Parametric Studies for a Hydrogen Peroxide Rocket Engine

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Abstract

As the interest in green alternatives for currently used rocket propellants has increased over the past few years so has the need increased for enhanced insight into the working of rocket engines using these green propellants. The focus of this paper is on engines that employ the catalytic decomposition of hydrogen peroxide. A three-phase two-fluid model has been used for conducting parametric studies. Simulations show that an increase in pressure drop over the catalyst bed can be an indication of catalyst deactivation. It is also shown that the required catalyst bed length increases with increasing inlet mass flux of peroxide.

1. Introduction

Hydrogen peroxide based rocket motors were extensively used in the ’50s and ’60s, but were gradually replaced by propellants with better performance characteristics; notably hydrazine and hydrazine derivatives [1]. However, because of the toxic and carcinogenic nature of hydrazine and the associated costs for transportation, handling and storage, interest has grown in the past few years into alternative, less-toxic propellants, also known as green propellants. Hydrogen peroxide has been identified as one such green propellant. By decomposing hydrogen peroxide exothermally in a catalyst bed, it can be used either as a monopropellant or as the oxidiser in a bipropellant system.

Designing a hydrogen peroxide rocket motor requires knowledge about the influence of parameters such as the ratio of catalyst bed length to catalyst bed diameter, inlet mass flux and catalyst reactivity on overall performance parameters such as pressure drop over the bed, specific impulse and thrust. As experiments are often expensive and time consuming, and parameters of interest are sometimes very difficult to measure, models can be useful tools within the design process.

To date very few models have been published that describe the hydrogen peroxide flow and its decomposition in a propulsion system. This is despite the availability of a number of models in the chemical reactor engineering community that describe the multiphase flow through packed beds [2]. However, the liquid and gas velocities inside the reactors typically found in these models are far lower than typically found in hydrogen peroxide rocket motors [3] and they do not incorporate chemical reactions and the associated changes in temperature. Flow models that describe more representative systems are described below.

Zhou and Hitt [4, 5] described a one-dimensional mixture model for a hydrogen peroxide flow through a channel in a miniaturised propulsion system to determine the required bed length to obtain complete decomposition. The mixture model had a shared pressure, temperature and velocity field and it was assumed that evaporation of the liquid components take place at the respective normal boiling points of each component. They found that the activation energy plays a key role on the temperature at which thermal decomposition becomes important, but mentioned at the same time that these values are difficult to determine and are scarce in literature. They also showed that, for a higher concentration of peroxide, the maximum temperature increases but that longer beds are required for complete decomposition. Moreover they showed that the required bed length is inversely proportional to the inlet mass flux. Finally they mentioned that the effect of axial heat conduction and mass diffusion on the required catalyst bed length is minimal.

Bonifacio and Russo Sorge [6] developed a one-dimensional single phase model for hydrogen peroxide decomposition in a monolithic reactor and studied the influence of the pre-exponential factor of the Arrhenius reaction rate and the inlet mass flux on the steady state performance. They assumed a high concentration hydrogen peroxide gas flow that entered the catalyst bed at room temperature and showed a significant influence of the channel size on the transient behaviour of the monolithic bed. They concluded that the absence of thermal decomposition in their model was one the main causes of the difference between simulation and experiments for a range of reactor pressures. They also suggested that the absence of a boiling liquid phase resulted in a far lower inlet mass flux at which flooding - a situation where decomposition and evaporation rates are not high enough to convert the liquid into gas before it leaves the catalyst bed - takes place compared to experiments.

Pasini et al [7] presented their one-dimensional two phase mixture model for a pellet based catalyst bed that was mainly used to perform parametric studies. The model was formulated as a mixture model with a shared pressure, temperature and velocity field. Decomposition was modelled by considering the adsorption of reactants onto the catalyst material and desorption of the reaction products from the catalyst material. The pressure drop caused by the presence of the catalyst material was modelled with the Ergun relation. To close the model they used experimentally determined values for the constants in the Arrhenius reaction rate equation, the number of active adsorption site and its relative occupancy. They found their model in good agreement with experimental results.

As they are all mixture models [8], none of these is capable of investigating the influence each phase in the catalyst bed has on the performance. Design optimization is thus influenced by fluid mixture properties. As there is a large difference in the density of the liquid and gas phase and a large difference in steady state temperature between the two fluid phases, it is expected that optimizing a catalyst bed design results in different solutions for each phase. Other features, such as pressure drop over the catalyst bed, might be difficult to predict because models based on a mixture of liquid and gas do not always encompass the necessary details of the contribution of each phase.

This paper presents a parametric study of the influence of catalytic reactivity on the pressure drop over the catalyst bed. It will also investigate the claim of Zhou and Hitt that the required catalyst bed length is inversely proportional to the inlet mass flux. For this purpose a three-phase two-fluid simple flow model has been developed by the authors. This model treats each phase separately contrary to the mixture models that have been published so far. The general features of this model are discussed below. After that a description of the results is given followed by a discussion.

2. The Simple Flow Model

2.1 General features

The model follows the same principles as that developed by Ju et al [9], which was used to describe the flow of a flashing propellant through a metered dose inhaler. This model, a schematic of which is shown in figure 1, contains a reservoir (tank), which contains a fixed mass of pure volatile liquid and vapour, and an expansion chamber (catalyst bed), where the liquid flashes. An inlet nozzle provides the link between the reservoir and the expansion chamber and an exit nozzle provides the link between the expansion chamber and the atmosphere. A common feature of the present model and that of Ju et al [9] is that mass, momentum and energy are conserved within the tank and bed through internal changes within each volume; mass, momentum and energy transfer from tank to bed take place by an inflow condition and the coupling between the bed and the atmosphere is established via a nozzle. In contrast to the model of Ju et al [9] here the fluid phases are multicomponent, a third phase is introduced in the catalyst bed representing the solid catalyst material, there is momentum transfer between the catalyst bed and the fluid phases and mass transfer is described by chemical reactions and evaporation.

The liquid phase in the tank consists of water and hydrogen peroxide which has a fixed mass percentage of peroxide of 87.5%; in practice this concentration changes in the catalyst bed due to the hydrogen peroxide decomposition and evaporation. The gas phase consists of air, which is residing in the catalyst bed prior to injection of hydrogen peroxide; oxygen, formed by chemical reactions; water vapour, formed by chemical reactions and evaporation; and hydrogen peroxide vapour, formed by evaporation. The chemical reactions take place partly at the surface of the catalyst material and partly in the fluid. As a consequence of the presence of the solid catalyst a force is exerted on the fluid phases resulting in a pressure drop over the bed.

The tank contains a pressurant gas section and a liquid propellant section. The model is set up such that during a simulation only liquid propellant is flowing into the catalyst bed. The liquid peroxide in the catalyst bed will partly decompose into water and oxygen and partly evaporate as vapour. The products that leave the catalyst bed are assumed to be all in the gaseous state. To account for the fact that the liquid volume fraction is not spatially uniform within the bed due to reactions progressing as one moves down the bed and due to channeling, a non-uniform relative liquid

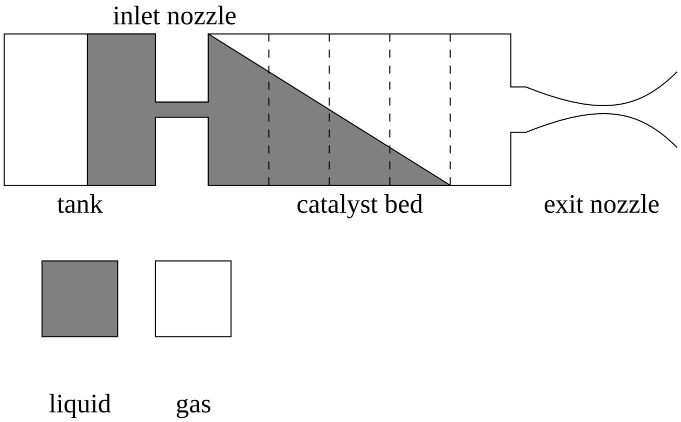

Figure 1: Schematic representation of the flow model

volume fraction distribution is assumed within the catalyst bed. This is achieved by subdividing the catalyst bed into 5 sections and assuming a relative liquid volume fraction distribution over the four upstream sections such that the volume fractions are in the ratio 4:3:2:1. As the simulation proceeds these sections are first completely filled up with liquid, before liquid is allowed to enter the last section. The point that happens is defined as the moment at which the catalyst bed is flooding. Numerical experiments have shown that the results are independent of this arbitrary distribution of the liquid volume fraction.

The pellets are assumed to be homogeneously distributed over the bed, which is the same approach as used by Pasini et al [7]. Any wall influences are disregarded which would require higher dimensional models and therefore are left out of consideration. The pellets are further assumed to have an euclidian shape, so that any porosity of the pellet itself can be left out of consideration. As a consequence all the catalytic decomposition is taking place on the outside surface of the pellet. Moreover it is assumed that the concentration at the surface is the same as of the bulk flow. Although not explicitly stated, these assumptions were also used by Pasini et al [7].

Due to decomposition liquid hydrogen peroxide is consumed and water is produced resulting in a decrease of hydrogen peroxide concentration in the liquid. However, Corpening et al [10] pointed out that at the same time water preferentially evaporates from the liquid, resulting overall in a near constant hydrogen peroxide concentration. Pasini et al [7] assumed that these two transfer mechanisms keep each other more or less in equilibrium, which allows the assumption that evaporation is such that the concentration of hydrogen peroxide in the liquid phase stays constant. The same assumption is applied for our model.

In reality there is not a well-defined interface between the liquid and the gas phase. In fact, most of the gas will be present in the form of bubbles and slugs in the liquid phase. However, the current model cannot solve for this and therefore the factor ϵ_{bub} is introduced which is the volume fraction of the gas in the liquid-gas mixture. This volume fraction influences the total pressure drop over the catalyst bed as well as the moment at which flooding of the catalyst bed is predicted. In a real catalyst bed ϵ_{bub} would vary from 0 to 1 depending on the distance from the injector, but in the present model we take an average value. As the value is arbitrary simulation results will be shown for different values of ϵ_{bub}.

2.2 Source term definition

Decomposition of hydrogen peroxide is generally given by [11]:

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2 \tag{1}$$

The reaction constant, k, associated with this decomposition is modelled by Arrhenius kinetics and generally given by:

$$k = A_0 \exp\left(\frac{-E_A}{R_c T}\right) \tag{2}$$

where A_0 is the pre-exponential factor, E_A the activation energy, R_c the universal gas constant and T the temperature.
The pressure drop per unit length for each phase is generally given by:

$$\left(\frac{\Delta p}{L}\right)_\alpha = \epsilon_\alpha \left(\frac{\mu_\alpha u_{0,\alpha}}{K_{rel,\alpha} K} + \frac{\rho_\alpha u_{0,\alpha}^2}{\eta_{rel,\alpha}\eta}\right) \tag{3}$$

where μ is the dynamic viscosity, ρ the density, u_0 the superficial velocity and ϵ the volume fraction. The subscript α refers to the phase to which the equation is applied. The parameters K and η are given by:

$$K = \frac{D_p^2}{150}\frac{(1-\epsilon_s)^3}{\epsilon_s^2} \tag{4}$$

$$\eta = \frac{4D_p}{7}\frac{(1-\epsilon_s)^3}{\epsilon_s} \tag{5}$$

where the subscript s refers to the solid phase and D_p the diameter of the catalyst pellets.
The first term between brackets describes the viscous interaction with the catalyst bed while the second term describes the momentum exchange between the fluid and the catalyst bed due to inertia. $K_{rel,\alpha}$ and $\eta_{rel,\alpha}$ are parameters that account for the partial obstruction by the presence of the other fluid phase and are therefore influenced by the value of ϵ_{bub} chosen. A much more rigorous mathematical description of this model can be found in [12].

3. Results

Three sets of simulations have been performed. In the first set the catalytic reactivity for decomposition of the liquid on the catalyst surface was slightly changed for every simulation case. This was achieved by defining the strength of the source as a percentage, where a percentage of 100% was taken as the reference case. The source strength varied from 50% to 150%. The variation of the source strength can be interpreted as either a change in catalytic reactivity or as comparison of different types of catalyst material and their corresponding differences in catalytic activity. A second set of simulations was performed by changing the inlet mass flux for each run. This was achieved by varying the delivery pressure of the hydrogen peroxide, which ranged from 50% to 300% of the reference case. The required catalyst bed length for a given inlet mass flux was determined in the third set of simulations. The inlet mass flux ranged from 15 to about 40 $kgm^{-2}s^{-1}$. It should be noted that the required catalyst bed length is defined as the minimum length for which no liquid is exhausted through the outlet nozzle for a given inlet mass flux.
Each simulation was run until steady state conditions were reached. Analysis was then performed only for steady state conditions. To reduce the total simulation time, all computations have been performed on Iridis 3, the supercomputer of the University of Southampton. Relevant initial conditions for the reference case are shown in Table 1. The geometry parameters are applicable to an instrumented catalyst bed we have used for testing at Southampton [14]. As can be seen in this table the propellant tank volume as well as the volume for the pressurisation gas is very large. This is to ensure a constant delivery pressure.
For the first set of simulations the focus is on pressure drop over the catalyst bed, shown in Figure 2 against normalised catalyst reactivity for different values of ϵ_{bub}. The figure shows that the pressure drop is higher for smaller ϵ_{bub}. The difference between $\epsilon_{bub} = 0.3$ and $\epsilon_{bub} = 0.4$ is markedly larger than the difference between $\epsilon_{bub} = 0.4$ and $\epsilon_{bub} = 0.5$. Furthermore the figure shows that for a decreasing source strength the pressure drop increases non-linearly.

The second set of simulations focus on the claim of Zhou and Hitt that the required catalyst bed length is inversely proportional to the inlet mass flux [4]. For this purpose the fraction of the catalyst bed volume that is occupied by the mixture of liquid and gas is plotted against inlet mass flux. The result is shown in figure 3. The figure shows that for an increasing inlet mass flux the volume fraction of the liquid-gas mixture increases. It also shows that for higher values of ϵ_{bub} the volume fraction is higher. The inlet mass fluxes reported in this work are much lower than those reported by Zhou and Hitt. To compare the results a couple of simulations were performed for similar inlet mass fluxes as reported in the work of Zhou and Hitt. The results are shown in Table 2. For this set of simulations the ratio of the catalyst bed length to the catalyst bed diameter was set to 15 by adjusting the catalyst bed length. This value was reported by Zhou and Hitt as the required ratio. Case a and b show the limiting values for ϵ_{bub} above which flooding occurs at the inlet mass flux shown. Case c shows the resulting liquid-gas mixture volume fraction for low inlet mass flux with a value for ϵ_{bub} corresponding to case b.

Table 1: Initial and boundary conditions

parameter	value	unit
pressure	101325	Pa
temperature	293	K
pre-heat temperature	423	K
time step	$1 \cdot 10^{-4}$	s
pellet diameter	0.003	m
pellet length	0.004	m
bed diameter	0.016	m
bed length	0.12	m
inlet nozzle throat diameter	$0.4 \cdot 10^{-3}$	m
inlet nozzle throat discharge coefficient	1.00	$-$
exit nozzle throat diameter	$1.6 \cdot 10^{-3}$	m
exit nozzle throat discharge coefficient	1.00	$-$
HTP concentration	87.5	%
pre-exponential factor catalytic decomposition [6]	$1 \cdot 10^{8}$	$-$
pre-exponential factor liquid thermal decomposition [13]	$4 \cdot 10^{3}$	$-$
pre-exponential factor gas thermal decomposition [13]	$1 \cdot 10^{13.5}$	$-$
activation energy catalytic decomposition [6]	52500	$J\,mol^{-1}$
activation energy liquid thermal decomposition [13]	49000	$J\,mol^{-1}$
activation energy gas thermal decomposition [13]	207000	$J\,mol^{-1}$
tank pressure	$20 \cdot 10^{5}$	Pa
propellant volume	$1 \cdot 10^{6}$	m^3
pressurant volume	$1 \cdot 10^{6}$	m^3
nozzle throat area to nozzle exit area	2	$-$

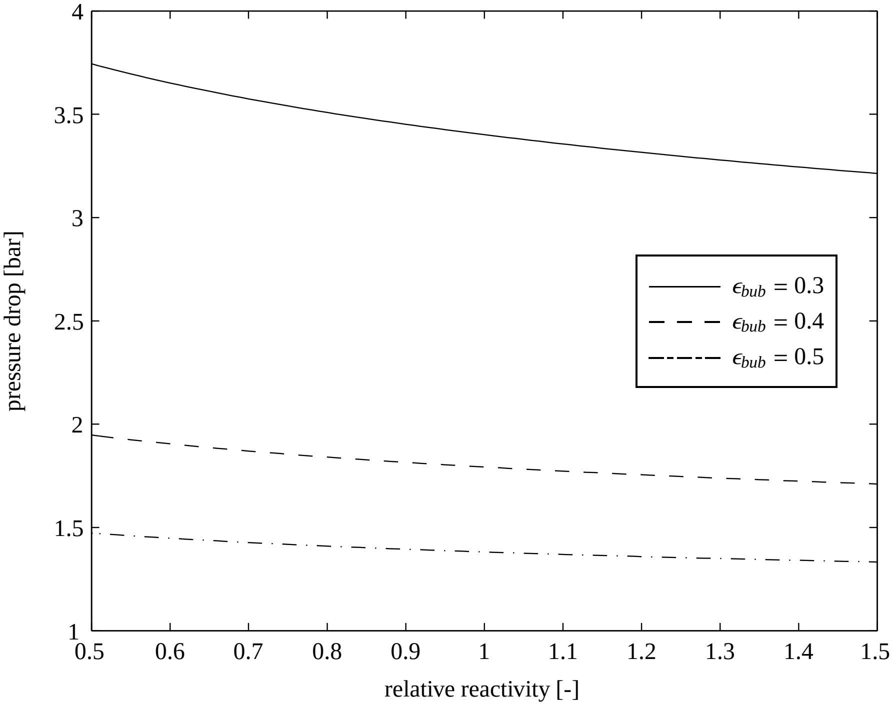

Figure 2: Total pressure drop as a function of the catalyst reactivity for different values for ϵ_{bub}

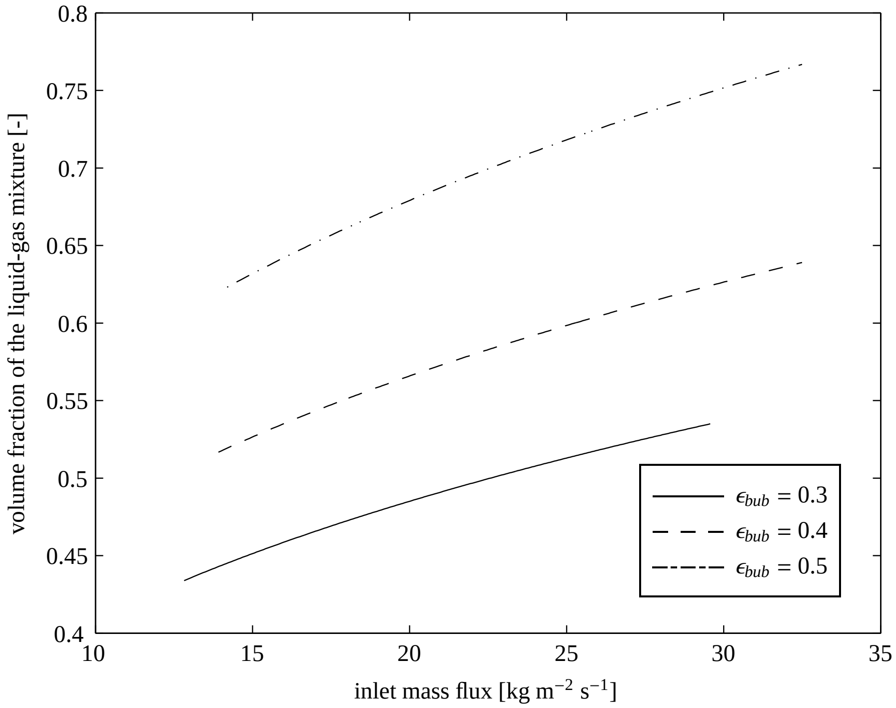

Figure 3: Liquid-gas mixture volume fraction as a function of inlet mass flux for different values of ϵ_{bub}

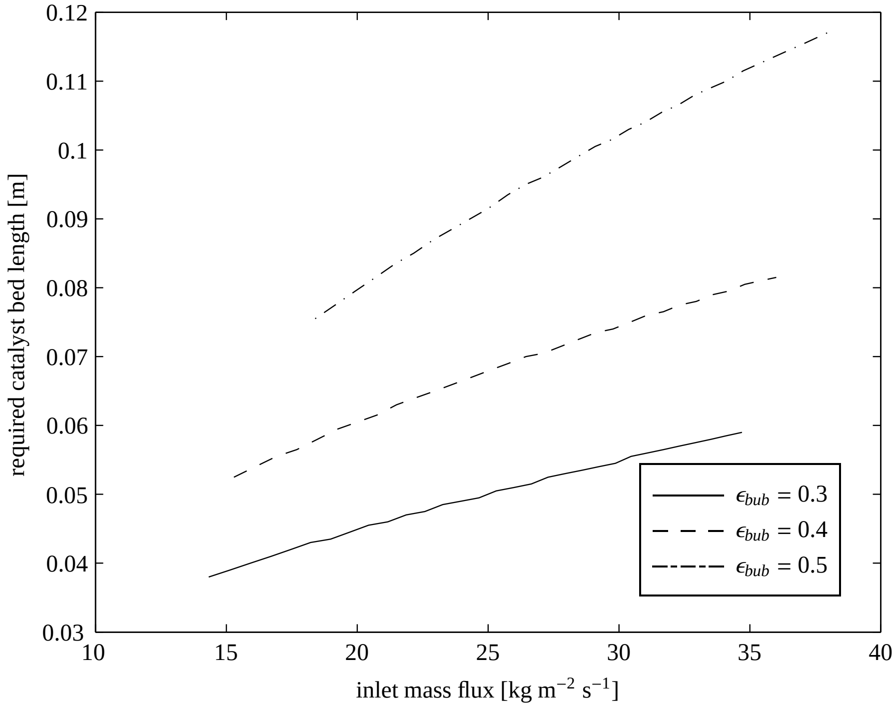

Figure 4: Minimum catalyst bed length as a function of inlet mass flux for different values of ϵ_{bub}

Figure 4 shows the minimum required catalyst bed for which no flooding takes place as a function of the inlet mass flux for three different values of ϵ_{bub}. It clearly shows that for a higher inlet mass flux the required bed length increases. This effect is stronger for higher values of ϵ_{bub}. It can also be seen that for a low value of ϵ_{bub} the required bed length is smaller than for high value for equal inlet mass flux.

Table 2: Liquid-gas mixture volume fractions for high inlet mass fluxes

case	mass flux	ϵ_{bub}	liquid-gas mixture volume fraction
a	387.9 $kgm^{-2}s^{-1}$	0.36	1.00
b	796.7 $kgm^{-2}s^{-1}$	0.24	1.00
c	401.9 $kgm^{-2}s^{-1}$	0.24	0.67

4. Discussion

As is shown in figure 2 in the previous section, for decreasing catalytic activity the pressure drop over the catalyst bed increases. This can be understood by examining the pressure drop model more closely. Equation 3 gives the general form of the pressure drop in each fluid phase. The parameters $K_{rel,\alpha}$ and $\eta_{rel,\alpha}$ account for the obstruction of the flow caused by the presence of the other fluid phase. In the limit, if only one of the phases, let us say gas, is present then $K_{rel,g} = \eta_{rel,g} = 1$. For the liquid phase both parameters are zero however, as no liquid is present ($\epsilon_l = 0$) this does not influence the total pressure drop. If both phases are present, the value for $K_{rel,\alpha}$ and $\eta_{rel,\alpha}$ is between 0 and 1.

$K_{rel,\alpha}$ and $\eta_{rel,\alpha}$ are dependent on ϵ_{bub} to the power 3 or 4 [12]. Consequently, the combined pressure drop in the case of a two phase flow is larger than the pressure drop for a single phase flow. Simulations show that for a two phase flow typically about 90% of the total pressure drop arises from the gas phase.

In the case of reduced relative activity it will take longer for the liquid peroxide to decompose. The location in the catalyst bed from where liquid is no longer present will thus move downstream. This means that the total length over which a two phase flow exists is larger. As the pressure drop for a two phase flow is larger than for a single phase flow, the pressure drop over the bed will therefore increase.

This result is a good example of the kind of detail that is lost when employing mixture models. As mixture models assume a shared pressure, velocity and temperature field no distinction can be made between the contribution of the different phases to the total pressure drop. Two-fluid models such as the present model, however, do catch this detail.

In figure 3 it is shown that, for an increasing inlet mass flux, the volume of the catalyst occupied by liquid increases. This suggests that for higher inlet mass fluxes the catalyst bed should be longer to convert all the liquid into gas by either decomposition or evaporation. This is supported by figure 4 which shows that the minimum required catalyst bed length to avoid flooding increases for a higher inlet mass flux. This is in contrast with the claim of Zhou and Hitt [4] that the catalyst bed length is inversely proportional to the inlet mass flux.

Zhou and Hitt use considerably higher inlet mass fluxes - 400 to 800 $kgm^{-2}s^{-1}$ against 10 to 35 $kgm^{-2}s^{-1}$ in this paper. As is shown in Table 2, for the same values of ϵ_{bub}, case *b* and *c*, the volume fraction of the liquid-gas mixture is higher for the higher inlet mass flux. Also shown in the table is that for a lower inlet mass flux, flooding takes place at a higher value of ϵ_{bub}, case *a* and *b*. From this can be concluded that the trends, even at much higher inlet mass fluxes, are similar to those shown in figure 1 and figure 4.

An obvious difference between this model and that of Zhou and Hitt is that their model has a spatial discretisation while this model considers the catalyst bed as one large control volume. To prevent liquid coming out of the nozzle the liquid is arbitrarily distributed over the 5 sections, but as was mentioned in [12] a change of distribution has no influence on the results of the simulation. Thus it is not clear why our model gives results that we believe are intuitively correct, whereas Zhou and Hitt's model does not.

5. Conclusion

It has been shown that an increase in pressure drop over the catalyst bed during steady state operation can be a result of catalyst deactivation. As the reactivity of a catalyst decreases, the liquid-gas mixture volume fraction increases. As the flow of each fluid phase is partly obstructed by the presence of the other fluid phase the pressure drop increases. This result is in contrast to those provided by mixture models and arises from the details of the interaction between the two

phases, which the mixture models are unable to capture.
It was also shown that for increasing inlet mass flux the required catalyst bed length increases. This is contrary to the claim made by other workers that the catalyst bed length required for full decomposition is inversely proportional to the inlet mass flux.

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