A coupled transport model for water splitting within a porous metal oxide thermochemical reactor using the random walk particle tracking method

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ABSTRACT

Water splitting using an iron-based looping processes is a promising method to produce high purity hydrogen. The cyclical, heterogeneous oxidation and reduction reactions are carried out within high surface area stable porous structures as the solid reactant. The random walk method is used to simulate chemical reaction and species transport, as it is capable of handling stiff reaction kinetics and varying hydrodynamic dispersion tensors caused by pore-level velocity fluctuations. The original random walk formulation is extended to account for bulk density variations and source terms due to the chemical reaction. The species transport equation is recast in the form of the Fokker—Planck equation, and the trajectories of fluid particles are obtained by solving an appropriate Langevin equation that has additional drift terms as a result of spatial variations in bulk density and dispersion tensor. The source term is accounted for by changing the composition of fluid particles based on the reaction kinetics. The extended approach for each new term is validated against exact solutions or highly resolved finite difference solutions. Finally, a new coupled model for bulk fluid flow, species transport, and chemical reaction in porous media is developed and applied to simulate a bench-scale water splitting reactor with a porous iron-silica fixed bed structure. Excellent agreement with the measured hydrogen production rate at different operating conditions is obtained.

Introduction

Clean and renewable sources of energy are critical for long term human development. Hydrogen produced from sustainable resources is an ecologically-benign fuel which can be used in electrochemical cells as well as for direct combustion. There are numerous processes that generate hydrogen from water, fossil and renewable biomass resources. These processes include reforming and pyrolysis as well as electrolysis and thermolysis [1—4]. Currently, the leading technology for producing hydrogen in large quantities is steam reforming of

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methane [5]. Solar thermal chemical cycles, especially cycles involving metal/metal oxide systems, have recently drawn a lot of attention [6,7]. In these processes, hydrogen is produced from water by oxidizing a metal, and the subsequent metal oxide is reduced back to metal using solar heat in a thermal reduction step [8,9].

Mehdizadeh et al. [10] reported a novel strategy for making magnetically stabilized porous structures to produce hydrogen through the looping process. This process involves the production of hydrogen from steam at high temperatures (800 °C) by oxidizing the iron in the porous structure and reducing the iron oxide to elemental iron by flowing a reducing agent such as carbon monoxide, thus completing one cycle of the looping process (see Eq. (1)). Carbon monoxide required for the reduction step is obtained from gasification of coal and therefore the energy content of coal is transferred to hydrogen with high purity which can be utilized as a clean fuel.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{1a}$$

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2 \tag{1b}$$

This process involves mass, momentum, and species transport in porous media with significant chemical reactions between the solid and the gas phase. A detailed analysis or simulation that can account for those complex physical and chemical mechanisms is highly desirable in order to develop a better understanding of the process and provide useful guidelines for optimal operating conditions and engineering design.

Simulating the reaction of steam within a porous structure can be performed at the pore level in which the exact geometry of the porous media is used and fluid flow is simulated within the pore spaces. This method requires a high resolution representation of the porous media. Moreover the method is computationally expensive since all relevant small pore-level scales must be resolved. As an alternative, continuum models are developed by treating solid and fluid phases as interpenetrating continua using the method of volume averaging [11]. The computational cost of solving continuum models is significantly lower. However, effective transport properties of the solid matrix are required.

Species transport in porous media consists of macroscopic advection due to bulk fluid flow, dispersion due to irregular flow patterns caused by the presence of the solid matrix, and diffusion due to molecular motion. For advection dominated flows, the commonly used finite volume or finite difference methods for solving transport problems using an Eulerian formulation suffer from numerical dispersion and artificial oscillations. They require highly resolved grids and small time steps to overcome the associated errors [12,13]. The shortcomings of these methods are more pronounced when applied to heterogeneous porous media with small scale features [12].

Lagrangian methods, on the other hand, inherently have zero numerical dispersion and are suitable for heterogeneous porous media [12,14]. Typically computational costs of particle methods are relatively higher than those of Eulerian methods, but they are easy to parallelize and consequently computational time can be reduced significantly [15].

Due to unique features of the Lagrangian particle based methods, they are widely used in modeling solute transport within porous media. Ground water and contaminant flow simulations are essentially performed on large heterogeneous domains that involve several length scales and hence stochastic particle tracking methods, such as random walk (RW), are very well suited to obtain accurate results with high stability and efficiency. As a result, the majority of studies reported in the literature considers the reaction and transport of species within the liquid inside the porous underground reservoir [15–17]. Moreover, similar Lagrangian methods are developed and employed to simulate turbulent flows and solve the reaction-diffusion equations for propagating laminar flames [18–22].

In the present paper, the random walk particle method is used to simulate water-splitting processes within porous iron-silica structures. The coupling of bulk fluid flow and mass transport in this process requires modification to the conventional random walk particle tracking method. The extended method with such modifications is validated against known exact solutions for special cases or high resolution finite difference solutions when no exact solution is available. The model is then used to predict hydrogen production rates within a laboratory scale reactor at different operating conditions, and results are compared with experimental measurements.

Mathematical model

The volume averaging method is employed to develop the continuum scale model. The intrinsic volume average of a quantity ϕ is defined as [11]:

$$\langle \phi \rangle^F = \frac{1}{V_F} \int_{V_F} \phi dV \tag{2}$$

where V_F is the volume filled with the fluid phase of a representative elementary volume (REV) [23] of the porous medium. The superficial average is the average over the total volume of all phases within a porous medium:

$$\langle \phi \rangle = \frac{1}{V} \int_V \phi dV \tag{3}$$

With the definition of porosity, $\varepsilon = \frac{V_F}{V}$, and the assumption of no macro-scale variation of ε, the intrinsic and superficial averages are related via:

$$\langle \phi \rangle = \varepsilon \langle \phi \rangle^F \tag{4}$$

The volume averaged mass conservation equation for the fluid phase within porous media can be written as:

$$\frac{\partial(\varepsilon \langle \rho \rangle^F)}{\partial t} + \nabla \cdot (\langle \rho \rangle^F \langle \mathbf{u} \rangle) = \langle \dot{r} \rangle \tag{5}$$

where $\langle \rho \rangle^F$ is the averaged fluid mixture density, $\langle \mathbf{u} \rangle$ is the superficial average of the velocity vector, and $\langle \dot{r} \rangle$ is the net superficial average rate of volumetric mass production or destruction.