Analysis of Reaction Kinetics for a Two-step Hydrogen Production Process Utilizing Porous Iron Powder

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Thermochemical water splitting is a hydrogen production process that has garnered significant attention in recent years. Unlike direct water splitting, which requires very high temperatures (2500 K), the dissociation of water into H_2 and O_2 via thermochemical water splitting uses reactive metals in a multi-step metal reduction-oxidation (redox) reaction. Many redox reactions have been proposed for hydrogen production, and this work considers the kinetics of thermochemical water splitting utilizing a porous iron powder in a fluidized bed reactor. Porous iron powder with particle diameters ranging from 45 to 150 μm is fluidized and heated within a furnace. The powder is classified as Geldart group B, and when fluidized, it exhibits good mixing, heat transfer and reactivity. A bench scale experimental facility was fabricated to carry out the investigations of hydrogen production via water splitting. The current analysis is limited to the water splitting (oxidation) step at different reactor temperatures. The temperature states for the fluidized bed under investigation are 450, 650 and 850 °C. The approximate reactive surface area of the iron powder is 60 cm^2/g, and thus the surface area of the 25 g sample in the fluidized bed is 0.158 m^2. For the duration of the experiments,18 to 26 minutes, the hydrogen yield is 0.37, 4.5 and 10.45 L for the 450, 650 and 850 °C, reactor temperatures respectively. The rate of hydrogen production decays exponentially with time.
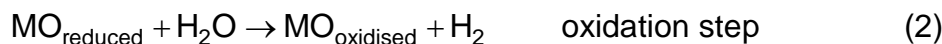
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1   Introduction

The abundance of hydrogen on earth, and its high energy per unit mass makes it attractive as an energy carrier. However, it is uncommon in its elemental form, due to its reactivity, and it is generally found combined with other elements, such as in water or hydrocarbons. In order to retrieve the hydrogen in elemental form, innovative separation methods are required. Currently available methods include electrochemical, biological, and thermal approaches. One promising technology for hydrogen production is thermochemical water splitting (TCWS). TCWS cycles have the potential to deliver overall system efficiencies in excess of 40% [7]. Direct water splitting requires very high temperatures (2500 K) to dissociate water into H_2 and O_2 [6], while thermochemical water splitting uses reactive metals to lower the reaction temperature [4] by splitting water through a series of two or more chemical reactions [2]. In addition, TCWS cycles release oxygen and hydrogen in two separate steps, hence avoiding any recombination which will eliminate any separation steps [2].

In a two-step reaction, the metal oxide is reduced as shown in reaction (1). In the water splitting (WS) step or oxidation step, reaction (2), the activated material is oxidized by the

water, releasing hydrogen. For reactions (1) and (2) M denotes the metal, which follows the convention utilized by Steinfeld [5].

$$MO_{oxidised} \rightarrow MO_{reduced} + O_2 \qquad \text{reduction step} \qquad (1)$$

$$MO_{reduced} + H_2O \rightarrow MO_{oxidised} + H_2 \qquad \text{oxidation step} \qquad (2)$$

Significant research activity with thermochemical water-splitting cycles began 40 years ago. Many Investigations were initiated in the 1970's as a result of the Energy Depot project that was carried out in 1960 [3]. The project aimed at investigating the opportunities to produce fuel from renewable sources. These investigations considered direct hydrogen production using a nuclear heat source. Currently over 350 thermochemical cycles have been identified [1]. Presently, there are two potential high temperature heat sources being considered for thermochemical hydrogen production, namely, concentrated solar energy or nuclear reactors. Several cycles were thermodynamically examined and tested in solar reactors, including zinc oxides and iron oxides. Other investigations have included titanium, cobalt, and manganese oxides, but the yield of hydrogen production is too low to be of any practical interest [5].

2   Experimental Facility

The water splitting step for the current investigation involves the conversion of iron (Fe) to magnetite (Fe_3O_4) and follows the reaction,

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4\ H_2 \qquad (3)$$
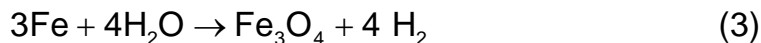
A bench scale hydrogen production process that utilizes a fluidized bed reactor was fabricated and tested at temperatures of 450, 650, and 850 °C as shown in Figure 1. The reaction utilizes porous iron powder with a mean particle diameter of 91 μm. The reaction chamber includes a 0.6 m long fused quartz tube, capable of operating up to temperatures of 1200 °C. The tube has an inside diameter of 21 mm and a wall thickness of 2 mm. A porous quartz frit, with pore sizes ranging from 40-90 μm, is inserted at the top of the tube to minimize particle carry-over. The powder is placed on a distributer made of a ceramic thermal insulation material with a service temperature up to 1650 °C. The tube is sealed with stainless steel fittings utilizing high temperature silicon O-rings that can withstand temperatures up to 300 °C. The quartz fluidization chamber extends through an electric furnace with a range of 100 to 1200 °C.

To prevent condensation in the system, a low flow (2.5 LPM) of high purity nitrogen gas is used to preheat the reactor. A gas heating section is constructed using nickel-chromium wire, grounded to the system at one end and electrically insulated with ceramic beads. The heat input is controlled with a DC power source. All fittings and tubing, including the quartz tube, are preheated to at least 300 °C prior to introducing steam through the system. During the preheat cycle, the nitrogen gas is vented to atmosphere. An estimation of the nitrogen gas remaining in the system after the preheat cycle is used to compensate for its contribution to the hydrogen production.

A steam generator, consisting of four 200W (maximum) cartridge heaters inside an aluminum chamber, is used in a boiling mode. The rate of steam generation is controlled with a pulse-width modulated signal and solid-state relay at a frequency of two Hertz. An AC power source provides power to the boiling chamber. Using a three-way valve, the steam is either directed to a condenser, which empties into a graduated cylinder, or the steam is directed to the fluidized bed reactor. When steam is directed to the condenser, the rate of condensate is measured to determine the mass flow rate of steam production, which is controlled by the heat input to the boiler. The mass flow rate of steam to the reactor is 0.075 g/s for all experiments considered.

The outlet gas from the reactor is directed through a condenser in which any excess steam is removed from the hydrogen gas flow. The condenser empties into a sealed cylinder, and the weight of the condensate is measured. From the cylinder, the hydrogen gas is directed into inverted water-filled graduated cylinders, and the volume of hydrogen accumulation is determined.

Stainless-steel sheathed E-type and J-type thermocouples are used to monitor and record the gas temperatures entering and exiting the quartz reactor chamber as well as the temperatures of the fittings. The electric furnace is also equipped with a K-type thermocouple that allowes estimation of the bed temperature.

The sequence of operating the experiment is as follows. The system is preheated to approximately about 300 °C with nitrogen. During this time, the boiler is heated, and the constant-power steam flow rate is determined. The nitrogen is then shut off, and the steam is directed into the gas heater section and reactor. Hydrogen production is determined by visual observation of accumulation in the graduated cylinders. A data acquisition board, in conjunction with a LabView virtual instrument panel, is used to monitor and log the temperatures at the inlet and outlet of the reactor, as well as the temperatures of the quartz tube fittings, boiler vapor temperature and pressure.
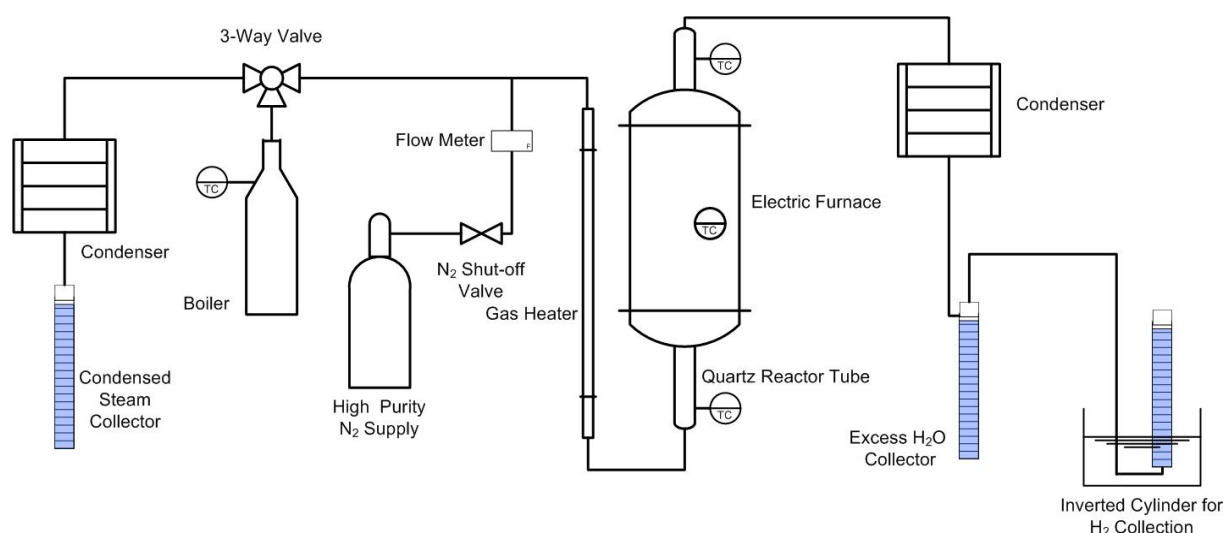

Figure 1:   Experimental fluidized bed hydrogen production facility.

Iron Powder Characterization

For the current reactor configuration, steam is introduced to a fluidized bed of iron powder. The powder has a particle density of 7800 kg/m^3 and an estimated surface area of 60 cm^2/g. This powder is classified as Geldart B. The powder particles, shown in Figure 2, are porous, and the mass fraction weighted average particle diameter is 91 µm.

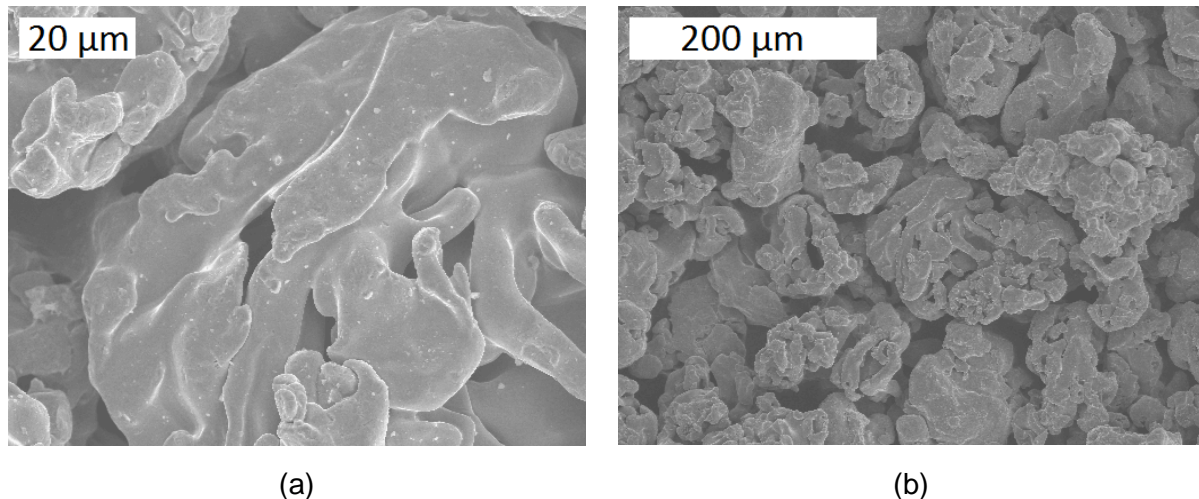| (a) | (b) |

Figure 2: SEM image of the iron powder at (a) 500X and (b) 110X magnification.

3   Hydrogen Production

Hydrogen production rates have been experimentally assessed for the oxidation (water splitting) reaction at various bed temperatures. The various reaction temperatures are measured at the particle bed and controlled by the electric furnace. The total volume of hydrogen collected for the duration of each experiment is limited by the amount of excess steam. Since the excess steam is collected in a container to be condensed and weighed, as illustrated in Figure 1, the volume limitation of the duration time is governed by the volume of the container.

The measured hydrogen volume for each reaction temperature is shown in Figure 3. As the temperature of the reactor increases, the amount of hydrogen produced increases. The total volume of hydrogen produced for 25g of iron is 0.35, 4.5 and 10.5 L for 450, 650 and 850 °C respectively. All volumes are measured at atmospheric conditions. The trend of increasing hydrogen production with increasing temperature is expected since the reaction rate increases exponentially with temperature, according to the Arrhenius equation.
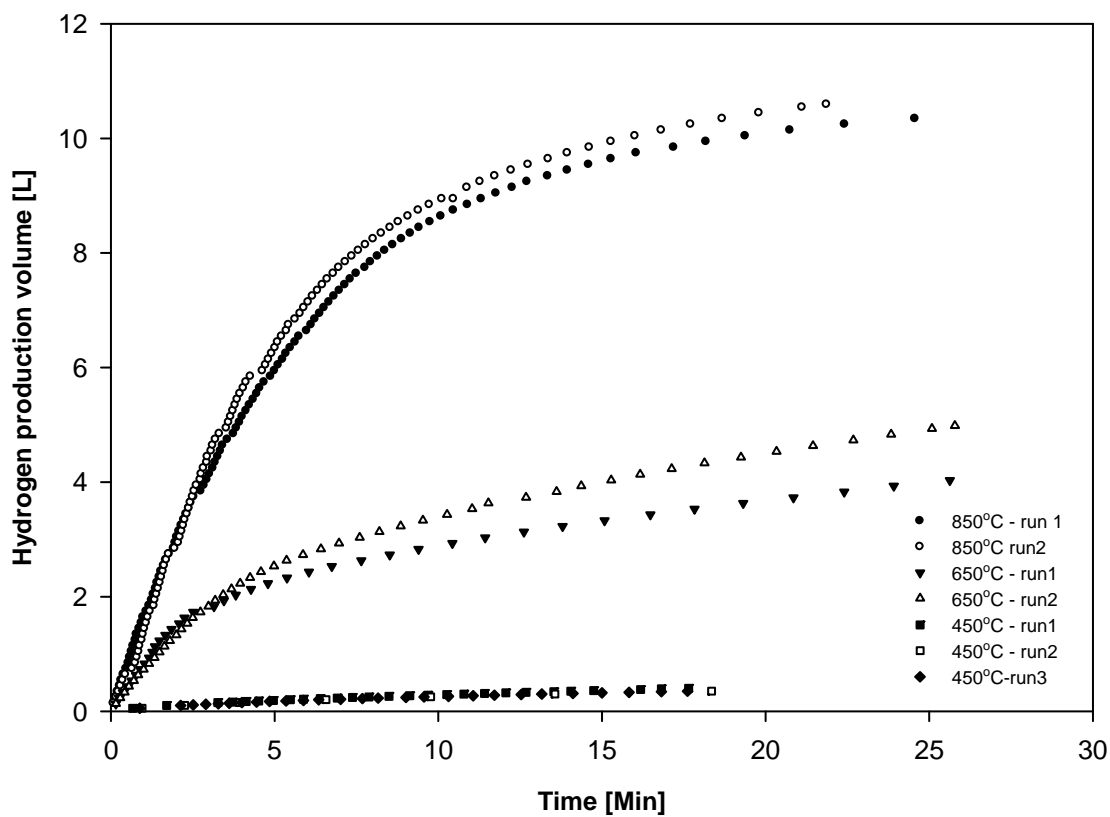
Figure 3:   Hydrogen production at various bed temperatures.

The rate of hydrogen production is determined by differentiating the hydrogen production curves. The time varying hydrogen production rates at different bed temperatures are shown in Figure 4. The rate exponentially decays and is highest at the start of the reaction. As the temperature of the bed increases, the rate of hydrogen production increases substantially. The initial rates of hydrogen production are on average 0.035, 0.75 and 1.9 LPM, for 450, 650 and 850 °C bed temperatures, respectively. The exponentially decaying reaction rate is a result of the decrease of the available particle surface area as the iron particles are coated with an oxide layer. This reduction in surface area is highly transient, and thus a transient conservation of species analysis is required to extract the intrinsic reaction rate constants from the measured hydrogen production. This remains for further investigation.

In all experiments, 25 grams of iron are used to react with water vapor. According to Eq. (3), the reaction of 25g Fe will result in the production of 1.2 g H_2 at equilibrium. The percent conversion of H_2 on a mass basis in shown in Table 2. At the highest temperature the percent conversion of hydrogen is about 72% of the theoretical maximum.
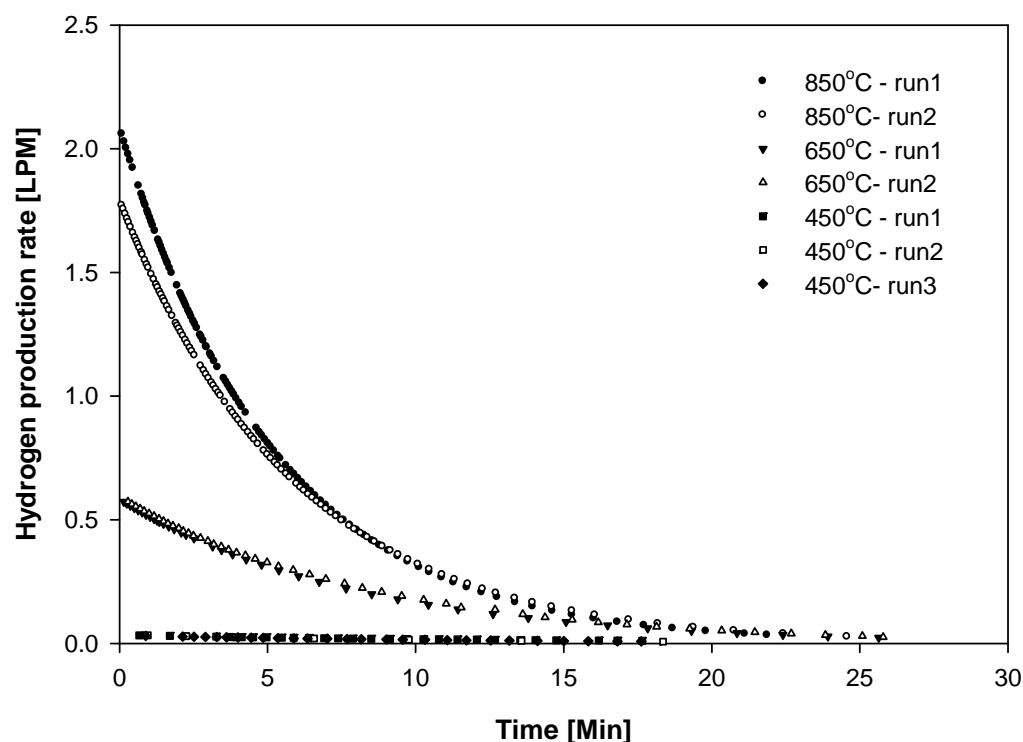
Figure 4:   Hydrogen production rates at various temperature settings.

Table 2:   Comparison of actual and theoretical equilibrium hydrogen production.

T [°C]	H$_2$ Produced [g]	%H$_2$ conversion
450	0.030	2.5
650	0.368	30.9
850	0.856	71.7
Equilibrium	1.194	

4   Conclusions

An experimental evaluation of the water splitting (oxidation) step in a two-step thermochemical cycle was conducted utilizing a fluidized iron powder. 25 g iron powder samples with 60 cm^2/g surface area were used for the fluidized bed experiments. Three temperatures for the iron particle bed were investigated: 450, 650 and 850 °C. It is found that the reaction rate increases substantially with increasing temperature, as expected. The hydrogen production rate reaches a maximum of 2 LPM at 850 °C. Further transient analysis is required to evaluate the intrinsic reaction rate constants for the current hydrogen production data.

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