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Heat and mass transfer in a copper oxy-chloride spray reactor for thermochemical hydrogen production

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ABSTRACT

A new predictive model is developed in this paper to analyze the height of the reactor for continuous production of copper oxy-chloride in the thermochemical Cu–Cl cycle for hydrogen production. The volumetric phase fraction is used to develop an energy balance and integrated spatially to determine the inlet temperature of nitrogen and steam mixtures for continuous production of copper oxy-chloride. The effects of the ratio of mixing power to mass of the suspended particle, the ratio of interfacial surface area of the gas film to the volume of liquid, and diameter of the steam/nitrogen bubble in the reactor, on the height of the reactor are reported for a production capacity of 3 kg of hydrogen per day. Results indicate that a smaller ratio of interfacial surface area to volume of liquid significantly reduces the height of the reactor.

Introduction

One of the major technical challenges of the Cu–Cl cycle for thermochemical hydrogen production is the hydrolysis step to produce copper oxy-chloride (Cu_2OCl_2). Recent advances in the Cu–Cl cycle have shown that in order to improve the efficiency of the cycle, the drying of the $CuCl_2$ particles from the electrolysis step and the hydrolysis step to produce Cu_2OCl_2 should be combined into one process. In order to achieve this objective, a spray roaster was determined as an effective means to integrate the cycle and avoid the dual processes. This paper investigates the heat and mass transfer processes of the reaction kinetics in the spray roaster to produce Cu_2OCl_2.

Extensive experimental studies were conducted by researchers at the Argonne National Laboratory (ANL) for a spray reactor [1,2] to determine the mass flow rate of steam required to produce Cu_2OCl_2, using a mixture of argon/steam to supply heat to the reactor. The results indicated that 100% yields of Cu_2OCl_2 were achieved when an ultrasonic nozzle is used to inject the reactants into the reactor at about 375 °C. The products were examined using X-ray diffraction (XRD) and scanning electron microscope (SEM) images. The results also indicated that a concurrent flow into the reactor chamber of $CuCl_2$ slurry and steam was preferable for efficient production of Cu_2OCl_2.

The excess steam required by spray reactor experiments conducted by ANL to produce Cu_2OCl_2 reduces the efficiency of the system. The cost of the plant increases with an

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increasing steam requirement to achieve continuous production of Cu_2OCl_2. Pope et al. [3] performed experimental studies to investigate the possibility of using nitrogen to reduce the steam requirement of the hydrolysis reaction in a fluidized bed reactor. The experimental results reported by Pope et al. [3] indicated that nitrogen will reduce the steam consumption, but the yield of Cu_2OCl_2 was not adequate for further development of the fluidized bed reactor. The gas film layer formed around the solid $CuCl_2$ particles during the hydrolysis reaction may be responsible for the incomplete conversion observed in the hydrolysis reaction.

This paper modifies the reaction by using nitrogen in the concurrent flow spray reactor proposed by Ferrandon et al. [4,5] to achieve continuous production of Cu_2OCl_2. Past studies have indicated that the chemical conversion effectiveness decreases as reactants are consumed [3]. Ferrandon et al. [6] reported that the conversion extent of the solid hydrolysis reactant indicated an optimal conversion of 4 mol–15 mol of steam per mol of HCl produced [7]. Further studies [8] indicated thermodynamic an optimal temperature of the hydrolysis reactor to be approximately 375 °C.

The numerical investigation in this study determines the molar flow rate of N_2 to sustain the reaction. The study also investigates the reactor size required to produce 3 kg of H_2/day, which is the target production rate of a pilot-scale system under construction at the University of Ontario Institute of Technology (UOIT). This paper investigates the heat and mass transfer mechanisms of the spray reactor to reduce the consumption of steam and continuously produce 3 kg of H_2/day. For an integrated Cu–Cl cycle with a hydrogen production rate of 3 kg/day, the corresponding required capacity of copper oxychloride production is about 13.3 kg/day in the spray reactor. The primary goals of this paper are to gain better understanding and insight into the effects of temperature, particle size, mixing power, interfacial reaction surface, and bubble dispersion in the spray reactor.

System description

The hydrolysis reaction can be represented by the following reaction:

$$2CuCl_{2(aq)} + H_2O_{(g)} \rightarrow Cu_2OCl_{2(s)} + 2HCl_{(g)} \quad (1)$$

The products are fed into the thermolysis (Cu_2OCl_2) reactor and the electrolytic cell (HCl). The efficient operation of the electrolysis process requires that the concentration of HCl is between 6 and 11 mol. Using the concurrent flow reactor suggested by Ferrandon et al. [5], the steam is injected with Ar at a flow rate of 400 mL/min at 370 °C for continuous production of Cu_2OCl_2. A steam to $CuCl_2$ ratio of 20 produced the desired amount of Cu_2OCl_2 for the spray reactor. Numerical investigations for a fluidized bed reactor reported by Daggupatti [9] reported a ratio of 17:1 for the steam to $CuCl_2$ for the reactor operating between 350 °C and 400 °C.

The spray reactor analysis is a complex transport problem involving atomization, heat and mass transfer, and phase change. The $CuCl_2$ slurry is sprayed into the reactor at about 150 °C, while the nitrogen/steam mixture is injected at about 375 °C. The path of the reaction is depicted in Fig. 1 for the particle. The analysis assumes that when slurry enters the reactor, the high temperature mixture of steam and nitrogen evaporates the water in the slurry so the steam concentration decreases accordingly in Fig. 1. The steam subsequently diffuses down a concentration gradient in Fig. 1 through the film surrounding the surface of the particle. The reaction rate is slower within the core of the solid particle as the reaction takes place on the solid surface. The gaseous surface diffuses back through the film again down a concentration gradient and through the main body of the slurry.

Reaction rate formulation

Considering a multiphase concurrent flow configuration in Fig. 2, the kinetic equations for the chemical reaction are used to determine the height of the reactor. It is assumed that the reaction rate is slower than the mass transfer. The reaction rate is best measured in terms of unit volume of the reacting phase rather than the interfacial surface between phases. The material balance for the reactor can be expressed as follows:

$$GdY = -\frac{LdX}{b} = -r_y dh = \frac{\text{moles of Y reacted}}{(\text{volume of liquid})(\text{time})} \left(\frac{\text{volume of liquid phase}}{\text{total volume}}\right)(\text{Height of element}) \quad (2)$$

where Y is the $CuCl_2$ slurry, X is steam, G is the molar flow rate of the inert gas in the gas phase, L is the molar flow rate of the inert gas in the liquid phase, r_y is the reaction rate, h is the height of the reactor, and b is the moles of steam consumed.

The model assumes that the slurry is insoluble in the steam, and the amount of the unreacted steam in the liquid is small compared to the steam in the gas phase. Each mole of reacting steam is replaced by fresh steam sprayed in the reactor. Integrating over the control volume, the height of the reactor can be estimated by

$$h = \frac{G}{f}\int_{y_1}^{y_2}\left[\frac{dY}{r_y}\right] = -\frac{L}{bf}\int_{x_1}^{x_2}\frac{dX}{r_y} \quad (3)$$

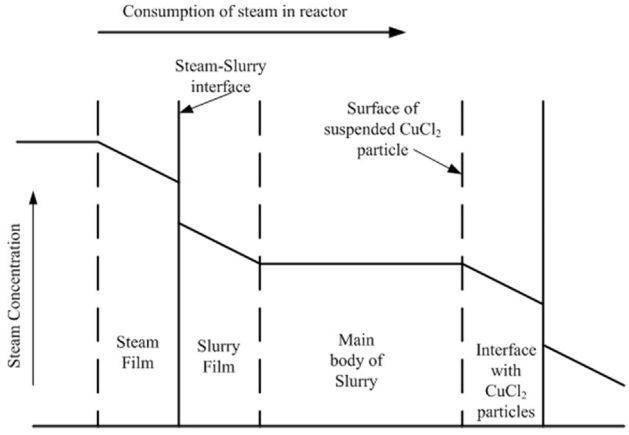

Fig. 1 – Reaction resistance in spray roaster for a droplet in the spray reactor.