



CRITICAL FLOW IN A CHEMICALLY REACTING TWO-PHASE MULTICOMPONENT MIXTURE

J. S. DUFFIELD, G. FRIZ and R. NIJSING

CEC Joint Research Centre, Ispra Establishment, I-21020 Ispra (Va), Italy

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Abstract—A model that describes the critical flow of chemically reacting, two-phase, multicomponent mixtures in channels of constant cross section is discussed. As a consequence of an assumed interphase thermal and mechanical equilibrium the applicability of the model is restricted to situations where one phase is intimately mixed with the other, such that choking is determined by the sound speed in the homogeneous mixture. It is shown that under certain conditions the highly non-linear temperature dependency of the reaction rate promotes the possibility of a multiplicity of steady state solutions to the problem.

Key Words: critical flow, two-phase, multicomponent, chemical reaction

1. INTRODUCTION

Much of the interest in critical flow has resulted from the safety assessment studies related to nuclear power reactors, particularly the investigation of Loss of Coolant Accidents (LOCA), and has concerned steam water mixtures. More recently however, the chemical industry has become interested in critical flow with the realization that two-phase conditions often exist in the vent line when chemical reactors and storage vessels are relieved following a thermal runaway event.

The concept of critical flow can be explained in simple terms as follows. To maintain a steady flow of a fluid through a channel a certain pressure difference is required to overcome the frictional forces. In the case of a compressible fluid the pressure drop along the channel causes a decrease in fluid density. By reason of continuity, a decrease in density results in an increase in velocity. The increased velocity in turn causes a higher frictional and an additional acceleration pressure drop. This mechanism leads to a continuous increase of the pressure loss along the channel. When the pressure gradient becomes infinite, critical conditions have been reached. In channels of constant cross section the steady state flow rate adjusts itself so that the choking plane coincides with the channel exit. This process is well known in gas dynamics and for ideal gases and special boundary conditions there exist analytical solutions to the problem.

If the fluid in the channel is not a pure gas, but a mixture of liquid and vapour phases, the mathematical description of the channel flow is more complicated. The pressure density interdependence is no longer given by the simple ideal gas law and the phases may have different velocities. An ongoing chemical reaction in the liquid phase adds a further complication as the fluid is now composed of different chemical substances (reactants, reaction products, solvents, dissolved gases, catalysts, etc.), the concentrations of which change along the channel. The chemical process may produce heat, the rate of which depends on the composition and the temperature of the fluid in a non-linear way. The treatment of this complex problem requires a numerical approach and is facilitated by the introduction of simplifying assumptions.

This paper presents results obtained from a homogeneous channel model for the critical flow of a multicomponent fluid mixture in which chemical reaction occurs in the liquid.

2. CRITICAL FLOW MODELS

Many review articles have been written describing critical two-phase flow, for example see Giot (1988), Wallis (1980), Weisman & Tentner (1978), Bouré *et al.* (1976), Ardron & Furness (1976); the common approach is to divide the models into two categories, namely equilibrium and

non-equilibrium models. Equilibrium models assume that both mechanical and thermal equilibrium exists and the two-phase fluid mixture behaves as a pseudo-fluid that can be described by the same equations as an equivalent single-phase flow, whereas non-equilibrium models allow for mechanical (phasic velocity) and thermal (phasic temperature) differences between the phases. A plethora of models exist in the literature that in some way or another account for these differences between phasic properties, some are purely empirical (e.g. Henry & Fauske 1971; Simpson & Silver 1962), others are physically based models where the phasic conservation equations for mass, momentum and energy are solved together with the accompanying constitutive laws that describe the interfacial transport processes (e.g. Ishii 1975; Bouré 1977; Ardron 1978; Richter 1983; Dobran 1987). The difficulty with these "mechanistic" models arises in the formulation of the constitutive relationships which requires a detailed knowledge of the flow structure, and all these models involve to some extent adjustable parameters such as a critical liquid superheat required to cause bubble nucleation, an initial bubble diameter and density of nucleation sites.

In situations where the transit time of the fluid in the channel is short compared to the relaxation times associated with the transfer of heat and mass, and the formation of new interfaces then non-equilibrium effects must be considered. This is the case for estimating the critical mass flow rates through nozzles, orifices and short tubes and for flow regimes such as annular flow where little interfacial momentum transfer occurs. Conversely, there appears general agreement that the equilibrium approach is successful in predicting the critical mass flux for the flow in long pipes and for flow patterns where the interfacial friction is significant, such as dispersed flow. For such a flow where one phase is intimately mixed with the other by far the most important relaxation process when considering its effect on the mass flow rate is thermal relaxation (Shepherd 1989). This mechanism controls the transfer of heat from the liquid to the interface and hence the phase change rate. Typical values of the time constant associated with this phenomenon are in the order of metres per second, which compares to a transit time of the fluid in a channel of length much less than 1 m. Fauske (1983) has shown that for channels of length greater than 10 cm there is sufficient time for thermal equilibrium to have been attained.

The problem this paper addresses is how critical flow is affected by an ongoing exothermic reaction in the liquid phase where a non-condensable gas is present as a reaction product. Physically this chemical process manifests itself by the appearance of a strongly temperature dependent source of heat production and a source of volume production homogeneously distributed over the liquid phase. Since the time constants associated with chemical reactions are normally many orders of magnitude smaller than those describing thermal relaxation the governing mechanism will remain that of thermal relaxation.

For the above reasons it has been decided to adopt the equilibrium approach in formulating the critical flow model.

3. MODELLING OF MULTICOMPONENT FLUID FLOWS

The following assumptions or simplifications have been made:

- steady state flow
- constant flow section
- thermal and mechanical equilibrium between the phases
- constant friction factor
- component distribution governed by phase equilibrium
- ideal liquid solution behaviour (Raoult's law)
- solubility of non-condensables described by Henry's law
- ideal gas behaviour.

3.1. Basic equations

Consider a pipe element of diameter d_h , with an inclination θ to the horizontal, then over the length dz there are the following contributions to the pressure drop, dp :

—by acceleration: $dp_{acc} = -\rho_m u du$

$$\text{—by friction:} \quad dp_{\text{fric}} = -\frac{2f\rho_m u^2}{d_h} dz$$

$$\text{—by gravity:} \quad dp_{\text{grav}} = -g\rho_m \sin \theta dz$$

where ρ_m is the mean density of the mixture, u is the mean fluid velocity, f is the Fanning friction factor and g the acceleration due to gravity. The total pressure drop along the pipe element dz is then the sum of the three contributions:

$$dp = -\rho_m u du - \frac{2f\rho_m u^2}{d_h} dz - g\rho_m \sin \theta dz. \quad [1]$$

As the flow is steady state and the flow section is assumed to be constant the continuity equation gives a constant mass flux, G and the pressure gradient along the pipe can be expressed in terms of G ,

$$\frac{dp}{dz} = -\frac{G^2 dv_m}{dz} - \frac{2fG^2 v_m}{d_h} - \frac{g \sin \theta}{v_m}. \quad [2]$$

The above equation can be readily integrated if a relationship is known between p and v_m . For example if the fluid is assumed to be a perfect gas and the flow is adiabatic and the gravity term is negligible, the following well known expression in gas dynamics for Fanno flow can be derived,

$$-\frac{dp}{dz} = \frac{2fG^2 v_m}{d_h} \left\{ \frac{1 + (\gamma - 1)M^2}{1 - M^2} \right\} \quad [3]$$

where M is the local Mach number and γ is the ratio of specific heats C_p/C_v . Critical conditions occur when the fluid velocity equals the local sound speed i.e., Mach number 1, and where of course the pressure gradient tends to ∞ . The situation is much more complicated if one considers a multicomponent mixture in which phase change and chemical reaction occurs, as the relationship between p and v_m is not described by a simple equation of state.

3.2. The interdependence of density, pressure, heat input and reaction rate for a multicomponent mixture

The central problem in modelling the pipe flow of a chemically reacting fluid is the interdependence between pressure, temperature, specific volume (or density) and composition at a given rate of chemical reaction and a given heat input from the outside.

The nomenclature used in the following section is a compromise between that familiar to chemical engineers and that familiar to mechanical engineers. This results in the component mole fraction in the liquid phase being denoted by x_i , the component mole fraction in the gaseous phase by y_i and the component mass fraction by X_i .

Consider a portion of a mixture which has the mass m , and is composed of an arbitrary number of components (NSUB). A part of the mass m is present in the liquid phase, the rest in the gaseous phase.

If m_{Gi} is the mass of component i in the gaseous phase and m_{Li} the mass of component i in the liquid phase one can define:

$$X_{Gi} \equiv \frac{m_{Gi}}{m} \quad \text{gas mass fraction of component } i$$

$$X_{Li} \equiv \frac{m_{Li}}{m} \quad \text{liquid mass fraction of component } i. \quad [4]$$

The mass fraction of component i in the mixture is then:

$$X_i = X_{Gi} + X_{Li}. \quad [5]$$

The composition of the *separate phases* is described in terms of mole fractions. The gas phase mole fraction of substance i is given by:

$$y_i = \frac{X_{Gi}/M_i}{N_G} \quad [6]$$

where M_i is the component molecular weight and N_G is the total number of moles in the gaseous phase.

Similarly, the liquid phase mole fraction is given by:

$$x_i = \frac{X_{Li}/M_i}{N_L} \quad [7]$$

where N_L is the total number of moles in the liquid phase.

If the heat of mixing is excluded the single component enthalpies can be summed to obtain the specific enthalpy of the two-phase mixture, h_m :

$$h_m = \sum_{i=1}^{NSUB} (h_{Li}X_{Li} + h_{Gi}X_{Gi}) \quad [8]$$

where h_{Li} is the liquid specific enthalpy and h_{Gi} is the gas specific enthalpy of component i at temperature T and pressure p . Similarly, the mixture specific volume, v_m , is given by:

$$v_m = \sum_{i=1}^{NSUB} (v_{Li}X_{Li} + v_{Gi}X_{Gi}) \quad [9]$$

where v_{Li} is the liquid specific volume and v_{Gi} is the gas specific volume of component i at T and p .

The total pressure p in a multicomponent mixture is given by the sum of the component partial pressures. For ideal mixtures the partial pressure p_i of component i is given by the product of the component liquid mole fraction and the saturation pressure $p_{sat(i)}$ of the pure component i at the given temperature (Raoult's law). If a component i is non-condensable $p_{sat(i)}$ can be replaced by Henry's constant H .

The sum of the partial pressures yields the total pressure:

$$\sum_{i=1}^{NSUB} p_i = p = \sum_{i=1}^{NSUB} p_{sat(i)}x_i \quad [10]$$

If the gaseous phase is considered to be composed of ideal gases the partial pressure p_i of a component is equal to the product of the gas phase mole fraction and the total pressure, i.e.

$$p_i = py_i \quad [11]$$

The distribution of a component over liquid phase and gas phase is then given by,

$$\frac{y_i}{x_i} = \frac{p_{sat(i)}}{p} \quad [12]$$

To describe the ongoing thermochemical process in a reacting multicomponent two-phase mixture the time derivatives of the relevant parameters p , T , h , v and the component phasic mass fractions are required. If the energy conservation equation is used in the form,

$$\frac{dh_m}{dt} = v_m \frac{dp}{dt} + q_a \quad [13]$$

where q_a is the heat input rate due to conduction, friction and chemical reaction per unit mass, then [5–13] can be used to obtain the following linear relationship between the time derivatives of mixture specific volume and pressure:

$$\frac{dv_m}{dt} = A + B \frac{dp}{dt} \quad [14]$$

Substituting the above relation into [2] gives the following expression for the pressure gradient along the pipe:

$$\frac{dp}{dz} = \frac{G}{u} \frac{GA + \frac{2f}{d_h} u^2 + g \sin \theta}{1 + BG^2} \quad [15]$$

The factors A and B are rather complicated functions of mixture composition and component properties. Their physical meaning can be understood if one first considers a change at constant

pressure. The change in the specific volume of the mixture is then only a result of the heat source q_a and a change in the composition by chemical reaction; this is described by the factor A . In the absence of heat sources chemical reaction A is zero. In this case the $p \sim v_m$ interdependence is isentropic, and from this it follows that:

$$B = \left(\frac{dv_m}{dp} \right)_{\text{isentropic}} \quad [16]$$

B is related to the sound speed c_s of the homogeneous mixture:

$$c_s = v_m \sqrt{\left(-\frac{dp}{dv_m} \right)_{\text{isentropic}}} \quad [17]$$

and [14] can be written:

$$\frac{dv_m}{dt} = A - \left(\frac{v_m^2}{c_s^2} \right) \frac{dp}{dt} \quad [18]$$

If M is defined as the local Mach number of the two-phase mixture, i.e. $M = (u/c_s)$,

$$B = -\frac{M^2}{G^2} \quad [19]$$

and the pressure gradient along the pipe can then be written as:

$$-\frac{dp}{dz} = \frac{G}{u} \frac{GA + \frac{2f}{d_h} u^2 + g \sin \theta}{1 - M^2} \quad [20]$$

One should note the similarity between the above equation and [3] that describes single phase Fanno flow.

3.3. Flow conditions at the pipe entrance

To calculate the pressure distribution along the pipe length by integration of [15] the conditions at the pipe entrance are required. If the stagnation conditions are given one must know how the pressure and the other variables change during the acceleration phase from the stagnation conditions to the pipe entrance.

If the acceleration period is short compared to the residence time in the pipe it is justified to neglect in this phase of the calculation the chemical conversion, friction and gravity terms.

Thus only the acceleration pressure drop is considered,

$$dp = -\rho_m u \, du \quad [21]$$

and using [18] with $A = 0$,

$$\frac{dv_m}{dt} = -\left(\frac{v_m^2}{c_s^2} \right) \frac{dp}{dt} \quad [22]$$

gives:

$$\frac{dG^2}{dp} = -2\rho_m \left[1 - \left(\frac{u}{c_s} \right)^2 \right] \quad [23]$$

Integration of [23] from stagnation conditions $p = p_0$, $\rho_m = \rho_{m0}$, $u = 0$ and $G = 0$ up to the pipe entrance conditions yields all the necessary pipe entrance parameters as a function of the mass flux, G .

4. ILLUSTRATIVE CALCULATIONS

When in accident situations the fluid mixture comprises solely of condensable components, the fluid mixture entering the vent line is at saturation conditions. Under these circumstances there is a close coupling between the fluid temperature and pressure because of the evaporation process. The pressure decrease associated with the expansion of the fluid at the inlet of the vent line due

to acceleration, and in the pipe due to friction is accompanied by a decrease in temperature. This decrease in temperature will cause a reduction in any reaction in the vent line due to the exponential temperature dependence of the chemical reaction rate. Under these circumstances it is admissible to ignore chemical reaction in the vent line.

If the fluid mixture contains a non-condensable gas (produced by a chemical reaction), the situation is different. The total pressure is then not just the saturation pressure belonging to the mixture of condensable components, but a combination of this pressure and the partial pressure exerted by the inert gas. When the total pressure is dominated by the presence of an inert gas the expansion of the fluid due to pressure loss does not entail a latent heat of evaporation and hence is not accompanied by a significant reduction in the temperature of the liquid phase. Pressure and temperature are then largely uncoupled and under these circumstances the effect of an exothermic chemical reaction on critical flow behaviour may become important and should be considered.

The illustrative calculations presented below consider such a case which can be thought of as being prototypical of peroxide decomposition reactions.

4.1. Calculation procedure

The equation system is treated as an initial value problem and a marching procedure is applied to a Lagrangian mass element with a known value of G . The solution scheme is explicit and the timestep is automatically determined such that Courant and other criteria are not violated.

The practical problem is the determination of the mass flux G through a pipe or tube of a given length, diameter and inclination which is attached to a vessel. The procedure to solve this problem is summarized below:

- (1) Equation [23] describes the relationship between G and the pressure change from stagnation to pipe entrance conditions, p_{in} . Integrating this equation for different values of G gives the function:

$$p_{in} = p_{in}(G, p_0).$$

The maximum possible flow G_{max} is obtained by extending the integration to $dG/dp = 0$.

- (2) A value of G is chosen in the range:

$$0 < G < G_{max}.$$

- (3) Integration of [15] along the pipe, with the chosen value of G , from the inlet pressure $p_{in} = p_{in}(G, p_0)$ down to the outlet pressure p_{out} will give a certain pipe length. If critical conditions prevail, i.e. the pressure gradient becomes infinite or the Mach number becomes one, the critical length l_c is obtained. If critical conditions are not achieved, sub-sonic flow prevails and the pipe length is determined by noting when the pressure reaches the outlet pressure.
- (4) By changing G in narrow steps the function: $l_c = f(G, \text{stagnation conditions})$ is obtained and by inversion $G_c = f(l_c, \text{stagnation conditions})$.

Once the mass flux is known, the numerical integration of [15] gives all the other parameters (temperature, density, velocity, composition, etc.) as function of the distance from the pipe entrance.

4.2. System considered, initial and boundary conditions

The chemical system considered is a mixture of water, hydrogen peroxide and oxygen. The liquid phase is composed of 50% H_2O and 50% H_2O_2 , by mass.

The gas phase composition results from the partial pressures of water and hydrogen peroxide (which are functions of temperature) and the oxygen pressure which was chosen such as to obtain the desired stagnation pressure.

The chemical process is the decomposition of hydrogen peroxide:



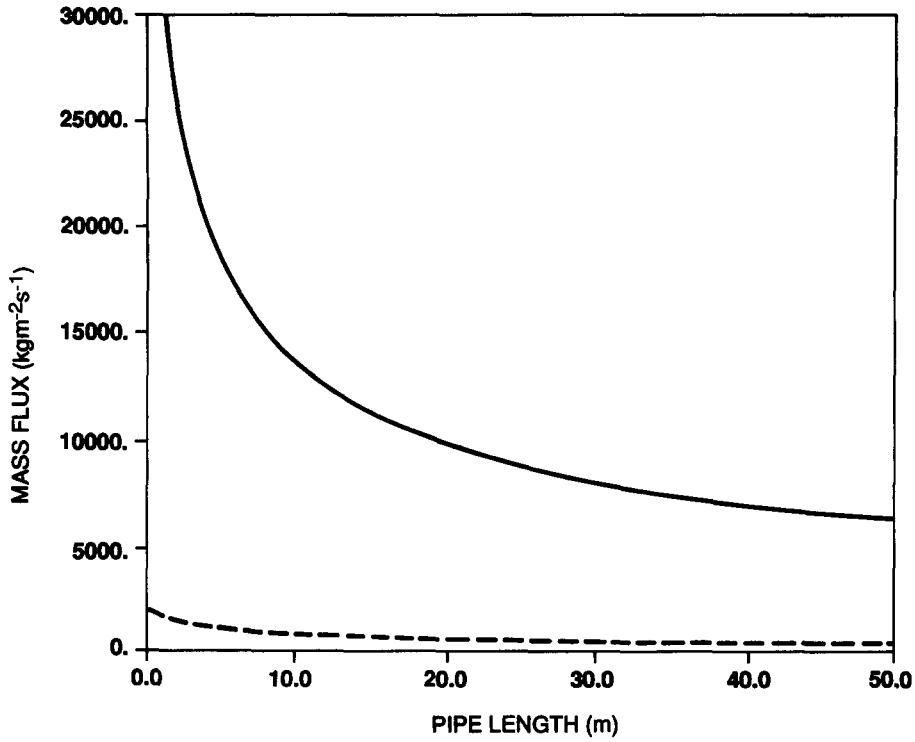


Figure 1. Critical mass flux for pipes of varying length, non-reacting hydrogen peroxide water system (—, $\epsilon_0 = 0$; ····, $\epsilon_0 = 1$).

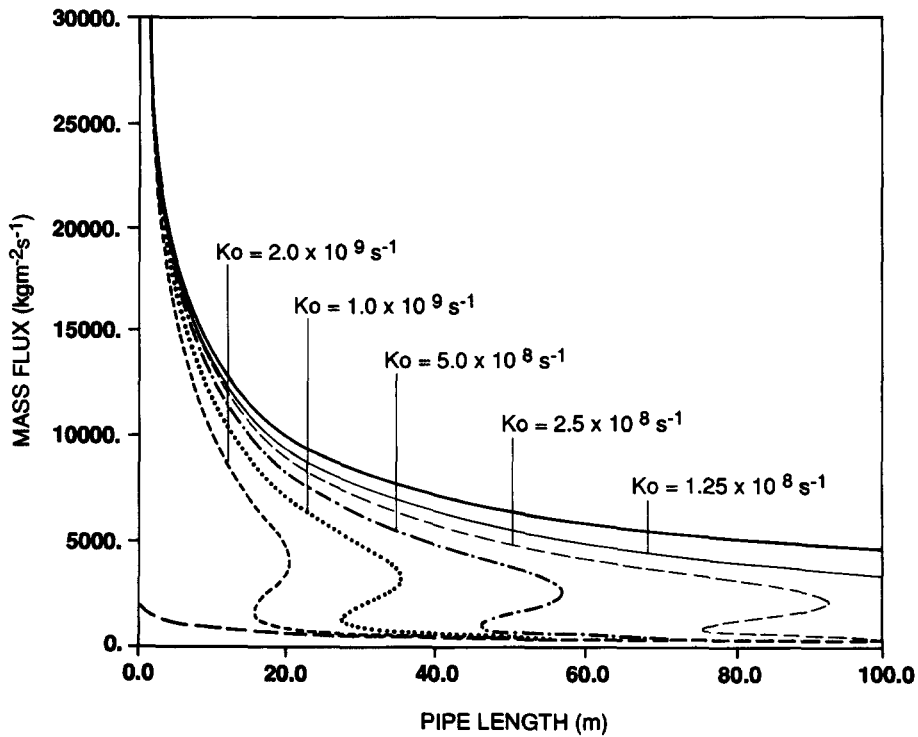


Figure 2. Critical mass flux for pipes of varying length, showing the effect of different liquid phase chemical reaction rates.

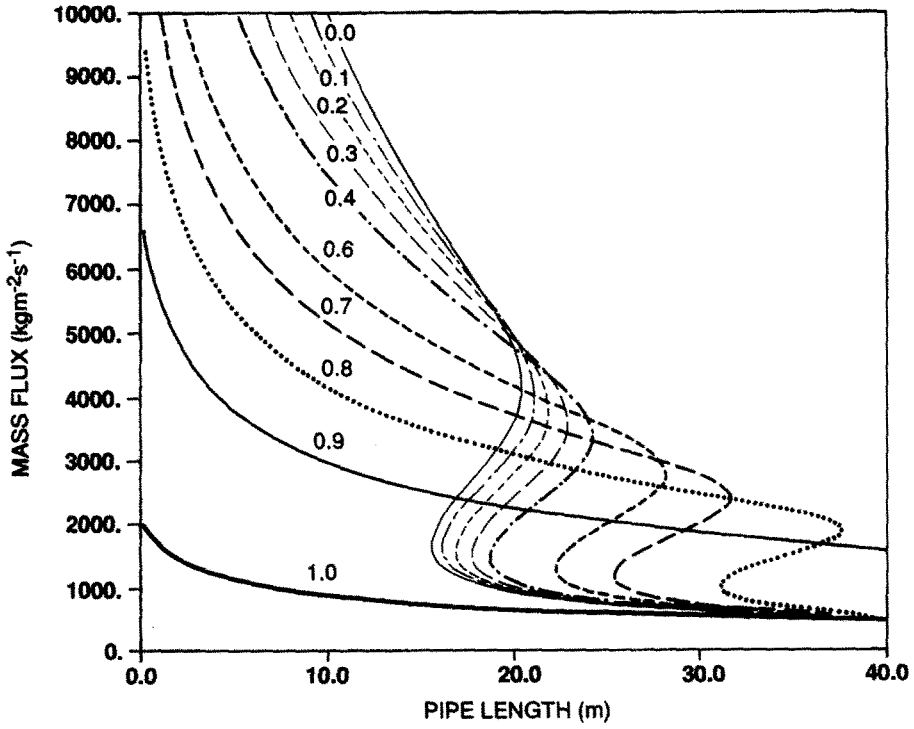


Figure 3. Critical mass flux for pipes of varying length, showing the effect of different stagnation void fractions.

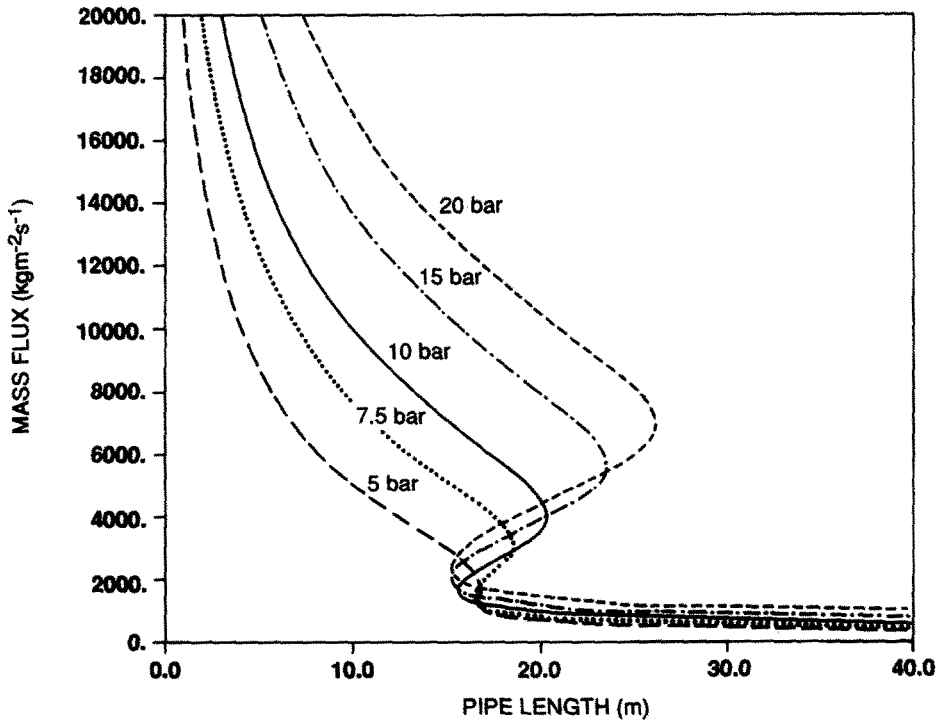


Figure 4. Critical mass flux for pipes of varying length, showing the effect of different stagnation pressures.

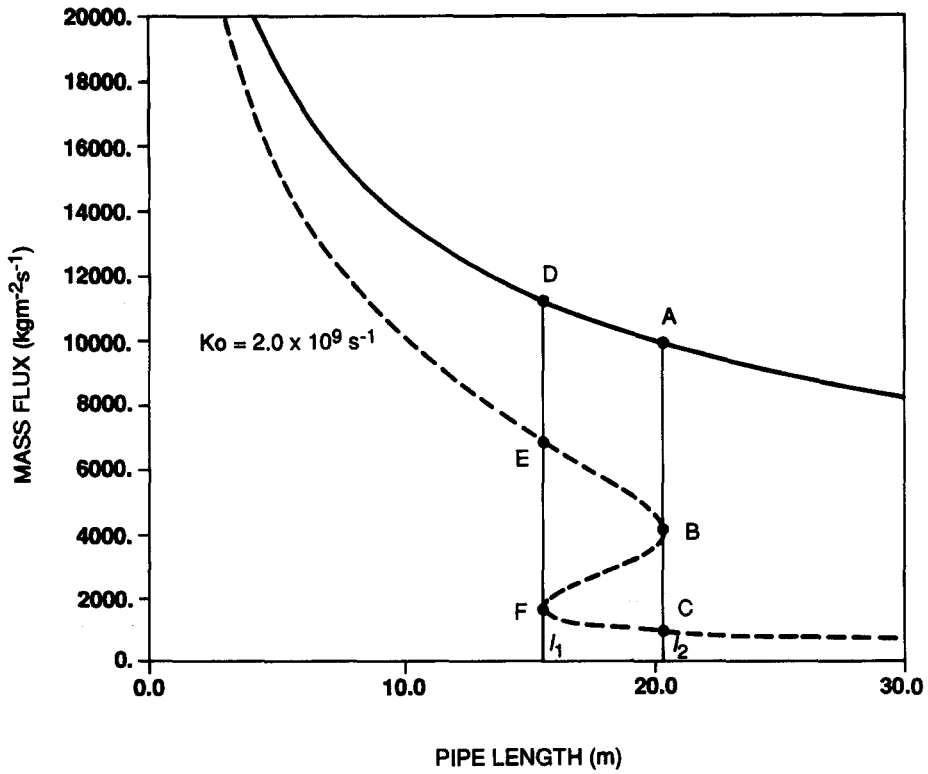


Figure 5. Critical mass flux for pipes of varying length, showing the effect of a liquid phase chemical reaction.

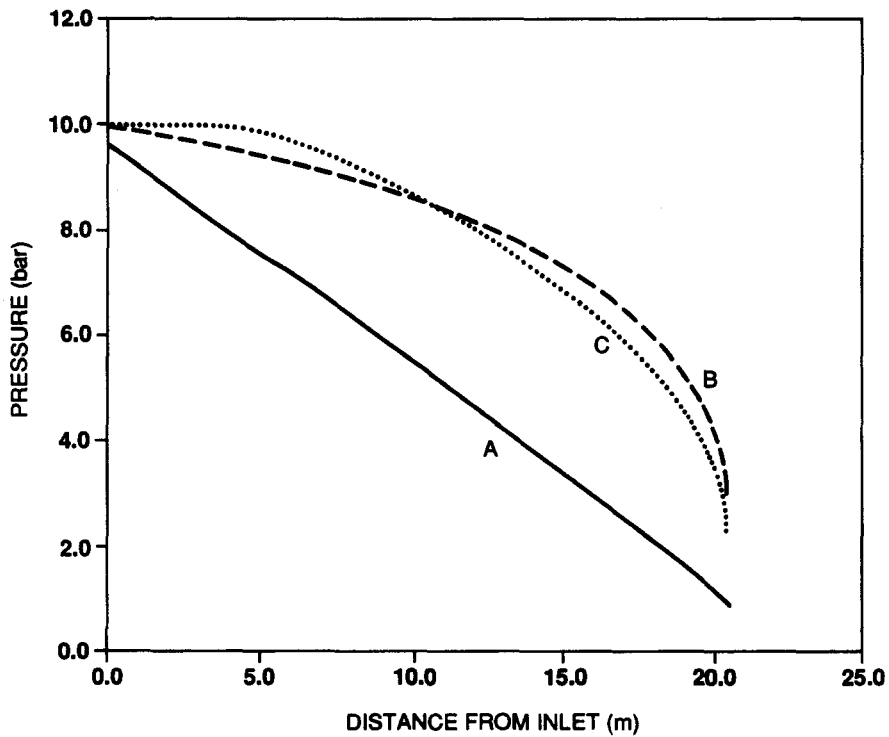


Figure 6. Variation of pressure along the pipe length.

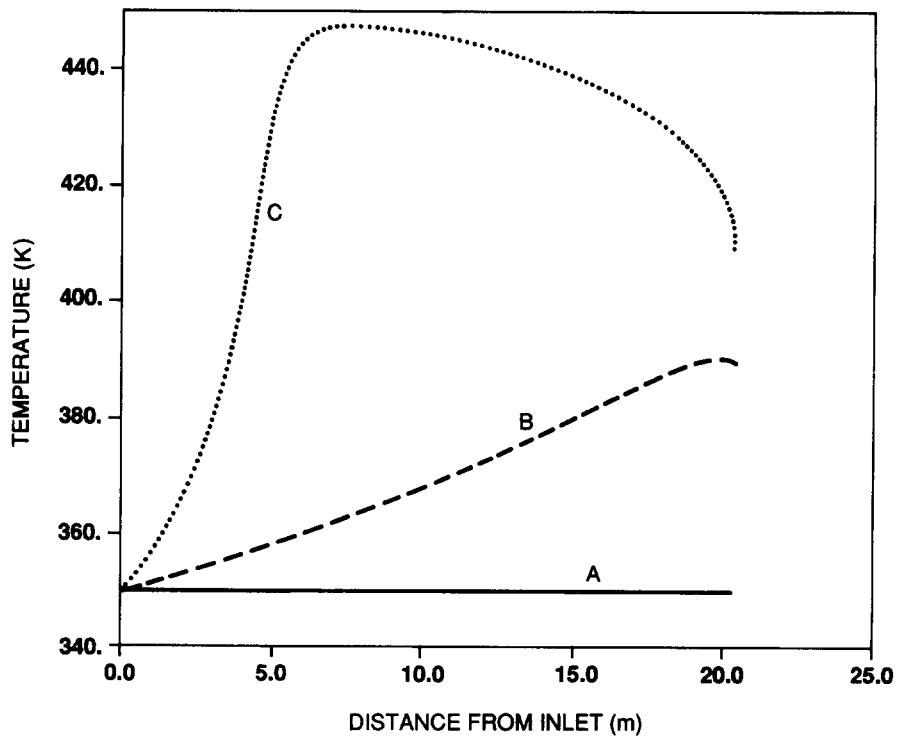


Figure 7. Variation of temperature along the pipe length.

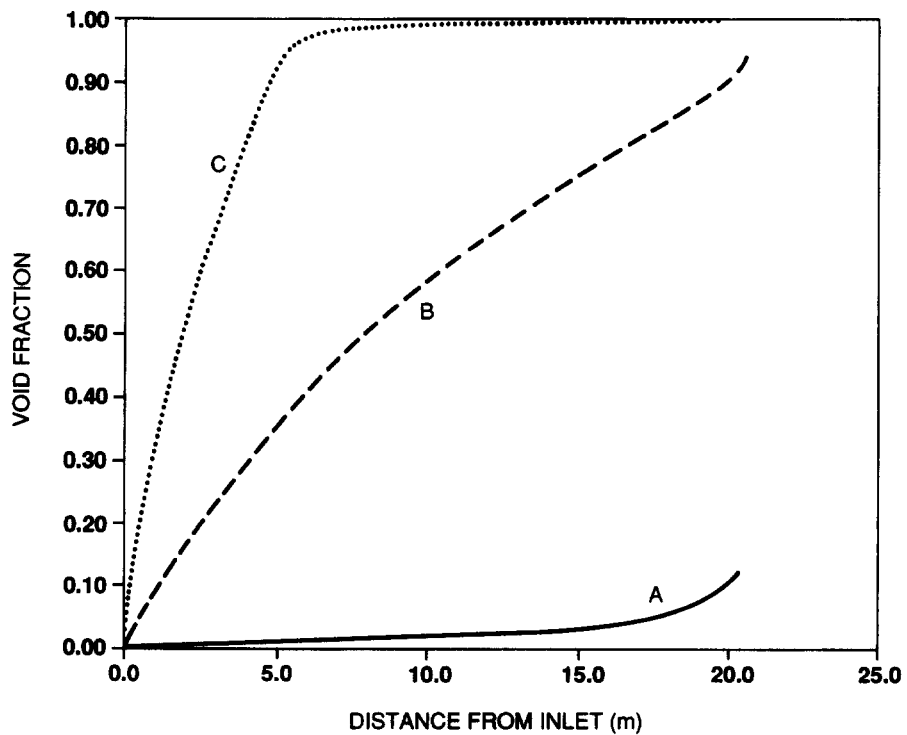


Figure 8. Variation of void fraction along the pipe length.

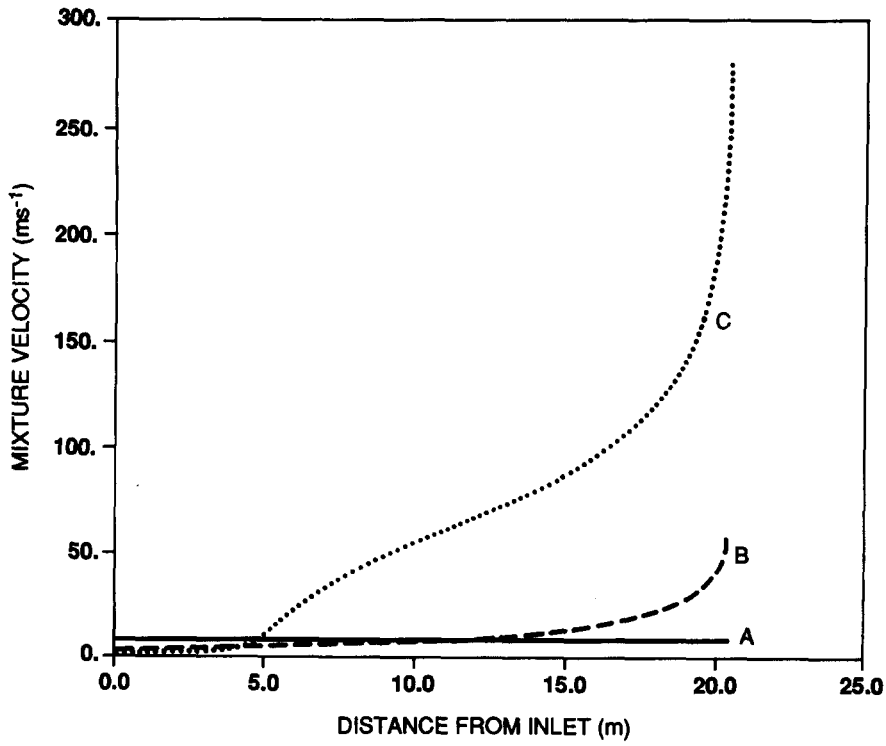


Figure 9. Variation of mixture velocity along the pipe length.

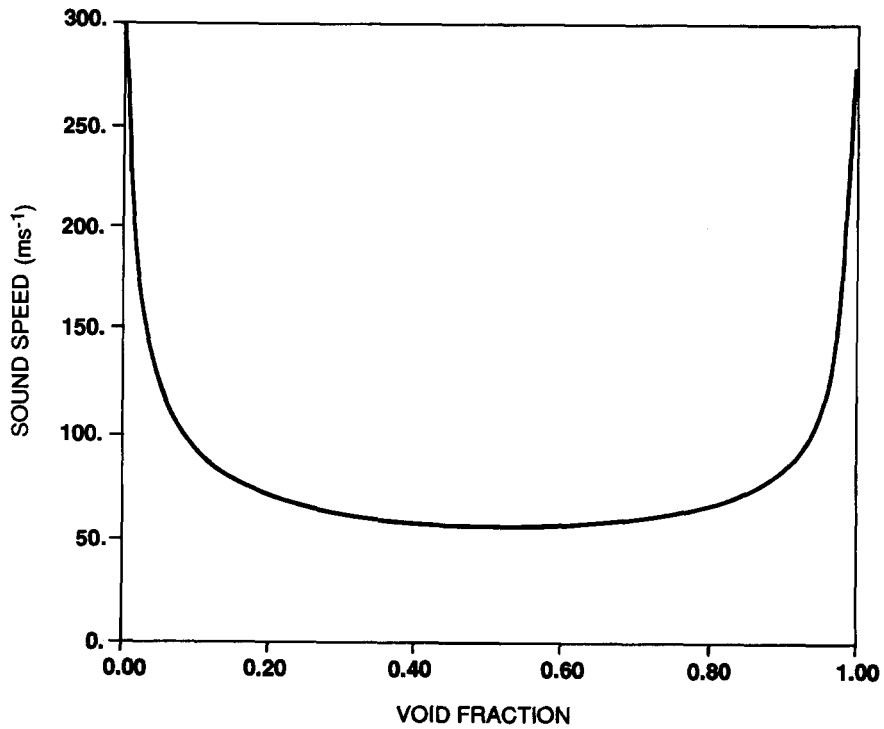


Figure 10. Variation of local sound speed with void fraction.

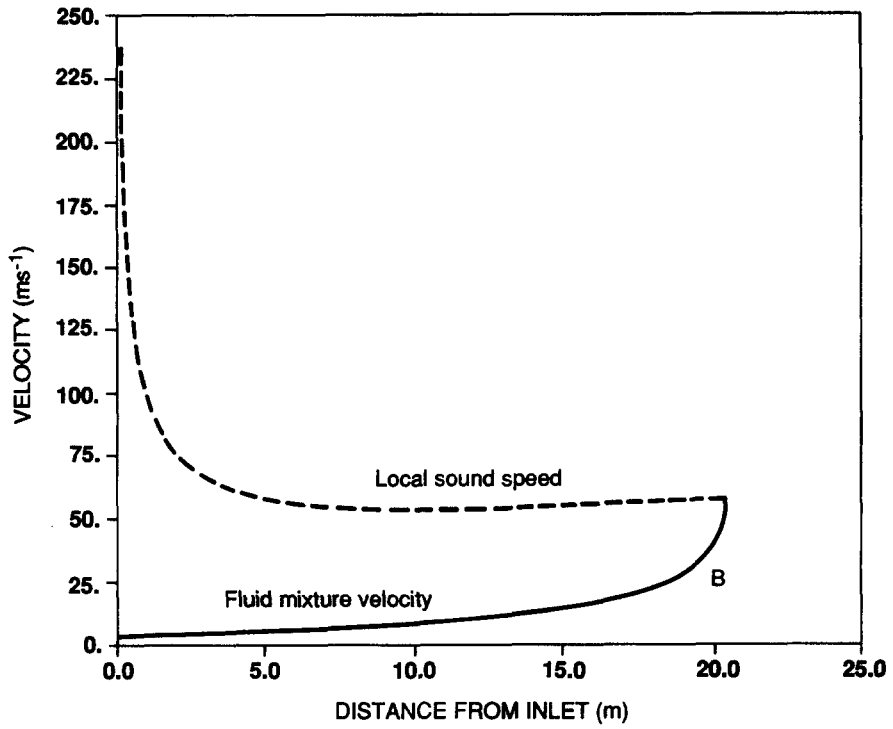


Figure 11. Variation of mixture velocity and local sound speed along the pipe length, high flow rate case B.

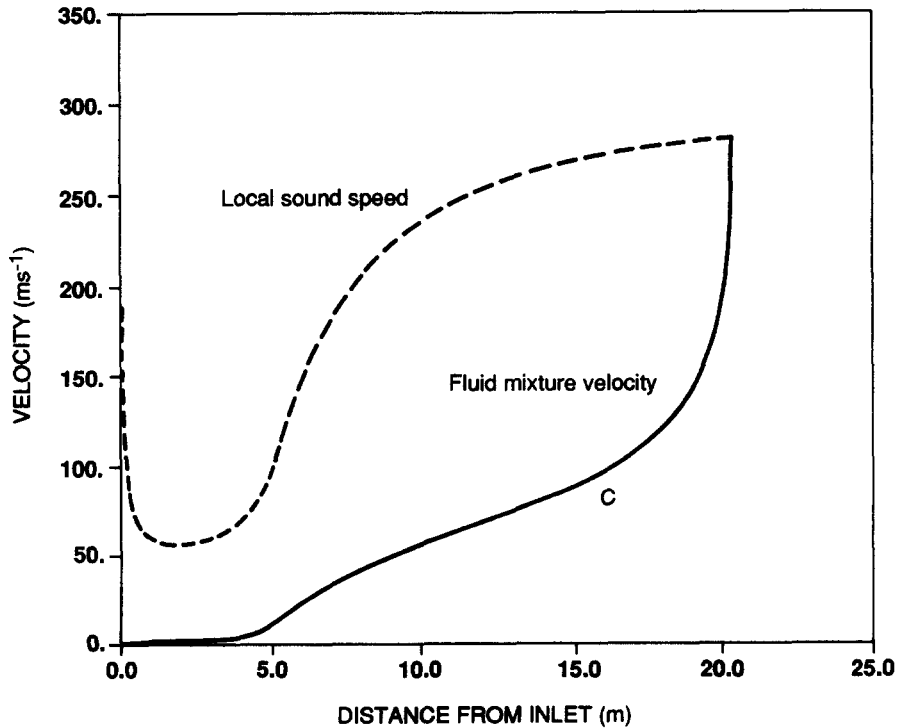


Figure 12. Variation of mixture velocity and local sound speed along the pipe length, low flow rate case C.

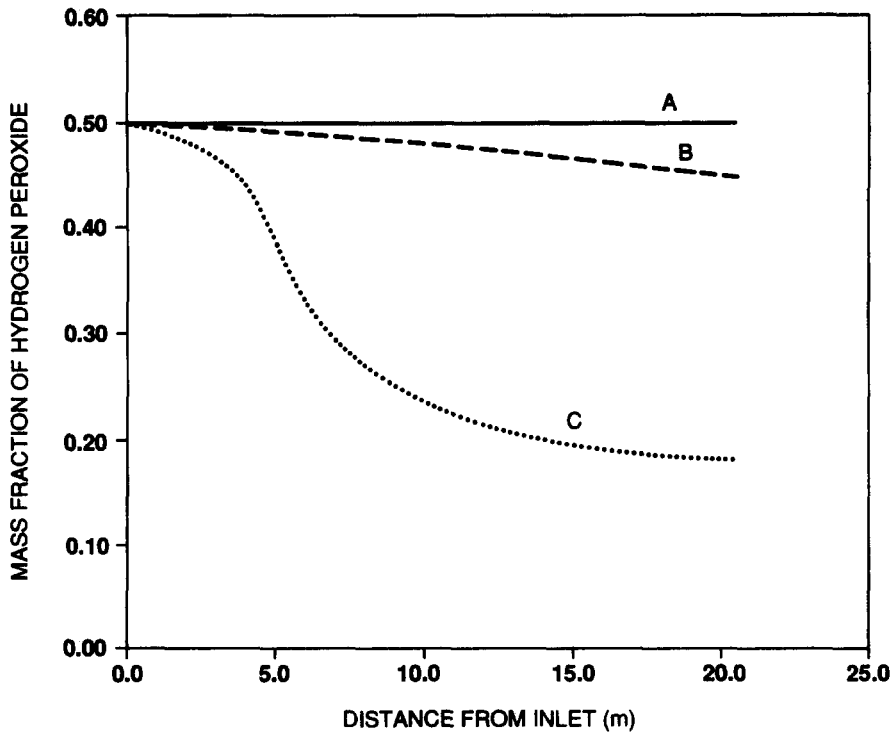


Figure 13. Variation of hydrogen peroxide mass fraction along the pipe length.

The instantaneous conversion rate of H_2O_2 is described by the first order reaction:

$$\frac{d}{dt} [\text{H}_2\text{O}_2] = -K_0 [\text{H}_2\text{O}_2] \cdot \exp\left(-\frac{E}{RT}\right)$$

where K_0 is the pre-exponential factor (s^{-1}), $[\text{H}_2\text{O}_2]$ is the molar concentration of hydrogen peroxide in the liquid phase (mol m^{-3}), E is the activation energy (J mol^{-1}), R is the molar gas constant and T is the absolute temperature.

The calculations presented in this paper correspond to the following conditions:

stagnation temperature:	$T_0 = 350 \text{ K}$
outlet pressure:	$p_{\text{out}} = 1 \text{ bar}$
pipe diameter:	$d_h = 2 \text{ cm}$
pipe inclination:	$\theta = 0$
Fanning friction factor:	$f = 0.005$
Activation energy:	$E = 7.52 \times 10^4 \text{ J mol}^{-1}$.

In addition the stagnation pressure p_0 , the stagnation void fraction ε_0 and the pre-exponential factor K_0 were varied sequentially within the range:

$$p_0 = 5, 7.5, 10, 15, 20 \text{ bar}$$

$$\varepsilon_0 = 0 \rightarrow 1 \text{ in steps of } 0.1$$

$$K_0 = 2.0 \times 10^9, 1.0 \times 10^9, 5.0 \times 10^8, 2.5 \times 10^8, 1.25 \times 10^8 \text{ s}^{-1} \dagger$$

4.3. Results

Figures 1–13 are a selection of the above calculational matrix and highlight some significant results. Figure 1 shows two curves $G_c = f(l_c)$ without chemical reaction, for the stagnation conditions $p_0 = 10 \text{ bar}$ and $T_0 = 350 \text{ K}$. Note that the saturation temperature (or bubble point

†The values for E and K_0 ($= 2.0 \times 10^9$) were experimental values for the reaction with ferric ions as a catalyst. These tests were performed at JRC with the PHITEC calorimeter.

temperature) of a pure water, hydrogen peroxide mixture at this pressure is 466 K. The upper curve corresponds to pure liquid inlet conditions ($\varepsilon_0 = 0$), the lower one corresponds to pure vapour inlet conditions ($\varepsilon_0 = 1$). The following figures will show results for the case where chemical reaction is considered.

Figure 2 shows the effect of chemical reaction for the case of stagnation pressure, $p_0 = 10$ bar and pure liquid ($\varepsilon_0 = 0$) inlet conditions. Five calculations are shown with different pre-exponential factors describing the chemical reaction; in addition the two "limiting" curves without chemical reaction from figure 1 are shown for comparison. The effect of the chemical reaction is to act like an "evaporator", shifting the curves towards the all vapour case from figure 1. The most striking feature, however, is the S-shape of the curves. As a consequence there exists a range of pipe lengths where three different mass flow rates are possible. This will be described as the "triple solution range".

For the case $p_0 = 10$ bar, $K_0 = 2.0 \times 10^9 \text{ s}^{-1}$ the influence of the stagnation void fraction is illustrated in figure 3. The position where a triple solution exists is shifted towards higher pipe lengths as the stagnation void fraction is increased. Figure 4 demonstrates the effect of a variation in stagnation pressure p_0 for the case $K_0 = 2.0 \times 10^9 \text{ s}^{-1}$ and $\varepsilon_0 = 0$. The minimum value of the triple solution remains roughly at the same l_c value but the extent over which a triple solution exists is reduced when the pressure is reduced. At a certain value of p_0 the triple solution feature disappears. Note that the saturation pressure corresponding to a bubble point temperature of 350 K of a pure water, hydrogen peroxide mixture is ≈ 0.3 bar.

Figure 5 shows a more detailed picture of the function $G_c = f(l_c)$ for the case $p_0 = 10$ bar, $T_0 = 350$ K, $\varepsilon_0 = 0$ and $K_0 = 2.0 \times 10^9 \text{ s}^{-1}$, and for comparison the case where no chemical reaction is considered. Let l_1 represent the lower limit and l_2 the upper limit of the triple solution range. These lengths define the points E, F and B, C on the curve where chemical reaction is modelled and points D and A on the curve with no reaction. The part of the curve between F and B is thought to be unstable as a *longer* pipe length leads to a *higher* mass flow keeping constant all other conditions. In addition a hysteresis effect is expected between points E–B–C–F–E. Figure 5 demonstrates that under the chosen conditions the effect of an ongoing chemical reaction in the vent line is important and that if the operating conditions are close to the unstable region an abrupt step reduction in flowrate could occur as signified by the portion of the curve B–C.

To understand the reasons for this behaviour it is necessary to investigate the development of the different parameters along the pipe, for a given pipe length. The length of pipe chosen for this exercise is that which corresponds to the points A, B and C in figure 5, i.e. $l_2 \approx 20$ m. The following figures therefore show the development of pressure, temperature, void fraction, velocity and phasic composition along the pipe for the case of no chemical reaction (A) and for the two solutions with chemical reaction (B and C).

Figure 6 shows the pressure distribution; the case with no chemical reaction (A) the flow is just sub-critical and the cases with chemical reaction show quite similar pressure distributions. The low flow case (C) leads to practically zero pressure gradient at the pipe entrance. When evaporation of the condensables (H_2O and H_2O_2) starts the pressure gradient changes significantly. Nevertheless the absolute pressure differences between case B and C remain small.

In figure 7 the axial temperature variation is given and here a significant difference is apparent between the three cases. The turn around in temperature in the curve C marks the onset of bulk boiling of the liquid phase, and with it the cooling effect associated with the latent heat of vaporization. The temperature distribution gives much more insight to the different flow situations than the pressure.

The same holds for the variation in the void fraction which is shown in figure 8. When the evaporation of the liquid phase begins (≈ 5 m, case C) the void fraction is already high, but the vapour phase is almost entirely composed of oxygen.

The axial variation of mixture velocity is shown in figure 9. One should note that the lowest entrance velocity results in the highest exit velocity. The higher volume production, due to oxygen production and evaporation, in case C is more important than the higher initial velocity of case B.

Figure 10 shows the variation of local mixture sound speed, as defined by [17], with void fraction. A strong minimum is seen at intermediate void fractions which is typical of homogeneous mixtures (see Wallis 1969). Note that in figure 10 variations in phasic composition are taken into account in the calculation of the sound speed.

Figures 11 and 12 compare (for the cases B and C) the axial variation of mixture velocity with that of the local sound speed. The mixture velocity strongly increases towards the pipe exit where it reaches the local speed of sound with practically a vertical slope. Critical flow conditions exist only at the pipe exit. The sound speed in case B remains near the minimum value ($\approx 60 \text{ ms}^{-1}$) shown in figure 10. However, the sound speed is a function of void fraction and the high exit void fraction in case C results in a much higher local sound speed. As a consequence critical conditions at the exit plane are reached in this case with a higher mixture velocity. What should also be noted from these figures is that mixture velocity remains quite low for an appreciable length of the pipe and approaches the sound speed only close to the pipe exit. The residence time of a fluid element can thus become appreciable (\sim seconds) and is orders of magnitude higher than that obtained from dividing the pipe length by the critical velocity or exit plane sound speed.

Figure 13 shows the axial variation of the mass fraction of hydrogen peroxide. During the residence time of a mass element in case C around 60% of H_2O_2 is consumed (from initially 50% H_2O_2 down to 18%). For case B this consumption is roughly 10%.

5. CONCLUDING REMARKS

A critical flow model for chemically reacting, two-phase, multicomponent mixtures in channels of constant cross section has been presented. Due to the assumption of mechanical and thermal equilibrium its application is restricted to long channels and to situations where one phase is intimately mixed with the other, such that choking is determined by the local sound speed in the homogeneous mixture.

The presence of an ongoing chemical reaction introduces a non-linearity into the system due to the strong temperature dependence of the reaction rate. It has been shown that in situations where the fluid mixture entering the channel contains a non-condensable gas and where one of the reaction products is also a non-condensable gas multiple solutions to the problem may occur. In this case there is a certain range of pipe lengths where identical boundary conditions lead to three different values of critical mass flow rate. Small perturbations may then cause the system to jump from one solution to another resulting in a step reduction in critical flow rate. This phenomenon could give rise to important industrial safety questions which relate to the emergency relief of chemical reactors through long vent lines and experimental confirmation of this phenomenon should be sought.

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