

A dynamic two phase flow model for a pilot scale sodium borohydride hydrogen generation reactor

T. Sousa^{1*}, C.M. Rangel¹

¹LNEG, Estrada Paço do Lumiar 22, 1649-038 Lisboa, Portugal

(*) e-mail corresponding author: tiago.sousa@lneg.pt

Abstract

A two-dimensional, non-isothermal, and dynamic model was developed to describe a sodium borohydride/hydrogen reactor for stationary use. All relevant transport phenomena were treated in detail and the kinetic model developed previously by the authors was introduced into the algorithm. In this paper the reactive solution was modeled as a two phase flow; with this approach the impact of the hydrogen production on the solution stirring could be observed and quantified. Results showed that not all ruthenium deposited on the nickel foam was used efficiently as catalyst. In fact, most of the reaction occurred in the surface of the catalyst foam and around 70% of the deposited catalyst was not used. It was also demonstrated the importance of the two phase flow approach for a correct simulation of the solution stirring and heat transfer.

Keywords: Sodium borohydride, Hydrogen storage, Two-phase flow, Modeling, Reactor simulation

1 Introduction

Sodium borohydride has been considered as a promising energy carrier. Over the last two decades it has been widely studied as hydrogen storage material and as fuel in fuel cells. This work is focussed on hydrogen storage and therefore direct sodium borohydride fuel cells will not be addressed, for more information on this issue reference [1] should be consulted. The application of NaBH₄ as hydrogen storage material for on-board systems was discarded in 2007 when the U.S. Department of Energy gave a no-go decision for this technology; however, this conclusion was only based on specifications for on-board vehicular storage. For other uses, such as portable and niche applications, there are not any specific targets, and several authors believe in the potential of NaBH₄ for these particular applications [2–4].

The main studied topic concerning this field has been the hydrolysis reaction, in particular new catalysts have been proposed and a much effort has been made to understand and increase the reaction efficiency. Several reviews were published regarding the experimental advances over the last years [2, 5–7]. In comparison with experimental testing very little work has been done on reactor modelling. So far, only three models have been reported [8–10]. Zhang et al [8] published the first work in this field in 2007. They developed a one dimensional (1D) numerical model for a 1 kWe system, which they had used previously for experimental testing. In this model they assumed homogeneous catalysis and to validate it they used the collected experimental data, mainly the temperature inside the reactor. The transport processes

involving multi-component and multi-phase were coupled with reaction kinetics, which was the subject of intensive study by the same research group. They used this model to predict reactor behaviour at different fuel concentrations, flow rates and reactor pressure; the obtained results compared reasonably well with the experimental data. By using only one dimension the impact on performance by the geometric parameters of the reactor is not totally taken into account, besides the variation of the dependent variables was only assumed to be on the flow direction. In 2011, Pinto et al. [9] developed a zero dimensional model to simulate a NaBH₄-based hydrogen generator with a polymer electrolyte membrane fuel cell (PEMFC) stack system. In this model the NaBH₄ reactor was simply modelled with the kinetic equation, which was enough because in this case the hydrogen pressure in the reactor was the only variable of interest. This model is quite useful to have an overview of the whole system, however it cannot be used for reactor design. More recently, Sousa et al. [10] published a three dimensional model for a pilot scale reactor. In this model all relevant transport phenomena were treated in detail and the kinetic model developed by the same authors was introduced into the algorithm. Results showed that the reaction rate was extremely affected by the mass transport resistance of sodium borohydride from the bulk to the catalyst surface. The main drawback of this model was the assumption of single phase flow during the hydrolysis reaction. Therefore, in this paper a two dimensional model of the same pilot scale reactor is presented taking into account two phase flow hydrolysis reactions.

2 Model Development

2.1 Model description and assumptions

The pilot scale reactor used in this paper was developed by Labtech Int. Ltd (Bulgaria) and tested in our laboratories, a detailed description of the reactor and experimental procedure can be found in [10]. The physical processes inside the reactor involved multi-component and two phase flow hydrolysis and heat and mass transfer. The proper reaction kinetics was also taken into account to govern the source/sink term in the species and heat balances. To describe the two phase flow we adopted the so-called bubble flow which is a simplification of the two fluid Euler-Euler model. Just like the Euler-Euler model it treats the two phases as interpenetrating media, tracking the averaged concentration of the phases. One velocity field is associated with each phase, and a momentum balance equation and a continuity equation describe the dynamics of each of the phases. Differences to the Euler-Euler model rely on the following assumptions: (1) the gas density is negligible compared to the liquid density; (2) the motion of the gas bubbles relative to the liquid is determined by a balance between viscous drag and pressure forces; (3) the two phases share the same pressure field.

A schematic representation of the reactor and computational domain is shown in Fig. 1. The governing equations were applied on a two dimensional plane which was divided into three regions: reactive solution; thermal fluid and metal walls.

2.2 Momentum balance

Based on the bubble model simplifications we end up with a set of equations to describe the two phase flow at the reactive solution region: momentum equation for the liquid velocity, continuity equation, and transport equation for the volume fraction of the gas phase. The momentum equation was computed as follows:

$$\phi_l \rho_l \frac{\partial \mathbf{v}_l}{\partial t} + \phi_l \rho_l \mathbf{v}_l \cdot \nabla \mathbf{v}_l = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \phi_l \rho_l \mathbf{g} \quad (1)$$

where, \mathbf{v}_l is the liquid volume fraction, ρ_l is the liquid density, \mathbf{v}_l is the liquid velocity, p is the pressure, $\boldsymbol{\tau}$ is the viscous forces and \mathbf{g} is the gravity. The continuity equation is

$$\frac{\partial}{\partial t} (\phi_l \rho_l + \phi_g \rho_g) + \nabla \cdot (\phi_l \rho_l \mathbf{v}_l + \phi_g \rho_g \mathbf{v}_g) = 0 \quad (2)$$

where, \mathbf{v}_g is the gas volume fraction, ρ_g is the gas density. The equation for the transport of the gas volume fraction is

$$\frac{\partial}{\partial t} (\phi_g \rho_g) + \nabla \cdot (\phi_g \rho_g \mathbf{v}_g) = 0 \quad (3)$$

Beyond these three equations several other constitutive relations are needed to solve the momentum balance, for more details reference [11] should be consulted.

To solve Eqs. (1), (2) and (3) boundary conditions needed to be applied. At the solution/wall interfaces was assumed no slip boundary condition, and at the solution/hydrogen interface the boundary condition was set as slip.

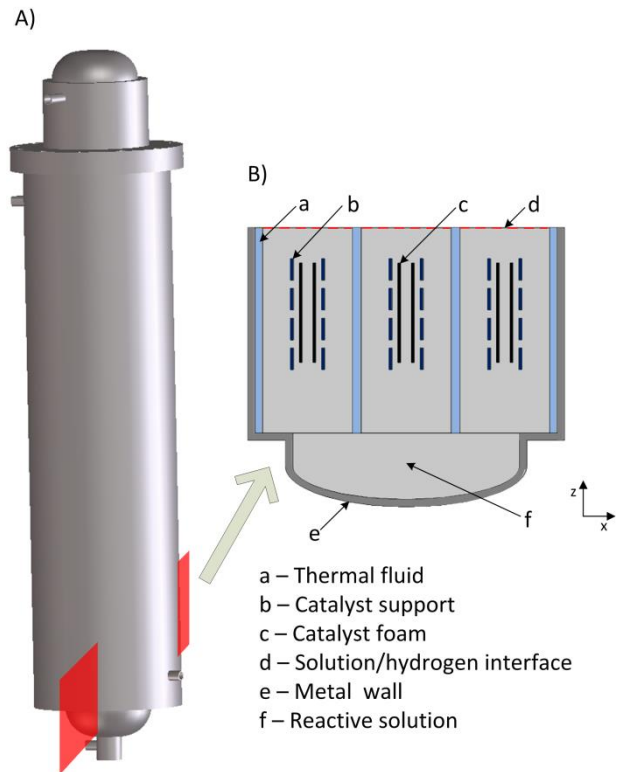


Fig. 1. Schematic representation of the pilot scale reactor (A) and computational domain (B) used in this work.

2.3 Species balance

The species balance was solved to calculate the variation of NaBH_4 concentration in the solution. The concentration of NaBH_4 was given by the following equation:

$$\frac{\partial [\text{NaBH}_4]}{\partial t} + \mathbf{v} \cdot \nabla [\text{NaBH}_4] - D_{\text{NaBH}_4} \nabla^2 [\text{NaBH}_4] + \mathbf{v} \cdot \nabla [\text{NaBH}_4] = R_{\text{NaBH}_4} \quad (4)$$

where, D_{NaBH_4} is the diffusion coefficient of NaBH_4 and R_{NaBH_4} is the reaction rate expression.

The reaction rate is zero everywhere except on the catalyst surface. In these regions it is assumed the expression developed by the authors for the kinetic behaviour of NaBH_4 on Ru/Ni-foam catalyst [10].

Boundary conditions were also required to solve Eq. (4). In this case it was only necessary to set the concentration of NaBH_4 at the initial instant ($t = 0$ s).

2.4 Conservation of energy

The temperature distribution in all regions of the computational domain was obtained by a single equation:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \mathbf{v} \cdot \nabla T = \nabla \cdot (\lambda \nabla T) + Q \quad (5)$$

where, C_p is the heat capacity, λ is the thermal conductivity and Q is the heat source. The heat source was zero everywhere except at the catalyst region. The hydrolysis reaction, with a reaction heat of $-2.1 \times 10^5 \text{ J mol}^{-1}$, is extremely exothermic; therefore, as hydrogen is generated heat is released from the catalyst sites. In the solution region it was assumed that heat was only transported through the liquid phase, since gas concentration was very low. This assumption proved to be very useful in terms of computational time and convergence.

To solve Eq. (5) several boundary conditions had to be applied in the different regions of the computational domain. For the metal walls region we set natural convection at the exterior walls of the reactor, in this boundary condition we assumed room temperature to be $20 \text{ }^\circ\text{C}$. For the thermal fluid region we assumed a constant velocity on the z direction (taken from previous model [10]) and set $45 \text{ }^\circ\text{C}$ as inlet temperature; at the outlet we simply assumed outflow as boundary. At last, for the solution region we only need to set outflow at the solution/hydrogen interface. As initial conditions ($t = 0 \text{ s}$) we assumed that the thermal fluid, metal walls and hydrogen storage regions were at $45 \text{ }^\circ\text{C}$. The NaBH_4 solution at the initial instant was at $40 \text{ }^\circ\text{C}$.

It was shown by Cess [12] that radiation effects could influence to some extent forced convection heat transfer, especially in low density applications for which Reynolds numbers may be quite low. These conditions did not occur inside the reactor, therefore radiative heat was neglected.

3 Results

As mentioned before, in this work we developed a two-phase flow model to account for the effect of the hydrogen bubbles rising from the catalyst foam on the full hydrogen generation process. It was concluded in our previous work that the stirring of the reactive solution due to the hydrogen bubbles could have a massive impact on performance. Therefore, we tested several scenarios in order to take into account this phenomenon. In this short paper are shown results for three different catalyst loadings. As the catalyst loading was changed the reaction rate was affected, and consequently the concentration of gas on the reactive solution. The variation of the amount of catalyst exposed to the reactants was achieved by taking as 100% the amount of Ru catalyst experimentally deposited on nickel foam ($7.93 \times 10^{-3} \text{ kg m}^{-2}$) and actually used in the reactor.

3.1 Moles of NaBH_4

Fig. 2 shows the evolution of NaBH_4 moles obtained experimentally and model results. Three different cases were tested: (a) 100% catalyst loading ($7.93 \times 10^{-3} \text{ kg m}^{-2}$); (b) 70% catalyst loading and (c) 30% catalyst loading. As is possible to see only when catalyst loading was drastically decreased

(30% catalyst loading) we could match the experimental data. This fact can be related to two factors. First, the two dimensional computational domain could not capture the real reactor behaviour, besides the two dimensional representation of the catalyst foam was rather difficult which could lead to errors. Second, in this model we assumed that all catalyst sites were equally available for the hydrolysis reaction. However, from the obtained results we can observe a different behaviour, not all deposited Ru was available. This is thought to be partly due to unavailability of catalyst due to the resident time of gas bubbles and partly due to the thickness of the foam (1.6 mm). The reaction probably occurs on the surface of the foam decreasing in this way the overall process efficiency.

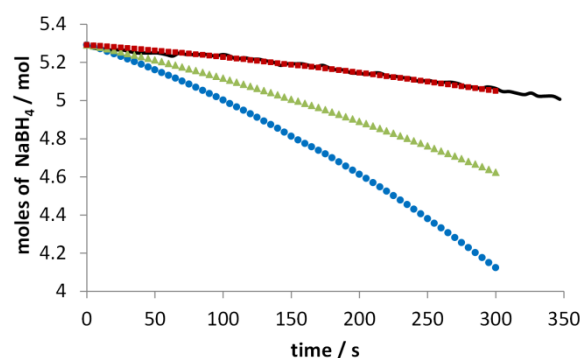


Fig. 3. Moles of NaBH_4 as a function of time. — experimental data; ● 100% catalyst loading; ▲ 70% catalyst loading; ■ 30% catalyst loading

3.2 Liquid phase velocity

Fig. 3 shows the liquid velocity for 100% catalyst loading and for 30% catalyst loading at $t = 350 \text{ s}$. As it is possible to see the reaction rate had a massive impact on the solution stirring. Without any mechanical stirring this phenomenon was responsible for the convective transport of the reactive species. An important observation is the fact that even when 100% of the catalyst loading was used the bottom of the reactor revealed very low velocity. Therefore, the solution was not perfectly stirred which could lead to a yield decrease because not all NaBH_4 reached the catalyst sites.

3.3 Temperature profile

Fig. 4 shows the temperature distribution for 100% catalyst loading and for 30% catalyst loading at $t = 350 \text{ s}$. As expected, temperature was higher at the interface catalyst foam/solution for both cases. In this region the reactive heat released during the hydrolysis reaction warm up the surrounding areas. This phenomenon was more extreme for the highest catalyst loading; the difference between the highest and lowest temperatures was $21.4 \text{ }^\circ\text{C}$. On the other hand and when 30% of the catalyst loading was used the temperature difference was only $5.4 \text{ }^\circ\text{C}$.

Taking into account that this last case was the one that better match the experimental data we can

conclude that the reactor design was able to control the temperature of the reactive solution.

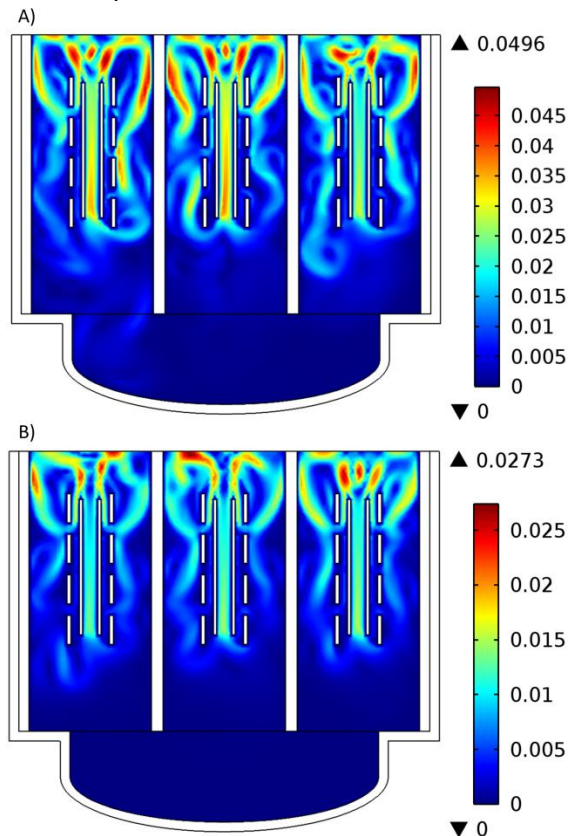


Fig. 3. Liquid phase velocity (m s^{-1}) at 350 s. A) 100% catalyst loading; B) 30% catalyst loading.

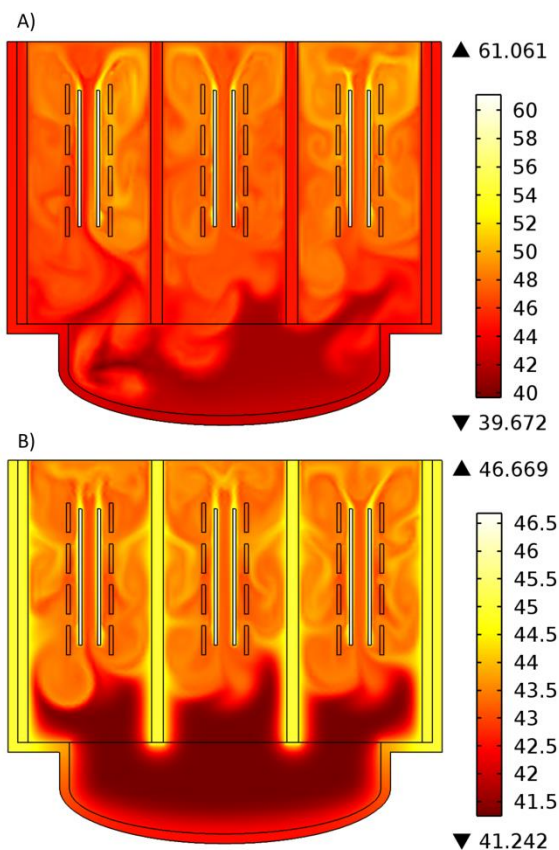


Fig. 4. Temperature ($^{\circ}\text{C}$) at 350 s. A) 100% catalyst loading; B) 30% catalyst loading.

4 Conclusion

In this paper, a dynamic, non-isothermal and two phase flow model was developed to simulate a pilot scale reactor and to observe the impact of the two phase flow on performance. Simulation results showed that the hydrolysis reaction would most probably occurred on the surface of the catalyst foam. This observation is extremely important for future catalyst support design and development. Besides, we concluded that the catalyst foam position plays an important role on the solution stirring. This position must be optimised in order to achieve an optimum mixture inside the reactor. Only in this way all NaBH_4 would be able to reach the catalyst sites. At last, the reactor design seemed to be able to deal with the heat transfer phenomenon.

5 References

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