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Vapor compression CuCl heat pump integrated with a thermochemical water splitting cycle

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ABSTRACT

In this paper, the feasibility of using cuprous chloride (CuCl) as a working fluid in a new high temperature heat pump with vapor compression is analyzed. The heat pump is integrated with a copper–chlorine (Cu–Cl) thermochemical water splitting cycle for internal heat recovery, temperature upgrades and hydrogen production. The minimum temperature of heat supply necessary for driving the water splitting cycle can be lowered because the heat pump increases the working fluid temperature from 755 K up to ∼950 K, at a high COP of ∼6.5. Based on measured data available in past literature, the authors have determined the *T–s* diagram of CuCl, which is then used for the thermodynamic modeling of the cycle. In the heat pump cycle, molten CuCl is flashed in a vacuum where the vapor quality reaches ∼2.5%, and then it is boiled to produce saturated vapor. The vapor is then compressed in stages (with inter-cooling and heat recovery), and condensed in a direct contact heat exchanger to transfer heat at a higher temperature. The heat pump is then integrated with a copper–chlorine water splitting plant. The heat pump evaporator is connected thermally with the hydrogen production reactor of the water splitting plant, which performs an exothermic reaction that generates heat at 760 K. Additional source heat is obtained from heat recovery from the hot reaction products of the oxy-decomposer. The heat pump transfers heat at ∼950 K to the oxy-decomposer to drive its endothermic chemical reaction. It is shown that the heat required at the heat pump source can be obtained completely from internal heat recovery within the plant. First and second law analyses and a parametric study are performed for the proposed system to study the influence of the compressor's isentropic efficiency and temperature levels on the heat pump's COP. Two new indicators are presented: one represents the heat recovery ratio (the ratio between the thermal energy obtained by internal heat recovery, and the energy needed at the heat pump evaporator), and the other is the specific heat pump work per mole of hydrogen produced. This new heat pump with CuCl as a working fluid can be attractive in other industrial contexts where high temperature heat is needed. One may replace a common heating technology (combustion or electric heating) with the present sustainable method that uses heat recovery and high efficiency temperature upgrading for heating applications.

1. Introduction

Hydrogen is recognized as an important component of the sustainable energy portfolio in the future for carbon-free society. From a sustainability perspective, hydrogen can be synthesized from water or biomass using primary energy sources which are considered sustainable (e.g., solar, wind, nuclear, hydro, geothermal, biomass, tidal, etc.). It is important to develop new commercially viable technologies which can produce hydrogen at high efficiency and reduced consumption of primary energy.

Water electrolysis is an existing commercial technology for sustainable hydrogen production. High temperature steam electrolysis – which can use a combination of sustainable thermal energy sources and electricity – represents an emerging new development for hydrogen production that promises higher efficiencies than conventional electrolysis. The main drawback of any electrolysis technique (either at low or high temperature) is the extensive need of electrical power. Regardless of the nature of the sustainable energy source, the conversion of heat to mechanical power introduces irreversibilities. Typical efficiencies of electricity production from sustainable thermal energy are as follows: concentrated solar 25% [1], geothermal plants 10–15%, ocean thermal conversion 3–5%, industrial heat recovery at typically 200 °C, 15% [2], nuclear reactors 34% [3], biomass through gasification and combined gas turbines/fuel cell systems, maximum ∼40–50% (based on gasifier efficiency up to 70% [4], and gas turbine/fuel cell systems effi-

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Nomenclature

COP	coefficient of performance
COP_{ex}	exergetic coefficient of performance
C_P	specific heat, kJ/mol K
f	function
h	molar specific enthalpy, kJ/mol
H	flow enthalpy, kJ
k	proportionality coefficient, Eq. (8), K^{-2}
n	number of moles, mol
P	pressure, Pa
Q	heat flux, kJ
R	universal gas constant, kJ/mol K
s	molar specific entropy, J/mol K
T	temperature, K
v	molar specific volume, m^3/mol
W	work, kJ
X	vapor quality

Greek letters

α	volumetric thermal expansion coefficient, K^{-1}
β	density thermal coefficient, Eq. (9), kg/m^3 K
η	efficiency
ρ	density, kg/m^3
χ	internal heat recovery ratio

Subscripts

0	reference value
ev	evaporator
(g)	gas
inp	input
(L)	liquid
m	melting
oxy	oxy-decomposer
P	pump
r	reaction
ref	reference
(s)	solid phase (crystal)
s	sensible heat
sat	saturation

ciency, 60–70% [5]). The irreversibilities associated with electricity generation lead to reduced overall thermal-to-hydrogen efficiency of hydrogen production through water electrolysis of about 20% (assuming 40% efficiency of electric power generation and 50% efficiency of water electrolysis).

A promising alternative to electrolysis is thermochemical cycles for water splitting. The main energy input needed by such systems is high temperature heat. Some electricity is still needed to transport materials, operate pumps, compressors, electrochemical reactions (when applied), and so forth. In all cases, the electricity usually represents a small fraction of the total energy input inventory. There are many types of thermochemical cycles currently under investigation, but the technology has not yet reached a large industrial commercialization stage.

Past literature shows that over 200 types of thermochemical water splitting cycles have been considered [6–8]. The copper–chlorine (Cu–Cl) cycle requires a heat source of 805 K. This cycle is under development by a consortium of North American institutions, co-led by Atomic Energy of Canada Limited (AECL) and the University of Ontario Institute of Technology in Canada (see [9] for a review of the recent status). The sulfur–iodine cycle has been developed in Japan, USA, France, etc. as described in [10]. A recent comparative study shows that the sulfur–iodine and copper–chlorine cycles have similar hydrogen production efficiencies; however, the first requires a much higher level of thermal energy source temperature (1123 K). The Westinghouse hybrid sulfur process and UT-3 cycle are among the most advanced in terms of their development [11]. The minimum temperature required to drive these cycles is about 1025–1175 K, for which possible sustainable energy sources are solar radiation or nuclear energy. Thus, the development of such thermochemical cycles occurs alongside the development of advanced solar concentrators and future generations of nuclear reactors that can operate at very high temperatures to either generate hydrogen or to co-generate both hydrogen and electricity [3].

Regarding the minimal temperature for driving the thermochemical cycle, a lower temperature allows a wider range of sustainable thermal energy sources. From past literature (e.g. [8]), cycles that require the lowest temperatures are as follows: Cu–Cl cycle 805 K, Li–N–I cycle 750 K and Fe–S–I cycle 725 K. The Li–N–I cycle has been proposed by the Argonne National Laboratory, US, and comprises three steps from which one is at ambient temperature. The main chemical involved in this cycle is lithium nitrate, which by thermal decomposition generates oxygen. The Fe–S–I cycle – also known as Yokohama Mark 3 – comprises also three steps with one at ambient temperature, one at 100 °C and the other at a high temperature. The main recycled chemical of this cycle is iron sulfate. The Cu–Cl, Li–N–I and Fe–S–I cycles draw special attention because they can be coupled to nuclear reactors of the current generation. For the current CANDU (CANada Deuterium Uranium) reactors, which produce nuclear heat at ~575 K, heat upgrading options must be considered in this case. Also, other thermal energy sources like industrial waste heat, biomass combustion, concentrated solar power and geothermal energy could be candidates for linkage to the aforementioned cycles, for example, by a heat pump that upgrades their temperature up to the required level. Among those three above cycles, the Cu–Cl cycle is in the most advanced stage of development, currently under development at a large lab scale demonstration [9].

Several studies have been published regarding possible solutions to upgrade the temperature of sustainable thermal energy sources, and linkage of such sources to a Cu–Cl water splitting plant. The main focus concerns the integration of a Cu–Cl plant with a CANDU nuclear reactor. In Refs. [12–14] are proposed various heat pumps that use organic (biphenyl, cyclohexane) and titanium-based working fluids to upgrade the source temperature. The mechanical energy needed to drive the heat pump is assumed to be sustainable/renewable at the origin. There are at least two major technical constraints when devising a thermo-mechanical heat pump for high temperatures: finding a suitable working fluid, and obtaining a coefficient of performance (COP) high enough to justify the use of a heat pump. If the COP is close to 1, then one would better use electric heating than a heat pump. The previous heat pumps have potential for improvement of the COP when heat recovery is applied.

Implementing internal heat recovery within the Cu–Cl cycle is essential for obtaining a high COP [3] presented a graphical description of a Cu–Cl plant with heat recovery sources. For example, the oxy-decomposer is a chemical reactor in the Cu–Cl cycle that needs heat input at the highest temperature, about 805 K. In this reactor, oxygen and molten cuprous chloride (CuCl) are produced and delivered as hot streams at a temperature close to the average reactor's temperature of 805 K. These streams must be cooled for further processing at lower temperature. There is an opportunity for heat recovery, through a heat pump that operates at a source temperature close to that of the products from which it recovers heat. Apart from the oxygen and molten cuprous chloride, the Cu–Cl plant has a high temperature exothermic reactor that can deliver heat at normally 725 K, but in principle, can be made to operate at