In order to correctly size relief systems for a runaway chemical reaction, it is necessary to determine the following:

- the chemical system involved, according to the mechanism of pressure rise,
- the rate of gas generation during relief of the runaway,
- the vessel flow regime, and
- the vent flow regime.

Chemical systems can be classified according to whether the system pressure is caused by condensables (vapour pressure systems), noncondensables (gassy systems) or both (hybrid systems). This project is concerned with gassy systems.

The rate of gas generation during a runaway reaction increases with time as the reaction accelerates. Gassy systems are 'untempered' in that there is no latent heat to cool the reactant mass, so that the venting process cannot control or limit the reaction rate. A gassy reaction will therefore always reach the maximum adiabatic temperature for the runaway with the corresponding very high reaction rate. However, if the relief system operates early in the runaway, much of the relief process will occur at a lower gas generation rate rather than the maximum.The rate of gas generation can be measured as a function of temperature in a suitable adiabatic calorimeter[3,4].

The vessel flow regime determines the phase (vapour, liquid or two-phase) of the fluid entering the vent and if two phase flow is predicted, the degree of vapour-liquid disengagement. In general, the fluid entering the relief device can be considered to be in one of three categories:

- All Vapour/Gas - total disengagement between vapour/gas and liquid.

- Homogeneous Two-Phase Mixture - zero disengagement. Vapour & liquid are intimately mixed in the vessel, so the fluid entering the vent has equal quality to that in the vessel.

- Churn-Turbulent or Bubbly Flow Regimes - partial disengagement. Venting of a two-phase mixture in which the fraction of liquid entering the vent is less than the average in the vessel.

The fact that two-phase relief occurs is due to the phenomenon of level swell. The chemical reaction will generate gas and the bubbles produced will attempt to rise through the liquid to disengage at the surface. These bubbles occupy volume, so that whilst they are within the liquid the bulk liquid level rises or 'swells'. Two-phase flow occurs if the liquid level reaches the height of the relief device.

From understanding the vent flow regime, the vent mass flux can be determined. Two general categories of flow can be described: flashing and nonflashing flow. For gassy systems the nonflashing two-phase flow equations of Tangaren[1] can be used. These give

similar results for a frictionless system to the Omega method of Leung[2], which can also be used for long relief lines.

DIERS Sizing Method

The DIERS[3] (AIChE Design Institute for Emergency Relief Systems) research project looked at the sizing of pressure relief systems in the 1980's and short-cut sizing methods were proposed for gassy systems (as well as others). The equation recommended for gassy systems is simply:

$$A = \frac{m_r Q_m}{m_e \nu G} \tag{1}$$

where

$$Q_m = \frac{V_e}{P_m}\frac{T_r}{T_e}\left(\frac{dP}{dt}\right)_{m,e} \tag{2}$$

Thus, the above approach is based on the maximum gas generation rate, $\left(\frac{dP}{dt}\right)_{m,e}$, developed by the reaction, even though all the contents of the reactor may have vented due to two-phase flow before this peak gas generation rate occurs. This method is frequently very conservative and often yields large vent sizes which would be impractical to install.

Sizing Methods Which Account For Mass Loss During Relief

Leung[5] derived a vent sizing equation for gassy reactions when homogeneous two-phase relief occurs. However, he cautioned against its use because it can undersize the relief system in cases in which the reactor flow regime is not homogeneous.
Jasbir Singh[4] also derived a simplified vent sizing equation for gassy reactions. This also assumes homogeneous two-phase relief, but offsets this potentially unsafe assumption by using a gas generation rate which is the average of the rate when relief first begins and the peak rate. This method can reduce the calculated vent area by a factor of three compared with the DIERS equation.

A rigorous solution, is also presented by Jasbir Singh and is given in equations (3) & (4) below. The equations take account of vessel emptying via the vent. This theory is then utilised within a computer program called VENTSIZE, which, as well as other functions, uses the adiabatic pressure-time relationship of a runaway chemical reaction to predict the required vent size.

$$\left(\frac{dP}{dt}\right)_v = m_r\beta - F\beta(t - t_v)(1 - x) - \frac{P}{V_g}F\nu \tag{3}$$

where

$$\beta = \frac{V_e}{V_g}\frac{1}{T_e m_e}\left(T_r\left(\frac{dP}{dt}\right)_e + (P - P_l)_e\left(\frac{dT_r}{dt}\right)\right) \qquad (4)$$

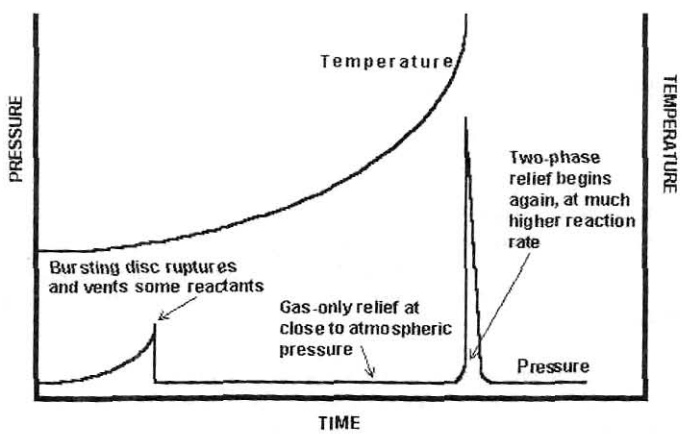
WORST CASE RELIEF ASSUMPTIONS FOR GASSY RUNAWAY REACTIONS

Two-phase relief has two effects:

- it removes reactants from the reactor (this acts to decrease the required relief system size),
- it gives a lower volumetric relief rate (at a given pressure and relief area) than gas-only relief (this acts to increase the required relief system size).

For a gassy runaway reaction, the worst case relief assumptions will be those which give rise to least early mass loss by two-phase venting, since this leaves more reactants in the reactor at the higher temperatures (and reaction rates) which occur towards the end of the runaway. This is illustrated in Figure 1 in which the early relief is of gas only and two-phase relief begins only later at much higher reaction rates.

Figure 1 Possible Worst Case Behaviour Of A Gassy System During Relief



The extreme case of the situation shown in Figure 1 is the DIERS gassy reaction assumptions. These are essentially that gas-only relief (no mass loss of reactants) occurs for the whole of the runaway except that two-phase relief begins just as the reaction rate reaches its peak. Most real situations will not be as bad as DIERS assumptions. Either some two-phase relief will occur prior to the peak reaction rate being attained, or gas only relief will occur for the entire duration of the runaway.

In order to obtain a more realistic relief size than calculated using the DIERS equation, it is necessary to model the level swell and gas/liquid disengagement which occurs in the reactor over the entire course of the vented runaway reaction. The safe, worst case assumptions for this level swell modelling are those which give rise to the most gas/liquid disengagement and hence the least early mass loss. The possible flow regimes that can be modelled using DIERS methodology[3] are:

- homogeneous,
- bubbly, and
- churn-turbulent.

Of these, churn-turbulent gives the most disengagement (lowest mass loss) and is therefore chosen as the worst case.

DEVELOPMENT OF A DYNAMIC MODEL

In order to model the level swell behaviour throughout the course of a vented gassy reaction, a dynamic model was required. SAFIRE[3] which was developed for DIERS structures its physical property routine in a such a way that it cannot handle a pure gassy reaction. VENTSIZE[4], although it uses the churn-turbulent model to determine whether two-phase venting will occur or not, assumes two-phase venting to be homogeneous. As discussed above, this is not a safe assumption for gassy reactions. It was therefore decided to develop a new dynamic model.

DIERS produced the coupling equation (shown below), a gas/vapour mass balance at the vessel/vent junction, which utilises vessel and vent models to calculate the volumetric discharge rate from the vessel and the weight fraction of gas entering the vent. This can be used for the churn-turbulent and bubbly flow regimes, but the churn-turbulent version is shown here.

$$\frac{xGA_{ven}}{U\rho_g \lambda A_{vess}} = \frac{1}{1 - C_o \lambda a} \qquad (5)$$

where,

$$a = \frac{(1-x)}{rx} \quad , \quad r = \frac{\rho_l}{\rho_g} \quad , \quad \& \quad \lambda = \frac{2\alpha}{1 - C_o \alpha}$$

Therefore, using the coupling equation (5) with equations (3) & (4) should give more accurate, yet conservative results.The parameter, C_o, is a tuning factor within the churn-turbulent model. The best estimate value[3] is 1.5 and that has been used in the work described in this paper.

The dynamic model which has been written to do this is named NIRVANA (New Improved Relief Venting Analysis). This model has been written for research purposes and is not intended to be made commercially available. It has been written in FORTRAN 77 and SI units are used throughout. NIRVANA assumes the vent is a bursting disc and once open, the type of discharge (either single-phase or two-phase flow) is determined

using the churn-turbulent model. From there, the mass flux and weight mass fraction of gas entering the vent are calculated before the pressure in the vessel is determined. A flowchart of the program can be seen in Figure 2.

CALORIMETRIC DATA

For any ERS design, experimental data is required for the rates of heat and gas generation. This needs to be measured in a specially developed adiabatic calorimeter whose thermal inertia (heat capacity of calorimeter and sample/heat capacity of sample) is very close to unity. Examples of this are the adiabatic dewar[6], VSP[3] and Phitec[4].

Data for use in NIRVANA was obtained from two sources; firstly, measurements made by Jaswant Singh using adiabatic dewar and bench scale apparatus (similar to VSP calorimeter) from Zeneca, and secondly, measurements made on behalf of the Health & Safety Laboratory using the Phitec calorimeter. Two organic peroxides were tested:

- Trigonox 21 (T21) - Tert-butyl peroxy 2-ethyl hexanoate.
- Trigonox 42S (T42) - Tert-butyl peroxy 3,5,5-trimethyl hexanoate.

Both are highly reactive and decompose exothermically to produce gaseous products. Before any of the tests, the peroxides were mixed with an inert solvent, Shellsol T, in a 20 wt% peroxide - 80 wt% solvent mixture to dilute the peroxides and reduce the reaction rate.

The results shown in this paper use the data generated from the decomposition of T21 in an adiabatic dewar, as shown in Figure 3.

MODELLING OF TEST DATA

Prediction Of Calorimetric Data

This section describes how both NIRVANA & VENTSIZE were used to predict the calorimetric test from which the kinetic data used in the codes was obtained, i.e. using the calorimetric data described above and modelling the adiabatic dewar as the reactor. The dimensions used are described here:

Volume = 1litre = $1 \times 10^{-3} m^3$
Cross Sectional Area = $4.4356 \times 10^{-3} m^2$

The set pressure was fixed at 2×10^7 Pa so as not to allow venting. Figure 4 shows the comparison between NIRVANA & VENTSIZE against the experimental data.

Both models over predict the rate of pressure change with time. VENTSIZE giving higher values than NIRVANA. The probable reason as to why both models over predict, is that both use linear interpolation methods in their calculation procedures and this over estimates true rate values. Another reason may be inaccuracy in the gas-space volume of the dewar which was assumed in the modelling.

Numerical Sensitivity

A subroutine in NIRVANA gives the user the option of introducing divisions (time steps) between experimental time points. (Both NIRVANA and VENTSIZE use the time/temperature/pressure data points from calorimetric experiments as input) It was written to increase the accuracy of the calculation of mass loss from the reactor during two-phase flow. Using the same set case as before, Figure 5 shows how changing the time step affects the predicted peak pressure in the reactor and mass lost due to two-phase flow.

The results show how both the peak pressure and mass lost become relatively more stable above a time step division of one fifth than below it. This indicates how numerically sensitive predictions can be. All the runs of NIRVANA reported here used a time step division of one fifth.

Evaluation of Complete Pressure-Time Profile

To compare the output from the two computer models, a specific case was defined, i.e. a reactor volume, $V_{vess} = 7.5\ m^3$, initial gas space volume fraction, $a_o = 0.15$ & set pressure, $P_{set} = 3x10^5$ Pa. Both models require a predicted vent area and this was calculated using equation 1. As previously mentioned, this value would frequently be very conservative, but for the purposes of evaluating a pressure-time profile to compare models, it was suitable.Different simulations assumed both churn-turbulent and homogeneous flow. The results are shown in Figures 6 -9.
The plots indicate the rate of change of pressure and mass in the reactor with time. They show, that for the same case for churn-turbulent flow (Figures 6 & 7), VENTSIZE predicts higher mass losses than NIRVANA, and that NIRVANA predicts higher peak pressures than VENTSIZE. This suggests that VENTSIZE is less conservative than NIRVANA and confirms the suspected behaviour discussed above. In both cases, gas-only venting was predicted for most of the relief process, with two-phase relief beginning at close to the peak rate. For these runs, with the very large DIERS vent size, the final predicted peak pressure (close to the experimental peak rate) was less than the bursting pressure of the (already open) disc.

Comparison with Figures 8 & 9, which are for the homogeneous venting assumption, show that for homogeneous venting, only very small pressure increases above atmospheric occurred once the disc had burst, compared with a pressure peak of around $2x10^5$ Pa for the churn-turbulent assumption in Figures 6 & 7. This confirms the expectation that churn-turbulent vessel behaviour is worse than homogeneous.

Effect Of Varying Vent Area

The pressure-time profiles, Figures. 6 - 9, were produced using a vent area calculated from DIERS methodology. In this section, NIRVANA was used to predict further profiles using smaller vent areas. The results are shown in Figure 10. From these predictions, it can be seen that;

- venting occurs at approximately 4650s,
- the experimental peak rate of pressure rise occurs at approximately 6400s,
- at this point, the predicted pressure rise increases with decreasing vent area,
- the simulations using the two largest vents predicted two-phase flow.
- a second smaller pressure peak is obtained for these two simulations which predicted two-phase flow.

Further simulations are planned which will look at conditions which give rise to two-phase relief and at vent areas which are smaller fractions of the DIERS vent area, given by equation 1.

CONCLUSIONS

- The worst case assumptions used for modelling the relief of a gassy reaction are minimum early mass loss (gas-only venting) together with final two-phase venting. The corresponding worst case level swell assumption is churn-turbulent with C_0=1.5.

- A new dynamic model, NIRVANA, has been developed which uses the material balance proposed by Jasbir Singh together with a rigorous application of the churn-turbulent model using the DIERS coupling equation.

- Due attention needs to be paid to the size of the time-step used in dynamic modelling of gassy reactions in order to avoid numerical instability.

- NIRVANA is more conservative for gassy system vent sizing than VENTSIZE, which assumes homogeneous two-phase flow whenever the churn-turbulent model predicts two-phase flow

FUTURE WORK

Further work is planned to extend the parametric sensitivity study using NIRVANA. The code is to be partially validated using Laboratory-scale vented runaway reaction tests at the Health and Safety Laboratory. A heat transfer model will be added to the code to facilitate this.

Acknowledgements

Sponsorship by EPSRC, HSE and ZENECA under a CASE award is gratefully acknowledged. The Hazard Evaluation Laboratory kindly provided access to the VENTSIZE code.

NOMENCLATURE

A	Area of Vent	m^2	t	Time	s
a	Parameter in Eqn. 5	-	U	Single Bubble Rise Velocity	m/s
C_o	Parameter in Calculating Superficial Gas Velocity	-	V	Volume	m^3
F	Mass Venting Rate	kg/s	x	Weight Fraction of Gas	-
G	Two-Phase Mass Flux	kg/m^2s	α	Void Fraction	-
m	Mass	kg	β	Rate of Pressure Rise per unit Mass of Reactant	Pa/s.kg
P	Pressure	Pa	λ	Parameter in Eqn. 5	-
Q	Gas Generation Rate	m^3/s	ν	Specific Volume of Two-Phase Mixture	m^3/kg
r	*Parameter in Calculating a*	-	ρ	*Density*	kg/m^3
T	Temperature	K			

Subscripts

e	Experimental	r	Reactor
g	Gas	v	Vented
i	Initial	ven	Vent
l	Liquid	vess	Vessel
m	Maximum		

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Figure 2 Simplified Flow Chart For NIRVANA

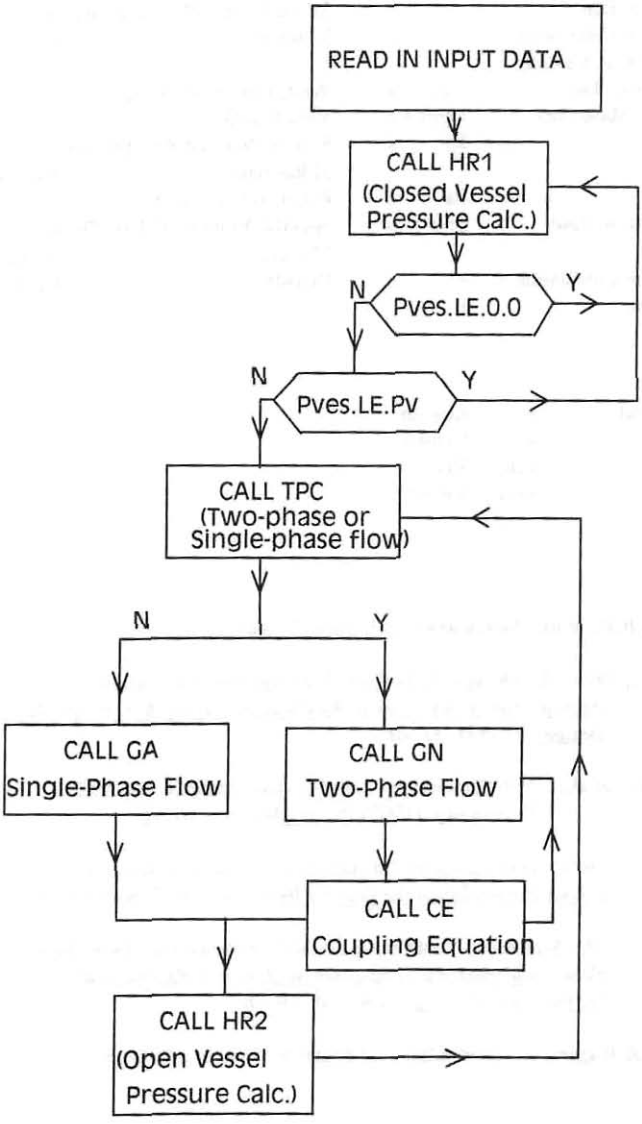

FIGURE 3

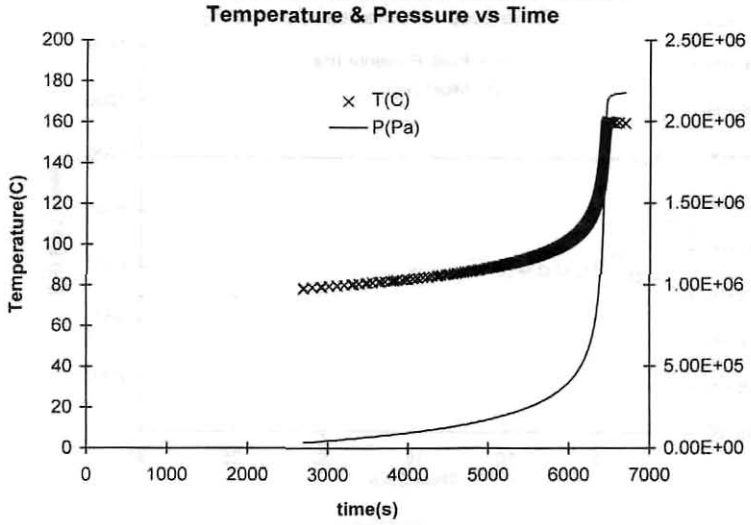

FIGURE 4

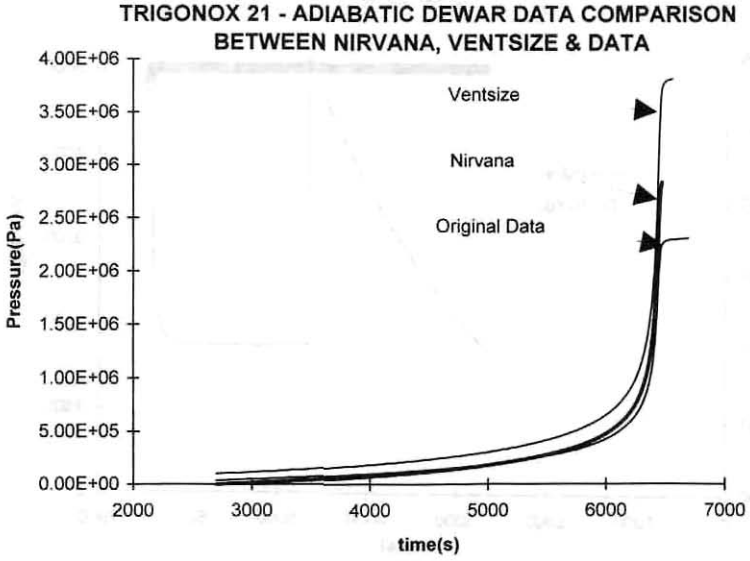

FIGURE 5

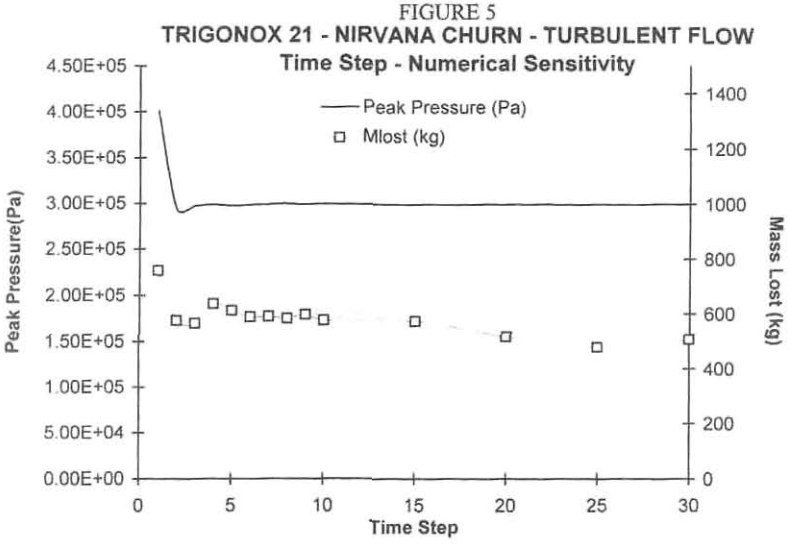

FIGURE 6

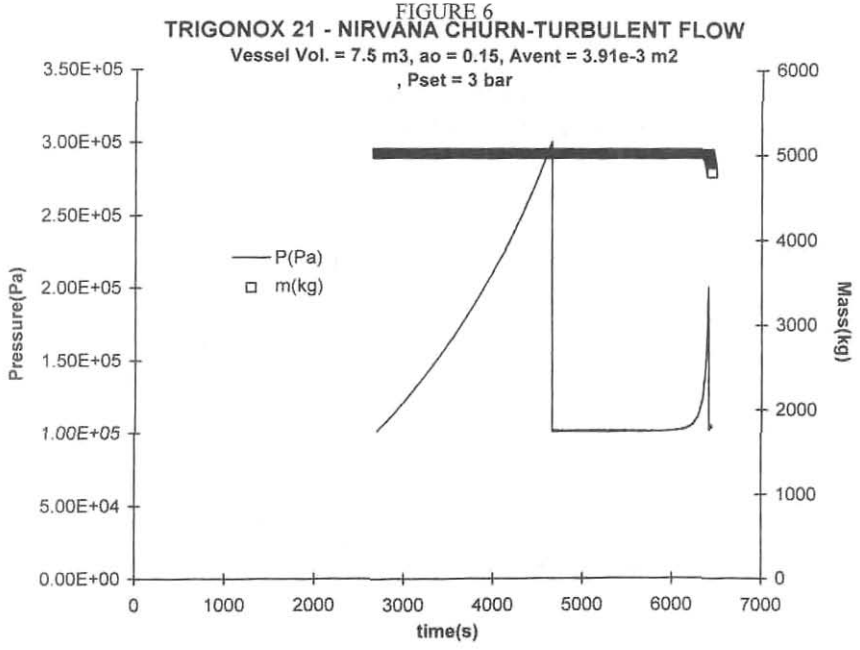

FIGURE 7

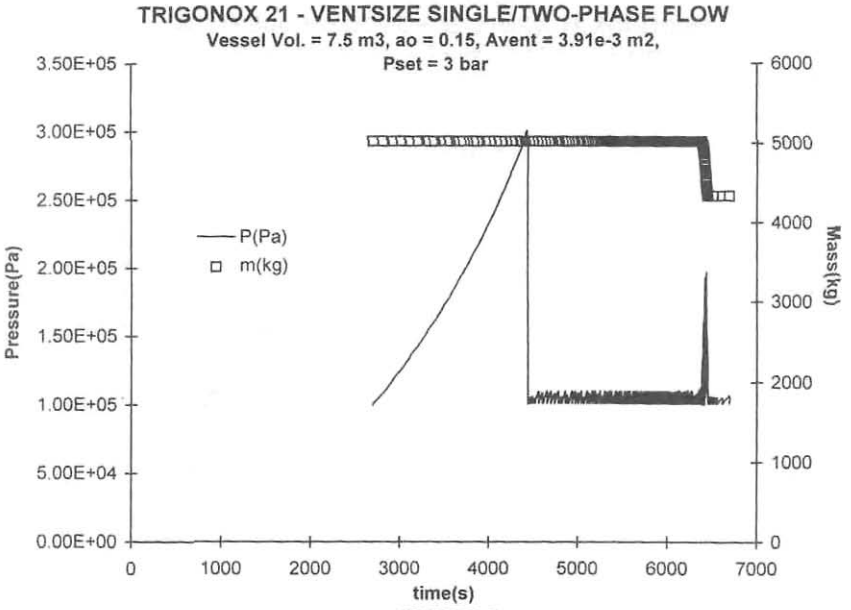

FIGURE 8

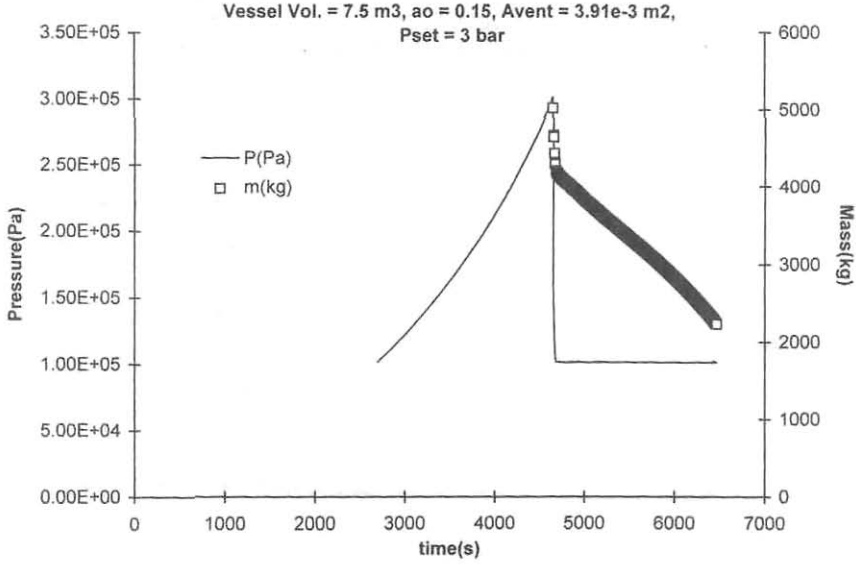

FIGURE 9

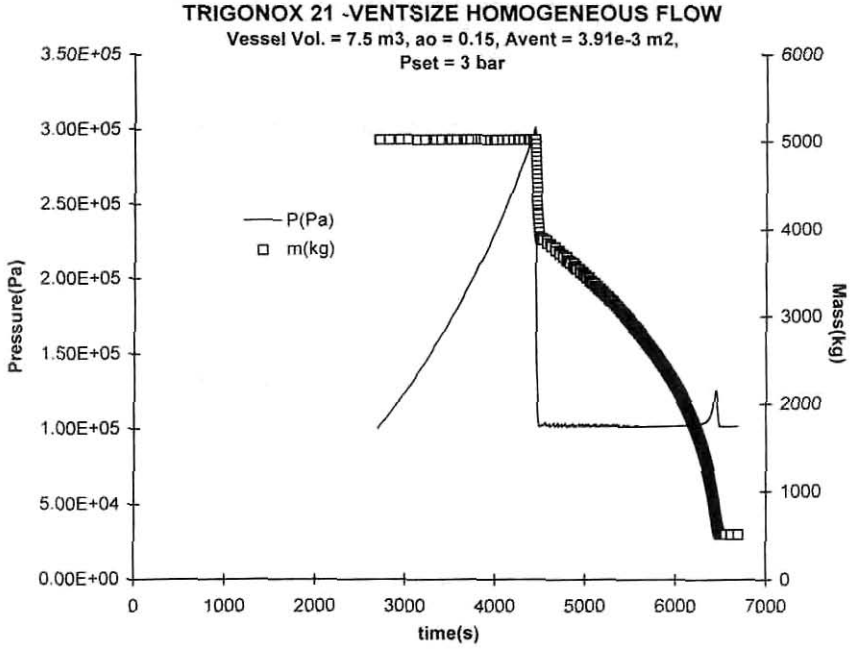

FIGURE 10