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Photocatalytic water splitting in a fluidized bed system: Computational modeling and experimental studies

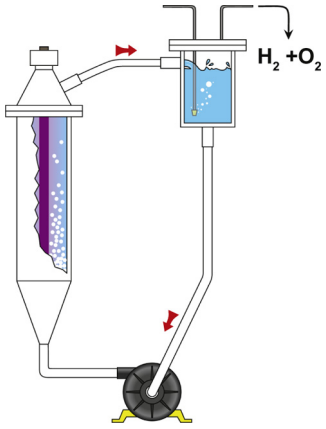
Kevin Reilly, David P. Wilkinson, Fariborz Taghipour*

Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver V6T 1Z3, Canada

HIGHLIGHTS

- UV-irradiated fluidized bed photocatalytic system was applied to water splitting.
- The parasitic Pt-catalysed back reaction can be reduced through novel designs.
- A model describing the performance was developed and validated experimentally.
- The model can be applied to the optimization of photocatalytic systems.

GRAPHICAL ABSTRACT



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ABSTRACT

Photocatalytic water splitting in a novel, UV-irradiated fluidized bed reactor system with Pt-deposited titanium dioxide (TiO_2) particles has been explored as an alternative approach to hydrogen production. A model describing the water splitting performance of the fluidized bed system was developed through a holistic approach combining fluidized bed theory, mass transfer effects, an optical model, and a proposed mechanism for the parasitic Pt-catalysed back reaction of H_2 and O_2. The model was validated experimentally using fluidizable Pt-deposited TiO_2 particles. It was found that the efficiency of the fluidized bed water splitting system is dependent on the rate of mass transfer in the gas–liquid separator, while the overall rate of hydrogen evolution was found to vary with the height and density of the photocatalyst bed in the reactor; all of which are functions of the fluidization flow rate. It is shown that maximizing the rate of mass transfer in the gas–liquid separator can greatly diminish losses due to the Pt-catalysed back reaction of H_2 and O_2, yielding significant gains in efficiency and the overall rate of hydrogen production. The application of the model to the design of the fluidized bed water splitting system, the sub-systems and the photocatalyst particles is discussed.

1. Introduction

Photocatalytic water splitting over heterogeneous semiconductor photocatalysts has long been sought after as an affordable and efficient solar-to-chemical energy conversion process. While many photocatalyst materials have been developed since the initial discovery of

* Corresponding author.
E-mail address: fariborz.taghipour@ubc.ca (F. Taghipour).

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Nomenclature

a	liquid-gas interfacial area [cm^2/cm^3]
A_c	reactor cross-section area [cm^2]
Ar	Archimedes number [ ]
B_{ex}	bed expansion [ ]
C_{cat}	photocatalyst mass concentration [g/cm^3]
C_F	H_2 conc. in the liquid bulk in the fluidized bed reactor (mol/cm^3)
C_L^*	H_2 conc. at the L-G interface (mol/m^3)
C_s	H_2 conc. in the liquid bulk within the separator (mol/cm^3)
d_p	particle diameter (cm)
d_p^*	dimensionless particle diameter [ ]
D	diffusion coefficient [cm^2/s]
g	gravitational acceleration constant [cm/s^2]
Ga	Galileo number [ ]
H	Henry constant [M/atm]
H_{bed}	static bed height [cm]
H_{ex}	expanded bed height [cm]
I	light intensity [ein/min·cm^2]
k_L	mass transfer coefficient [cm/min]
k_La	overall mass transfer coefficient [min^{-1}]
k_L'	mass transfer coefficient [min^{-1} cm^{-3}]$^{0.5}$
k_L''	aggregate mass transfer coefficient [cm^{-3} min]$^{0.5}$
k_r'	back reaction rate constant [cm^3/g min]
k_s	mass transfer coefficient [m/s]
m	constant [ ]
M*v*	Mass number [ ]
n	expansion coefficient [ ]
N_G	interface-gas mass transfer rate
N_L	liquid-interface mass transfer rate
N_S	solid-liquid mass transfer rate
p_{H_2}	hydrogen partial pressure [atm]
P_{abs}	overall rate of photon absorption [ein/min]
P_i	total rate of photons entering the reactor [ein/min]
r_p	particle radius [cm]
R_o	radius of outer reactor wall [cm]
R_i	radius of the inner annulus [cm]
q	volumetric flow rate [cm^3/s]
q_e	elutriation flow rate [cm^3/s]
q_{mf}	flow rate at minimum fluidization [cm^3/s]
r_r	rate of back reaction [mol/min]
r_d	H_2 generation rate [mol/min cm^3]
r_{net}	net H_2 evolution rate [mol/min cm^3]
R_d	overall H_2 generation rate [mol/min]
R_{net}	net H_2 evolution rate [mol/min]
RTE	Radiation Transfer Equation
S	photocatalyst surface area
S_L	rate of photons entering the reactor per lamp length
Sc	Schmidt number [ ]
Sh	Sherwood number [ ]
U	superficial velocity [cm/s]
U_e	particle settling velocity [cm/s]
U_t	terminal velocity [cm/s]
U^*	dimensionless terminal velocity [ ]
V_{bed}	expanded bed volume [cm^3]
V_s	separator volume [cm^3]
W_{cat}	photocatalyst mass [g]
W_{max}	maximum mass of catalyst [g]
α	photon attenuation coefficient [cm^3/g]
ε	bed voidage [ ]
ε_0	voidage of the static bed [ ]
θ_c	"contact time" of a packet of fluid at the liquid-gas interface [min]
μ	fluid viscosity [cP]
ρ_p	bulk particle density [g/cm^3]
ρ_f	fluid density [g/cm^3]
σ	aggregate attenuation cross section [cm^2/g]
$\sigma_{abs,l}$	probability of photon absorption by the liquid phase [cm^2/g]
$\sigma_{abs,p}$	probability of photon absorption by the particles [cm^2/g]
$\sigma_{scatter}$	probability of photon scattering by the particles [cm^2/g]
τ_F	fluidized bed residence time [min]
τ_S	separator residence time [min]
ϕ	sphericity [ ]
Φ	photochemical efficiency [mol/ein]
Φ_{app}	apparent quantum efficiency [mol/ein]
ψ	function of the hydrodynamic parameters of the model

photocatalytic water splitting by Fujishima and Honda [1], the low cost, favorable energetics and high stability of TiO_2 has propelled titanium dioxide to become one of the most popular and widely studied photocatalysts [2,3].

Titanium dioxide and, indeed, most other photocatalysts typically require the addition of noble metal nanodeposits (Pt being the most commonly employed) on their surfaces to reduce charge recombination and allow water splitting to proceed at appreciable rates [2,3]. The presence of Pt or other noble metals, however, promotes the parasitic back reaction of hydrogen and oxygen to form waste heat and water, thus severely limiting the efficiency of the process. While attempts have been made to reduce this effect [4], efficient and low cost alternatives to noble metal co-catalysts have yet to be identified.

The parasitic back reaction is particularly prevalent in suspended photocatalyst slurries, as the evolved H_2 and O_2 remain in contact with the high surface area photocatalyst particles for extended periods of time. Though the photocatalyst particles may be immobilized onto supporting substrates in order to facilitate rapid separation of the product gases from the photocatalysts, the performance of immobilized film photocatalysts are generally limited due to poor radiation distribution, low photon capture, and mass transfer effects [5–9].

Despite the incredible progress in photocatalytic water splitting materials research, relatively little attention has been given to the design of the solar-to-hydrogen systems in which these materials could be employed. Indeed, few unique photocatalytic water splitting systems have been demonstrated at bench- [10–15] or pilot-scale [16–20]. Moreover, none of the pilot scale demonstrations could carry out *direct water splitting* and thus required the use of sacrificial reagents, such as methanol, as hole scavengers.

There have been remarkably few attempts to utilize the design of the reactor and its system to mitigate the effects of the parasitic back reaction and enhance the rate of hydrogen evolution [21]. Photocatalytic fluidized bed reactors have gained popularity for processes such as water treatment as they offer improved mass transfer, excellent radiation distribution, and a photocatalyst surface area-to-volume ratio approaching that of suspended photocatalyst nanoparticle systems [22–24], while also yielding fast and simple separation of the reaction products from the photocatalyst particles (much like immobilized photocatalyst film reactors). A photocatalytic fluidized bed approach to water splitting can greatly mitigate the parasitic back reaction while retaining the mass transfer, radiation distribution, and photocatalyst surface area-to-volume characteristics of the suspended nanoparticle systems.

Previously, we reported preliminary findings on photocatalytic water splitting in a UV-irradiated fluidized bed reactor where it was found that, on a per reactor volume basis, the fluidized bed approach