Experimental investigation of molten salt droplet quenching and solidification processes of heat recovery in thermochemical hydrogen production

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HIGHLIGHTS

- Thermal efficiency of a thermochemical cycle of hydrogen production is improved.
- Direct contact heat recovery from molten salt is analyzed.
- Falling droplets quenched into water are investigated experimentally.

ARTICLE INFO

ABSTRACT

This paper investigates the heat transfer and X-ray diffraction patterns of solidified molten salt droplets in heat recovery processes of a thermochemical Cu–Cl cycle of hydrogen production. It is essential to recover the heat of the molten salt to enhance the overall thermal efficiency of the copper–chlorine cycle. A major portion of heat recovery within the cycle can be achieved by cooling and solidifying the molten salt exiting an oxygen reactor. Heat recovery from the molten salt is achieved by dispersing the molten stream into droplets. In this paper, an analytical study and experimental investigation of the thermal phenomena of a falling droplet quenched into water is presented, involving the droplet surface temperature during descent and resulting composition change in the quench process. The results show that it is feasible to quench the molten salt droplets for an efficient heat recovery process without introducing any material imbalance for the overall cycle integration.

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1. Introduction

Worldwide energy demand is increasing rapidly due to the continuing increase in world population and the desires of developing countries to improve their living standards. A large portion of the world energy demand is met by fossil fuels, because of their availability and convenience. However, it is expected that fossil fuel production worldwide may peak in about 15 years and thereafter begin to decrease [1]. Also, the environmental damage caused by fossil fuel usage and their combustion products is a major problem [2,3]. Hydrogen is a potentially major solution to the problems of climate change. It burns cleanly to produce water without emissions. It is used in fuel cells to generate electricity directly. Its energy content per unit mass is 2.5 times higher than that of any

other conventional fuels [3,4]. Therefore, hydrogen is a promising energy carrier and storage medium for renewable energy resources [3–7]. Lu et al. [8] analyzed the feasibility of an optimal cascade hydropower system using hydrogen, produced from water electrolysis, as an energy storage medium. The authors showed that by using hydrogen production and storage in hydropower stations, more water resources can be used for electricity and hydrogen production, hence the amount of unused water is reduced and electricity generation reliability (EGR) is improved [8]. The economic viability of hydrogen production and storage from excess electricity in a 50 MW wind power plant was investigated by Kroniger and Madlener [9]. Their results showed that the power-to-fuel plant could be operated profitably at a hydrogen price of over 0.36 €/m³ with 100% utilization of the electrolyzer if the hydrogen is directly marketed instead of using it to store and re-generate electrical energy [9]. Coupled operation of a wind turbine and electrolyzer was investigated by Sarrias-Mena et al. [10].

Nomenclature

A	surface area (m^2)
B	bias
C_D	drag coefficient
c_p	specific heat at constant pressure (J/kg K)
d	droplet diameter (mm)
E_b	blackbody emissivity power (W)
g	gravitational acceleration (m/s^2)
h_c	convection heat transfer coefficient (W/m^2 K)
k	thermal conductivity (W/m K)
m	mass (kg)
Nu	Nusselt number
P	precision
Pr	Prandtl number
$\dot{q}_c$	convective heat transfer rate (W)
Re	Reynolds number
T	temperature (°C)
t	time (s)
U	uncertainty
v	velocity (m/s)

Greek symbols

α	thermal diffusivity (m^2/s)
β	fixed (bias) error
δ_k	measurement error
ε	emissivity
θ	angle between the incident ray and the scattering planes (rad)
λ	wavelength of the incident wave (m)
ρ	density (kg/m^3)

Subscripts

atm	atmosphere
d	droplet
g	gas
obj	object
s	surface
sur	surroundings
∞	ambient

The authors evaluated four different electrolyzer configurations under variable wind speeds and grid demand.

Most of the hydrogen currently produced in the world is derived from fossil fuels through different types of reforming processes [11,12]. Developing a sustainable, large-scale, low-cost method of hydrogen production from energy sources other than fossil fuels is required to reduce GHG emissions and accelerate the transition to a clean future. Water electrolysis and thermochemical cycles, using various clean and renewable heat sources, are alternative methods for sustainable hydrogen generation [13–15]. Han et al. [16] reported the effect of various operating conditions and design parameters on the performance of proton exchange membrane (PEM) electrolyzer cells. Their results show that PEM electrolyzer cell performance improves with a decrease in electrode thickness and membrane thickness due to lower diffusion overpotential and ohmic losses. At a current density of 1.5 A/cm^2, the performance loss due to the interfacial resistance between the electrode and the membrane contributes 31.8% of the total ohmic loss. An experimental study on hydrogen production from a 200 W solid oxide stack working in a reverse mode was presented by Penchini et al. [17]. The influence of steam dilution, water utilization and operating temperature on conversion efficiency and the stack's thermal balance was evaluated. The tests were performed at three different operating temperatures over a range of steam inlet concentrations from 50% to 90% and water utilization up to 70%. The net flows up to 2.4 ml/(min cm^2) of hydrogen and 1.2 ml/(min cm^2) of oxygen were measured [17].

A thermochemical cycle has a potentially higher overall efficiency compared to water electrolysis as heat is used directly to generate hydrogen to avoid the thermal energy losses in the heat-to-electricity conversion process. Water electrolysis has an overall heat-to-hydrogen efficiency of about 24%, based on the higher heat value of hydrogen, while thermochemical cycles can reach a heat-to-hydrogen efficiency up to about 50% [18].

A thermochemical water splitting process includes decomposition of water into oxygen and hydrogen using only heat in a fully thermochemical cycle, or a combination of electricity and heat in a hybrid cycle. The net reaction is as follows:

$$H_2O(l) \rightarrow H_2(g) + 1/2O_2(g) \qquad (1)$$

Several thermochemical water splitting cycles, using various sources of energy, have been studied in the past [19–23]. The sulfur–iodine thermochemical cycle, in which solar energy is used for the decomposition of sulfuric acid, was investigated by Huang and Raissi [24]. Xinxin and Kaoru [25] studied the sulfur–iodine (S–I) cycle for hydrogen production using nuclear energy. Energy and economic assessment of an industrial plant for hydrogen production by a sulfur-iodine thermochemical cycle was presented by Liberatore et al. [26]. The efficiency of the thermochemical cycle by itself was about 34%, based on the higher heat value. If this value is associated with the electrical energy production, including the efficiency of the solar plants, the total heat-to-hydrogen efficiency was obtained to be 21%. Varsano et al. [27] analyzed a sodium manganese mixed ferrite thermochemical cycle with a solar reactor receiver packed with pellets of a reactive mixture to investigate the feasibility of the process. The temperature at which the reactor operates is nearly constant within the range of 700–800 °C. About 130–460 micromole hydrogen per gram of mixture is produced during one hour operation of the reactor. An iron-chlorine thermochemical cycle was studied by Canavesio et al. [28]. The theoretical and experimental study was carried out at a laboratory scale to investigate the reaction pathway and the kinetics of the thermochemical cycle in order to improve its overall performance in terms of energy efficiency and hydrogen yield. Xu and Wiesner [29] presented a conceptual design of a two-step iron oxide cycle for production of hydrogen. Molten FeO is used as a storage and heat transfer medium. After five days, the hydrogen production was stabilized at 7 kg/min.

Alternative thermochemical cycles of hydrogen production were evaluated by Lewis et al. [30–32]. Their results showed that the copper–chlorine cycle is chemically possible and feasible concerning engineering aspects and energy efficiency. Dincer and Balta [33] have discussed several cycles for hydrogen production from nuclear energy. The Cu–Cl thermochemical cycle was shown a promising cycle for nuclear-based hydrogen production. Recent advances in thermochemical cycles of hydrogen production, using non-fossil energy sources such as nuclear or solar, were reported by Rosen [18]. The copper–chlorine cycle was shown to have significant potential because of the lower temperature requirement for heat supplies compared to most other thermochemical cycles.