DEVELOPMENT, ANALYSIS AND LIFE CYCLE ASSESSMENT OF INTEGRATED SYSTEMS FOR HYDROGEN PRODUCTION BASED ON THE COPPER-CHLORINE (Cu-Cl) CYCLE

By

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Abstract

The energy carrier hydrogen is expected to help solve many energy challenges we are facing today. Thermochemical water splitting using a Cu-Cl cycle, linked with renewable energy sources and/or the Generation IV nuclear super-critical water cooled reactor (SCWR), is a promising option for hydrogen production. The University of Ontario Institute of Technology (UOIT), Clean Energy Research Lab (CERL) has a research team working on the Cu-Cl hydrogen production cycle to demonstrate the process at the lab scale. This study aims to contribute to the development of hydrogen production using the Cu-Cl cycle by developing integrated multi-generation systems.

There are three key elements of the study. First, the Cu-Cl based integrated systems are developed for multi-generation. System I has a solar tower with molten salt energy storage integrated with a steam turbine, organic Rankine cycle and a LiBr-H$_2$O absorption cooling system. System II consists of a Generation IV SCWR integrated with the Cu-Cl cycle and a LiBr-H$_2$O absorption cooling system. System III has a solar tower with molten salt energy storage integrated with the Cu-Cl cycle, LiBr-H$_2$O absorption cooling system and a gas steam combined cycle. All three systems discussed in this thesis produce hydrogen as the main output. All the systems also have the capability of generating electricity and providing cooling, hot water and drying air. A novel configuration of the four-step Cu-Cl cycle is modeled in order to better understand and improve system performance and efficiency.

Second, in the analysis section, the Aspen Plus process simulation package is used to evaluate the characteristics of the entire cycle in terms of energy, exergy and cost effectiveness, to support the ultimate development of a pilot plant. Alternative designs for the heat exchanger network using Aspen Energy Analyzer are studied for better thermal management. The Aspen Plus simulation results for the four-step Cu-Cl cycle illustrate that the steam to copper molar ratio can be reduced to 10 from an initial value of 16 by decreasing the pressure of the hydrolysis reactor. Thermodynamic, economic and environmental analyses are then conducted for the simulated four-step Cu-Cl cycle using various engineering tools: exergy, cost analyses, life cycle assessment and exergoenvironmental and exergoeconomic analyses. Based on the conducted research for
the studied system under the baseline conditions, the total cost rate and environmental impact rate are determined to be 165 $/s and 37.6 Pt/s, respectively. Energy and exergy efficiencies of the four-step Cu-Cl cycle are also calculated to be 55.4% and 66.0%, respectively. Five optimization scenarios with the objective functions of exergy efficiency (single-objective), total cost rate (single-objective), environmental impact rate (single-objective), along with multi-objective exergoeconomic and exergoenvironmental optimizations are performed. Based on the single objective optimizations, it is determined that the exergy efficiency could be increased by up to 3.3% using exergy-based optimization, the cost can be reduced by up to 33% using cost-based optimization, and the environmental impact rate can be reduced by up to 39% using environmental impact-based optimization, at the expense of the nonoptimized objectives. In this regard, multi-objective optimization is conducted. Based on the exergoeconomic optimization, it is concluded that 0.80% higher exergy efficiency and 4.5% lower cost can be achieved, compared to baseline parameters. Furthermore, 0.46% higher exergy efficiency and 30% lower environmental impact rate can be achieved based on the exergoenvironmental optimization.

Third, the optimized four-step Cu-Cl cycle is integrated with the novel multi-generation systems. Exergy and exergoeconomic analyses and exergetic life cycle assessment are conducted for the multi-generation systems. Multi-objective optimizations of the present integrated systems are also performed. Multi-objective optimization results show that exergy efficiencies are 45.8%, 45.3% and 46.7% for the three integrated multi-generation systems for hydrogen production. Corresponding energy efficiencies are calculated to be 76.4%, 67.4% and 81.2%, respectively, considering that rejected heat from the systems are utilized as hot water and drying air.
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<td>Environmental impact per unit of exergy (Pt/kJ)</td>
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<tr>
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<td>Environmental impact rate (Pt/s)</td>
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<td>Cost rate ($$/s$)</td>
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<tr>
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<td>$\dot{m}$</td>
<td>Mass flow rate (kg/s)</td>
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<tr>
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<td>Annual number of operation hours</td>
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<td>Pressure (atm, kPa)</td>
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<tr>
<td>$Q$</td>
<td>Heat (kJ)</td>
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<tr>
<td>$T$</td>
<td>Temperature (°C, K)</td>
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<td>$U$</td>
<td>Overall heat transfer coefficient (W/m$^2$·K)</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume (m$^3$)</td>
</tr>
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</table>
\( W \)  Work (kJ)
\( \dot{W} \)  Work rate (kW)
\( Y \)  Environmental impact of a component (Pt)
\( \dot{Y} \)  Component related environmental impact (Pt/s)
\( Z \)  Purchased equipment cost ($)
\( \dot{Z} \)  Cost rate of owning and operating the cycle ($/s)

**Greek Symbols**

\( \eta \)  Efficiency
\( \gamma \)  Activity coefficient
\( \varphi \)  Maintenance factor

**Subscripts and Superscripts**

\( 0 \)  Ambient
\( ch \)  Chemical
\( d, dest \)  Destruction
\( e \)  Exit
\( elec \)  Electrolyzer
\( en \)  Energy
\( ex \)  Exergy
\( f \)  Fuel
\( gen \)  Generation
\( in \)  Inlet
\( kin \)  Kinetic
\( lm \)  Logarithmic mean difference
\( out \)  Outlet
\( p \)  Product
\( PF \)  Pollutant formation
\( ph \)  Physical
\textit{pot} & Potential & \\
\textit{s} & Step & \\

\textbf{Acronyms} & & \\
AP & Acidification Potential & \\
ACS & Absorption Cooling System & \\
AECL & Atomic Energy of Canada Limited & \\
ANL & Argonne National Lab & \\
BWR & Boling Water Reactor & \\
CEPCI & Chemical Engineering Plant Cost Index & \\
CERL & Clean Energy Research Lab & \\
CRF & Capital recovery factor & \\
Cu-Cl & Copper-Chlorine & \\
DC & Direct Current & \\
EES & Engineering Equation Solver & \\
EP & Eutrophication Potential & \\
EXCEM & Exergy-Cost-Energy-Mass & \\
ExLCA & Exergetic Life Cycle Assessment & \\
GA & Genetic Algorithm & \\
GHG & Greenhouse Gas & \\
GTC & Gas Turbine Cycle & \\
GWP & Global Warming Potential & \\
HHV & Higher Heating Value & \\
HTE & High Temperature Electrolysis & \\
HTF & Heat Transfer Fluid & \\
HTP & Human Toxicity Potential & \\
IGCC & Integrated Gasification Combined Cycle & \\
LCA & Life Cycle Assessment & \\
LCI & Life Cycle Inventory & \\

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>LCIA</td>
<td>Life Cycle Impact Assessment</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower Heating Value</td>
</tr>
<tr>
<td>Mg-Cl</td>
<td>Magnesium chlorine</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>ORC</td>
<td>Organic Rankine Cycle</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cell</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaics</td>
</tr>
<tr>
<td>PWR</td>
<td>Pressurized Water Reactor</td>
</tr>
<tr>
<td>RAD</td>
<td>Radioactive Radiation</td>
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<tr>
<td>S-I</td>
<td>Sulphur-Iodine</td>
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<tr>
<td>SCWR</td>
<td>Super-Critical Water Cooled Reactor</td>
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<tr>
<td>SMR</td>
<td>Steam Methane Reforming</td>
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<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
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<tr>
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<td>Specific Exergy Costing</td>
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<td>STC</td>
<td>Steam Turbine Cycle</td>
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<td>UOIT</td>
<td>University of Ontario Institute of Technology</td>
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CHAPTER 1: INTRODUCTION

1.1 Energy Challenges

Energy is used in all aspects of life and allows the existence of ecosystems, human civilization and life itself possible. Global energy demand tends to increase with increasing population. In this regard, energy has been a critical element in shaping local and external policies of countries, their economies, environmental policies, sustainable issues, social dimensions, etc. It is extremely important to produce, convert, transport and utilize energy sources and systems appropriately for a better service to the environment and societies, as well as their economies (Dincer and Zamfirescu, 2012). Today’s energy systems, which are based mainly on fossil fuels, cannot be considered as sustainable. Concerns about the energy supply security are increasing due to the reduction in fossil fuel resources, thereby increasing the energy carrier prices, local air pollution and contributes to global climate change. Petroleum is a central concern, with a share of more than one third of global primary energy consumption and more than 95% of the energy consumption in the transport sector. The negative environmental impact of coal mining, combined with the large contribution of coal usage to global carbon dioxide emissions, as well as the risks of the dwindling reserves of natural gas, are other factors of concern (Urbaniec et al., 2010).

The aforementioned reasons lead people into looking for more efficient, cheaper and ecofriendly options for energy conversion. Increases in energy demand will likely lead to a growth in nuclear and renewable energy utilization, partly to meet the objective of sustainability. The shift from fossil fuels to nuclear and renewable resources is expected due to the increase in energy demand, as well as concerns over environmental issues such as global warming. In the future, energy systems are expected to be multi-generation systems when it is economically feasible. Multi-generation systems combine various energy resources and energy conversion methods to assist in increasing the efficiency, while reducing the wastes and associated environmental impact. Hydrogen is a promising candidate as an energy carrier (not an energy source) that helps expand markets for renewable and nuclear energy resources, as well as contributes to
sustainability and environmental stewardship, and can act as a link between these technologies when they are utilized in hybrid systems (Dincer, 2012; Rosen, 2010).

1.2 Motivation
The energy carrier hydrogen is expected by many to become an important fuel that will help in solving several energy challenges we face today. This is because its oxidation does not emit greenhouse gases (GHGs) and does not contribute to climate change, provided it is derived from clean energy sources. Numerous researchers anticipate that hydrogen will replace petroleum products for the fuelling of transportation vehicles, which in turn decreases the dependence on petroleum. Industrial sectors, such as petrochemical, agricultural, food processing, plastics and manufacturing, use hydrogen heavily as commodity (Naterer et al., 2011a). Hydrogen complements the energy carrier electricity, which can be generated from a variety of primary energy sources and is widely used in a broad range of applications. These two energy carriers are expected to have complementary roles in the future, in part since hydrogen adds the capability of storage (Urbaniec and Ahrer, 2010). Hydrogen storage is a promising energy storage option. Renewable energy source based hydrogen production and storage system is considered to be effective for energy management since renewable energy systems have intermittent characteristics (Ozbilen et al., 2012a). Hydrogen exists in abundance in nature in the form of water, however, pure hydrogen needs to be produced. There are several methods of achieving this, including steam reforming of natural gas, coal gasification, water electrolysis and thermochemical water decomposition. Dufour et al. (2009) indicate that 96% of world’s hydrogen is produced using fossil fuels, and steam reforming of natural gas is the most commonly used method.

Hydrogen production using thermochemical water splitting cycles has the potential to be cleaner and more cost-effective than other production methods. Although hydrogen production systems using thermochemical cycles have not yet been commercialized, studies have shown that such systems can be expected to compete with the conventional H₂ production methods, including steam methane reforming (Lewis et al., 2009a; Pilavachi et al., 2009). Water can be directly split in one step, but the required process temperature is too high to be practical. However, a series of selected chemical
reactions can be utilized to achieve the same result at much lower temperatures (Funk, 2001). A variety of thermochemical water decomposition cycles have been identified (Funk, 2001), but few have progressed beyond the theoretical calculations and have not provided working experimental demonstrations. Considering several factors, including availability and abundance of materials, simplicity, chemical viability, thermodynamic feasibility and safety, the following cycles are identified as possible commercial significance: sulphur-iodine (S-I), copper-chlorine (Cu-Cl), cerium-chlorine (Ce-Cl), iron-chlorine (Fe-Cl), magnesium-iodine (Mg-I), vanadium-chlorine (V-Cl), copper-sulphate (Cu-SO₄), Ni-Ferrite (NiFe₂O₄), cerium-oxide (CeO₂/Ce₂O₃), ZnO/Zn and Fe₃O₄/FeO redox reactions and hybrid chlorine (Naterer et al., 2009; Steinfeld, 2002; Ishihara et al., 2008; Abanades and Flamant, 2006). Most of these cycles require process heat at temperatures as high as 800°C and above. Due to its lower temperature requirements (around 530°C), the Cu-Cl thermochemical water decomposition cycle has some advantages over other cycles (Naterer et al., 2013), including reduced material and maintenance costs. Moreover, several additional advantages exist with the Cu-Cl cycle, such as common chemical agents, a low electrochemical cell voltage and utilization of low-grade/waste heat to improve the cycle’s efficiency (Naterer et al., 2009).

Fossil fuels, nuclear energy and renewables can be used as energy sources for hydrogen production. Fossil fuels have significant negative impact on the environment. Renewables are usually considered the most environmentally benign alternative. An important challenge might be to obtain sustainable large-scale H₂ production, although daily production capacity of ~38,000 kg H₂ can be obtained using solar power towers and electrolyzers (Kolb et al., 2007). Nuclear energy for hydrogen production is advantageous for two main reasons: (i) nuclear plants do not emit GHGs during operation, and (ii) nuclear energy can contribute to large scale hydrogen production. However, nuclear reactors might not be available for every location in the world. For these reasons, thermochemical water decomposition linked with renewables and/or nuclear plants is seen as a promising alternative for H₂ production. The Generation IV SCWR (supercritical water cooled reactor) and heliostat solar towers are viewed as particularly suitable options for pairing with the Cu-Cl thermochemical cycle. SCWR operates at higher temperatures so it can facilitate co-generation of electricity and hydrogen (Naterer et al.,
Heliostat solar thermal tower, using molten salt as heat transfer fluid, can provide the required high temperature thermal energy for hydrogen production using the Cu-Cl cycle (Wang et al., 2011).

The four-step Cu-Cl cycle, which is currently under experimental investigation in the Clean Energy Research Lab at UOIT, should be designed, simulated and analyzed in a systematic way in order to better understand and improve the system efficiency, reduce investment and operating costs and corresponding environmental impact. Also, the Cu-Cl based multi-generation systems should be developed and analyzed to help increase the efficiency while reducing the wastes and associated environmental impact.

1.3 Objectives of Thesis

The main objective of this research is to show that hydrogen can be produced using the Cu-Cl thermochemical water decomposition cycle in an efficient, economical and environmentally benign way. Therefore, novel Cu-Cl based integrated multi-generation systems are introduced. Multi-generation systems are attractive due to their higher thermal efficiencies than individual cycles. A thermodynamic (energy and exergy), economic and environmental analysis have to be performed in order to justify the feasibility of the Cu-Cl based integrated systems.

The available studies in literature which evaluates the economic and environmental performance of the Cu-Cl cycle, based on a second-law analysis, use data (energy and mass flow) assuming the ideal cycle (stoichiometric reaction). Experimental studies, however, show that many challenges arise such as the excess steam requirements in the hydrolysis step. There is also no study in the literature that examines the Cu-Cl cycle’s environmental performance via exergy analysis using exergoenvironmental method. Furthermore, thermodynamic and environmental analyses of the Cu-Cl based integrated systems are not studied as yet.

Although lab scale experiments of individual reactions within the cycle have been conducted, an experimental set-up of the overall cycle is still nonexistent. Aspen Plus, a commercial process simulation package, is a useful tool to evaluate characteristics of the complete cycle, including energy, exergy and cost effectiveness, before building a pilot plant.
The objective of this PhD study is to show the viability of the hydrogen production via thermochemical water splitting using the Cu-Cl cycle by developing novel integrated systems. Analyses and assessment of the systems are performed using thermodynamic (energy and exergy), life cycle assessment, exergetic life cycle assessment, exergoenvironmental and exergoeconomic analyses. The main focus of this study is on the four-step Cu-Cl cycle (Option II), as it is under experimental investigation in the Clean Energy Research Lab at UOIT.

This PhD thesis consists of three main objectives:

1. To develop Cu-Cl based novel integrated systems with hydrogen storage and electricity conversion.
   - System I: Solar tower with molten salt energy storage integrated with a steam turbine, organic Rankine cycle, LiBr-H₂O absorption cooling system.
   - System II: Generation IV SCWR integrated with the Cu-Cl cycle and LiBr-H₂O absorption cooling system.
   - System III: Solar tower with molten salt energy storage integrated with the Cu-Cl cycle, LiBr-H₂O absorption cooling system and combined gas-steam cycle.

2. To simulate and analyze the four-step Cu-Cl cycle.
   - To simulate a new model for the Cu-Cl cycle using Aspen Plus to reduce excess steam requirement at hydrolysis reactor.
   - To develop and study new designs for heat exchanger network for thermal management within the Cu-Cl cycle.
   - To develop energy, exergy, exergoeconomic and exergoenvironmental models of the Cu-Cl cycle
   - To optimize the Cu-Cl cycle with respect to exergy efficiency, cost and environmental impact via multi-objective optimization.

3. To conduct analysis and assessment of the Cu-Cl based multi-generation systems.
   - To develop mathematical models of the multi-generation systems, conduct associated exergy analysis and exergoeconomic analysis.
   - To optimize the integrated systems with respect to exergy efficiency and exergoeconomic analysis via multi-objective optimization.
To develop an exergetic life cycle assessment model of the integrated systems in order to identify the most critical phases with respect to thermodynamic irreversibilities.

To compare the multi-generation systems with respect to energy and exergy efficiency and life cycle irreversibilities.

1.4 Summary of Approach and Rationale

In this research, three novel Cu-Cl based integrated systems are developed and analyzed and the areas of inefficiencies; their magnitude, causes and locations, are determined. Methods of improvements are suggested in order to increase thermodynamic performance of systems.

A new Aspen Plus model for the four-step Cu-Cl cycle is developed to provide a more realistic model. In the first stage of modeling, a detailed modeling of individual components in the Cu-Cl cycle is performed. Pressure of the hydrolysis reactor is then reduced to vacuum pressure in order to reduce excess steam requirements of the cycle. Thus, thermal energy requirement of the Cu-Cl cycle is in return reduced. Integration of the individual components is then completed, and a heat exchanger network to increase the energy and exergy efficiency of the system is built using Aspen Energy Analyzer.

Thermodynamic model based on Aspen Plus simulation results is developed to identify inefficiencies within the Cu-Cl cycle. Moreover, investment and exergy destruction costs, associated with the Cu-Cl cycle, are calculated and cost formation of the system is provided in order to evaluate the Cu-Cl cycle with respect to exergoeconomic variables. An environmental analysis is also conducted using a cradle to grave life cycle assessment with Eco-indicator 99 impact assessment method via SimaPro 7, as well as by creating environmental impact correlations from the literature in order to point out the components causing the highest environmental impact and suggest possibilities and trends for improvement based on the exergoenvironmental variables. Finally, the Cu-Cl cycle is optimized in Matlab using a multi-objective evolutionary algorithm which considers exergetic, exergoeconomic and exergoenvironmental objectives with respect to decision variables and constraints.
Furthermore, the optimized Cu-Cl cycle is integrated to multi-generation systems. The mathematical models using Engineering Equation Solver (EES) are developed for each integrated systems to perform exergy and exergoeconomic analyses. Multi-generation systems are also optimized in Matlab using multi-objective evaluationary algorithm with respect to exergetic and exergoeconomic variables. An exergetic life cycle assessment is also conducted to identify life cycle irreversibilities of each system.

1.5 Thesis Outline

This thesis is organized in 8 chapters as described below:

Chapter 1 gives introductory information. Chapter 2 presents an introduction to hydrogen production methods and energy sources that can be linked with them. The main focus is on thermochemical water splitting cycles, solar energy and Generation IV super-critical water-cooled reactor. Chapter 3 provides literature review on both methodology including energy, exergy, exergoeconomic, exergoenvironmental analyses and life cycle assessment, and the Cu-Cl thermochemical water decomposition cycle. Chapter 4 describes the Cu-Cl cycle in detail along with the integrated multi-generation systems. Chapter 5 explains the simulation framework and methodology, gives background information on Aspen Plus software, analyses and life cycle assessment that are going to be performed to the systems described in Chapter 4. Basic definitions and equations for thermodynamic, cost and environmental related analyses are outlined. Chapter 6 describes the Aspen Plus simulation model and heat exchanger network for the four-step Cu-Cl cycle. The conducted energy and exergy analyses, as well as exergoeconomic, exergoenvironmental analyses and life cycle assessment for the four-step Cu-Cl cycle and the integrated systems along with the associated multi-objective optimization are also presented. Chapter 7 illustrates the numerical results based on the developed models and the conducted analyses on the four-step Cu-Cl cycle along with the integrated systems. Chapter 8 summarizes the conclusions and provides the recommendations for future research.
CHAPTER 2: BACKGROUND

2.1 Hydrogen Production Methods

Hydrogen can be produced using several methods, such as water electrolysis, steam methane reforming (SMR), and thermochemical water splitting. These hydrogen production methods can also be linked with different kinds of energy sources including nuclear energy, fossil fuels and renewables. Currently, 96% of world hydrogen is produced using fossil fuels. Natural gas is the main raw material among them and SMR is the most common method (Dufour et al., 2009). Although hydrogen is a clean energy carrier, negative environmental impacts can arise during its production. Furthermore, since SMR is the most used method, large amount of GHGs are emitted during hydrogen production. Thermochemical cycles, specifically S-I and Cu-Cl cycles, are considered as promising options to produce hydrogen with lower environmental impact. Figure 2.1 shows the hydrogen production methods and energy sources linked with them. Global warming potentials per kg hydrogen produced for selected hydrogen production methods are presented in Figure 2.2.

Figure 2.3, on the other hand, proposes various paths through which the four kinds of energies to drive hydrogen production can be obtained from “green” energy sources. The electrical and thermal energy can be derived from renewable energies (like solar, wind, geothermal, tidal, wave, ocean thermal, hydro, biomass), or from nuclear energy, or from recovered energy. The photonic energy is comprised in solar radiation only. The biochemical energy that is stored in organic matter (in the form of carbohydrates, glucose and sugars etc) can be manipulated by certain micro-organisms that can extract hydrogen from various substrates or it can be chemically converted to thermal energy. Biochemical energy can be assisted by solar radiation to generate energy, depending on the case (viz. bio-photolysis or dark fermentation) (Dincer, 2012).

2.1.1 Hydrocarbon Based Hydrogen Production

Steam methane reforming (SMR), which is known as one of the least expensive method of producing hydrogen, has three main phases. Methane is first catalytically reformed at
high temperatures in order to produce carbon monoxide and a syngas mixture of hydrogen. A catalyst is generally used for the reforming reaction. Additional hydrogen can also be produced through the water-gas-shift reaction, which takes place at high and low temperature phases. Finally, a purification process is utilized by adsorption (Pilavachi 2009; Balat, 2009).

Figure 2.1: The main alternative methods of hydrogen production from energy sources (Adapted from Boehm et al., 2003).

Currently 23% of the world’s total energy comes from coal, and coal gasification is the primary method for producing hydrogen from coal. Although it is a well-established technology, it is not as common as SMR due to economic reasons (Jaber,
Syngas or artificial water gas (CO + H₂) from coal can be reformed to hydrogen. Hydrogen and oxygen concentrations in coal increase as coal rank goes down. Steam can be further shifted to hydrogen by establishing conditions to drive the reaction to produce additional hydrogen.

![Figure 2.2: GWP (kg CO₂-eq) per kg hydrogen production for several hydrogen production processes (Ozbilen et al., 2013).](image)

2.1.2 Water Electrolysis

Water electrolysis is a common method to produce hydrogen by water splitting which is achieved by passing an electric current through water. An anode, a cathode, power supply, and an electrolyte are treated as the main components of a basic water electrolysis unit, as shown in Figure 2.4. A direct current (DC) is applied and electrons flow from the negative terminal of the DC source to the cathode at which the electrons are consumed by hydrogen ions (protons) to form hydrogen. In keeping the electrical charge in balance, hydroxide ions (anions) transfer through the electrolyte solution to anode, at which the hydroxide ions give away electrons and these electrons return to the positive terminal of
the DC source (Zeng and Zhang, 2010). The alkaline process and the proton exchange membrane (PEM) process are two technologies to conduct water electrolysis. The efficiency and the current density are two important parameters. The energy efficiencies for the alkaline process and PEM process are 50-65% and 50-75%, respectively. The corresponding current densities are 0.1-0.4 A/cm² for the alkaline process, and greater than 1.6 A/cm² for PEM process (Dincer, 2012).

Figure 2.3: Paths of generation of basic form of energy from primary green energy sources (Dincer, 2012).

The high temperature electrolysis (HTE) of water is typically accomplished using yttria-stabilized zirconia as an electrolyte at high temperatures of 1100-1250 K. The cell voltage and current density in a typical HTE are 0.95-1.3 V and 0.3-1.0 A/cm², respectively. The HTE process has both thermodynamic and kinetic advantages over other conventional methods (Utgikar and Thiesen, 2006).
2.1.3 Biomass Based Hydrogen Production

Biomass is the fourth largest source of energy in the world, accounting for about 15% of the world’s primary energy consumption. There are many different routes to convert biomass into useful forms of energy products. Biomass based hydrogen production methods can be categorized into two: thermochemical conversion and biological conversion. Pyrolysis, gasification and supercritical water gasification are known as thermochemical methods, while fermentative hydrogen production, photosynthesis process and biological water gas shift reaction are biological methods. Gasification is the most common method in which biomass is converted into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range of 800-900°C. The process performs partial oxidation to convert carbonaceous feed stock into gaseous energy carrier consisting of permanent, non-condensable gas mixture. Biomass is converted completely to CO and H₂ in an ideal gasification, although in practice, some CO₂, water and other hydrocarbons are formed (Cohce, 2010; Kalinci et al., 2009; Saxena et al., 2008).

2.1.4 Thermochemical Water Splitting

All chemicals involve in a thermochemical cycle can be recycled except water which is the material source from which hydrogen is derived. Thermochemical cycles are attractive for various reasons: (i) they do not need catalysis to derive the chemical
reactions, (ii) there is no need of hydrogen oxygen separation membranes, (iii) the temperature of the required thermal energy source is in a reasonable range (600-1200 K), and (iv) there is no or very less requirement of electrical energy to drive the process.

2.1.4.1 S-I Cycle

Many institutions, including the Japan Atomic Energy Agency (Kubo et al., 2004), General Atomics (Schultz, 2003), CEA (France) (Anzieu et al., 2006) and Sandia National Laboratory (Moore, 2007), are actively investigating the S-I cycle. Moreover, General Atomics has a plant with a capacity of 2 kg hydrogen per day under development. The three-step S-I cycle is the most common one, although there are other types of S-I cycles. A simplified S-I cycle diagram is shown in Figure 2.5 and the main steps of S-I cycle are defined as follows:

- Step 1 (Hydrolysis step at 393 K):
  \[ \text{I}_2(l+g) + \text{SO}_2(g) + 2\text{H}_2\text{O}(g) \rightarrow 2\text{HI}(g) + \text{H}_2\text{SO}_4(l) \]  

- Step 2 (Oxygen production step at 1123 K):
  \[ \text{H}_2\text{SO}_4(g) \rightarrow \text{SO}_2(g) + 0.5\text{O}_2(g) + \text{H}_2\text{O}(g) \]  

- Step 3 (Hydrogen production step at 723 K):
  \[ 2\text{HI}(g) \rightarrow \text{I}_2(g) + \text{H}_2(g) \]  

The first step is an exothermic hydrolysis step which occurs at 393 K. The endothermic oxygen production step is the second step that occurs over 1100 K and the final step is the hydrogen production step, which is an endothermic reaction and occurs around 700 K (Wang et al., 2010).

2.1.4.2 ISPRA Mark 9 Cycle

ISPRA Mark 9 thermochemical cycle is a three-step cycle involving iron-chlorides. A simplified ISPRA Mark 9 cycle diagram is shown in Figure 2.6 and steps of ISPRA Mark 9 cycles are given as follows:

- Step 1 (Decomposition of Fe(III) chloride at 700 K):
  \[ 6\text{FeCl}_3 \rightarrow 3\text{Cl}_2 + 6\text{FeCl}_2 \]  

- Step 2 (Hydrolysis at 920 K):
  \[ 6\text{FeCl}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 12\text{HCl} + 2\text{H}_2 \]
• Step 3 (Chlorination at 420 K):

\[ 3\text{Cl}_2 + 2\text{Fe}_3\text{O}_4 + 12\text{HCl} \rightarrow 6\text{FeCl}_3 + 6\text{H}_2\text{O} + \text{O}_2 \]  

\[ \text{(2.6)} \]

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<tr>
<th>Steps</th>
<th>Chemical Reactions</th>
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<tbody>
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<td>Step 1</td>
<td>I(_2) + SO(_2) + 2H(_2)O \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4</td>
</tr>
<tr>
<td>Step 2</td>
<td>H(_2)SO(_4) \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2} \text{O}_2</td>
</tr>
<tr>
<td>Step 3</td>
<td>2\text{HI} \rightarrow \text{H}_2 + \text{I}_2</td>
</tr>
</tbody>
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Figure 2.5: An S-I thermochemical cycle for H\(_2\) production.

The hydrolysis reaction is conducted at 920 K, which is the highest temperature in the cycle. The attractive features of the ISPRA Mark 9 cycle are the small number of

<table>
<thead>
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</tr>
</tbody>
</table>

Figure 2.6: An ISPRA Mark 9 thermochemical cycle for H\(_2\) production.
reactions (three), use of the most abundant elements (Fe, Cl) and the low temperature requirement (a maximum temperature that is approximately 200 K lower than the maximum temperature in the S-I cycle) (Utgikar and Ward, 2006).

2.1.4.3 Mg-Cl Cycle

The Mg-Cl thermochemical water decomposition cycle is a hybrid process using heat and electricity to split water into hydrogen at a maximum temperature of 550°C. The Mg-Cl cycle consists of three main steps (two thermochemical and one electrochemical) as follows:

- **Step 1 (Hydrolysis step at 723-823 K):**
  \[ \text{MgCl}_2 (s) + \text{H}_2\text{O} (g) \rightarrow \text{MgO} (s) + 2\text{HCl} (g) \] (2.7)
- **Step 2 (Chlorination step at 673-773 K):**
  \[ \text{MgO} (s) + \text{Cl}_2 (g) \rightarrow \text{MgCl}_2 (s) + \frac{1}{2} \text{O}_2 (g) \] (2.8)
- **Step 3 (Hydrogen production step at 343-363 K):**
  \[ 2\text{HCl} (g) \rightarrow \text{H}_2 (g) + \text{Cl}_2 (g) \] (2.9)

A conceptual layout of the cycle with primary reactions is presented in Figure 2.7. In the hydrolysis step, a solid gas reaction takes place, in which hydrogen chloride (HCl) and magnesia (MgO) are produced during the hydrolysis of magnesium-chlorine (Mg-Cl2). This reaction is endothermic and has a temperature range of 450-550°C, which is the highest temperature requirement of the Mg-Cl cycle. The reactants of the hydrolysis step are H2O and MgCl2 (Balta et al., 2012).

In the chlorination step of Mg-Cl cycle, MgO (s) and Cl2 (g) enter as reactants to form MgCl2 (s) and oxygen at a reaction temperature of about 400-500°C. MgCl2 is then fed back to the hydrolysis step to form a closed internal loop that recycles all of the Mg compounds on a continuous basis. Hydrogen can be produced by a thermochemical or an electrochemical reaction in the third step of Mg-Cl cycle. Thermochemical dissociation of HCl is an energy-intensive process and the reaction occurs at high temperatures. The electrochemical process is a low temperature operation compared to thermochemical dissociation (Balta et al., 2012).
2.1.4.4 Cu-Cl Cycle
The AECL has identified copper-chlorine (Cu-Cl) as the most promising cycle for thermochemical hydrogen production with the next generation of CANDU SCWR due to its lower operating temperatures and potentially lower cost materials (Rosen et al., 2012). University of Ontario Institute of Technology (UOIT), AECL, Argonne National Laboratory (USA) and partner institutions are collaborating to scale this technology up to industrial capacities (Naterer et al., 2009).

<table>
<thead>
<tr>
<th>Steps</th>
<th>Chemical Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>MgCl₂ (s) + H₂O (g) → MgO (s) + 2HCl (g)</td>
</tr>
<tr>
<td>Step 2</td>
<td>MgO (s) + Cl₂ (g) → MgCl₂ (s) + ½ O₂ (g)</td>
</tr>
<tr>
<td>Step 3</td>
<td>2HCl (g) → H₂ (g) + Cl₂ (g)</td>
</tr>
</tbody>
</table>

Figure 2.7: Principal chemical reactions in the Mg-Cl cycle for thermochemical water decomposition and conceptual layout.

Several types of Cu-Cl cycles for thermochemical water decomposition are proposed in the literature, mainly characterized by the number of major chemical steps they incorporate and their types of groupings. Although all cycles consist of a series of chemical reactions, the net reaction for each cycle is

\[ \text{H}_2\text{O} (g) \rightarrow \text{H}_2 (g) + \frac{1}{2}\text{O}_2 (g) \]  

(2.10)

The Cu-Cl thermochemical cycle uses a series of intermediate copper and chlorine compounds. Its chemical reactions form a closed internal loop that recycles all chemicals on a continuous basis, without emitting any greenhouse gases or other substances (Naterer et al., 2008). Hence, water, thermal energy and electricity are the main inputs to
the Cu-Cl thermochemical cycle considered here. This subsection presents a conceptual layout and primary chemical reactions of the three-, four- and five-step Cu-Cl cycles.

The Five-Step Cu-Cl Cycle

A conceptual schematic diagram of the five-step Cu-Cl cycle is shown in Figure 2.8 along with its principal chemical reactions. The five main chemical reaction steps in the cycle are (1) HCl (g) production (hydrolysis) using equipment such as a fluidized bed, (2) oxygen production (copper oxychloride decomposition), (3) copper (Cu) production, (4) drying of cupric chloride and (5) hydrogen production. Some of the reactions are exothermic while others are endothermic, and the reaction temperatures differ for the steps. Heat exchangers are utilized to ensure appropriate temperatures are maintained and to allow for effective thermal management and waste heat recovery.

The first step of the cycle is the hydrogen production step in which solid copper particles from step 2 (Cu production) react with HCl from step 4 (HCl production). The hydrogen production step is an exothermic reaction which occurs at a temperature of 450°C. The products are hydrogen gas which is the desired output, and CuCl. The second step is the copper production step in which copper is produced from molten CuCl. Reaction temperature for this step is as low as 25°C. Moreover, this reaction requires electrical energy. While the product copper moves to the hydrogen production step, the other product CuCl₂ is transferred to the third step (drying). In the drying step, the molten CuCl₂ is dried to solid CuCl₂ which is used in step 4 (HCl production). CuCl₂ reacts with water in this step to produce HCl and CuOCuCl₂ at an approximate temperature of 450°C in a fluidized bed. In the O₂ production step, oxygen and CuCl are produced by splitting of CuOCuCl₂. Since the reaction temperatures are not the same for each step, heat exchangers are utilized prior to each reaction to obtain the required temperature.

The Four-step Cu-Cl Cycle

Option I

The four-step (Option I) copper-chlorine cycle combines step 2 and step 3 in Figure 2.8 to reduce transport and handling of solid particles. Drying of cupric chloride using a spray dryer or crystallization is eliminated. The aqueous cupric chloride is directly
sprayed into the hydrolysis reactor. The rest of the steps remain the same as seen in Figure 2.9.

<table>
<thead>
<tr>
<th>Step</th>
<th>Chemical reaction</th>
<th>T (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hydrogen production</td>
<td>2Cu(s) + 2HCl(g) → 2CuCl(l) + H₂(g)</td>
<td>450</td>
</tr>
<tr>
<td>2. Cu production</td>
<td>4CuCl(aq) → 2CuCl₂(aq) + 2Cu(s)</td>
<td>25</td>
</tr>
<tr>
<td>3. Drying</td>
<td>2CuCl₂(aq) → 2CuCl₂(s)</td>
<td>90</td>
</tr>
<tr>
<td>4. HCl production</td>
<td>2CuCl₂(s) + H₂O(g) → CuO•CuCl₂(s) + 2HCl(g)</td>
<td>450</td>
</tr>
<tr>
<td>5. O₂ production</td>
<td>CuO•CuCl₂(s) → 2CuCl(l) + 1/2O₂(g)</td>
<td>500</td>
</tr>
</tbody>
</table>

Figure 2.8: Conceptual layout of the five-step Cu-Cl cycle for hydrogen production and primary chemical reactions (modified from Naterer et al., 2009).
**Option II**

Option II of the four-step Cu-Cl is currently being demonstrated at UOIT. The conceptual layout and primary chemical reactions of this cycle are presented in Figure 2.10. In this case, step 1 (hydrogen production) and step 2 (copper production) of the five-step Cu-Cl cycle are combined to eliminate transport and handling of solid copper particles.

<table>
<thead>
<tr>
<th>Step</th>
<th>Chemical reaction</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. HCl production</td>
<td>$2\text{CuCl}_2(\text{aq}) + 2\text{H}_2\text{O(g)} \rightarrow \text{CuO}\text{•CuCl}_2(\text{s}) + 2\text{HCl(g)} + \text{H}_2\text{O(g)}$</td>
<td>375-400</td>
</tr>
<tr>
<td>2. O$_2$ production</td>
<td>$\text{CuO}\text{•CuCl}_2(\text{s}) \rightarrow 2\text{CuCl(l)} + \frac{1}{2}\text{O}_2(\text{g})$</td>
<td>500-530</td>
</tr>
<tr>
<td>3. Combined step</td>
<td>$4\text{CuCl(}aq\text{)} \rightarrow 2\text{CuCl}_2(\text{aq}) + 2\text{Cu(s)}$</td>
<td>20-80</td>
</tr>
<tr>
<td>4. Hydrogen production</td>
<td>$2\text{Cu(s)} + 2\text{HCl(g)} \rightarrow 2\text{CuCl(l)} + \text{H}_2(\text{g})$</td>
<td>430-475</td>
</tr>
</tbody>
</table>

Figure 2.9: Conceptual layout of the four-step Cu-Cl cycle (Option I) for hydrogen production and primary chemical reactions (modified from Orhan et al., 2011a).
The Three-step Cu-Cl Cycle

**Option I**

In the three-step Cu-Cl cycle, the hydrogen production step and the oxygen production step (copper oxychloride decomposition) are eliminated and combined with the hydrolysis reaction. Similar to the four-step Cu-Cl cycle (Option I), elimination of the solid transport is the main idea behind this configuration. The conceptual layout and the primary chemical reactions are shown in Figure 2.11.
Step | Chemical reaction | T (ºC)
--- | --- | ---
1. HCl production | $2\text{CuCl}_2(\text{aq}) + 2\text{H}_2\text{O}(g) \rightarrow 2\text{CuCl}(l) + 2\text{HCl}(g) + \text{H}_2\text{O}(g) + \frac{1}{2}\text{O}_2(g)$ | 400-600
2. Copper production | $4\text{CuCl}(\text{aq}) \rightarrow 2\text{CuCl}_2(\text{aq}) + 2\text{Cu}(s)$ | 20-80
4. Hydrogen production | $2\text{Cu}(s) + 2\text{HCl}(g) \rightarrow 2\text{CuCl}(l) + \text{H}_2(g)$ | 430-475

Figure 2.11: Conceptual layout of the three-step Cu-Cl cycle (Option I) for hydrogen production and primary chemical reactions (modified from Orhan et al., 2011a).

**Option II**

All of the reactions of the three-step Cu-Cl cycle (Option II) are demonstrated in proof-of-concept experiments at Argonne National Laboratory and the Atomic Energy of Canada Limited. This configuration is similar to Option II of the four-step Cu-Cl cycle, with the exception being that the drying step is eliminated. Figure 2.12 shows conceptual
layout of the three-step Cu-Cl cycle (Option I) for hydrogen production and primary chemical reactions.

<table>
<thead>
<tr>
<th>Step</th>
<th>Chemical reaction</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hydrogen production</td>
<td>$2\text{CuCl} \text{(aq)} + 2\text{HCl} \text{(aq)} \rightarrow 2\text{CuCl}_2 \text{(aq)} + \text{H}_2 \text{(g)}$</td>
<td>&lt;100</td>
</tr>
<tr>
<td>2. HCl production</td>
<td>$2\text{CuCl}_2 \text{(aq)} + \text{H}_2\text{O} \text{(g)} \rightarrow \text{CuO}•\text{CuCl}_2 \text{(s)} + 2\text{HCl} \text{(g)}$</td>
<td>340-400</td>
</tr>
<tr>
<td>3. Oxygen production</td>
<td>$\text{CuO}•\text{CuCl}_2 \text{(s)} \rightarrow 2\text{CuCl} \text{(l)} + \frac{1}{2}\text{O}_2 \text{(g)}$</td>
<td>450-530</td>
</tr>
</tbody>
</table>

Figure 2.12: Conceptual layout of the three-step Cu-Cl cycle (Option II) for hydrogen production and primary chemical reactions (modified from Lewis et al., 2009b)

2.2 Energy Sources

Various energy sources can be used for hydrogen production: fossil fuels (e.g. natural gas), renewables (e.g. solar, biomass, geothermal) and nuclear (e.g. SCWR). This section introduces solar and nuclear energy, which are considered in this research.

2.2.1 Solar Energy

There are four major types of solar concentrating systems: parabolic trough reflector, heliostat solar thermal power, parabolic dish collector, and double-concentration systems (Figure 2.13). Parabolic trough systems use linear parabolic concentrators to focus sunlight onto a solar tubular receiver positioned along their focal line. Parabolic solar troughs are usually aligned with their long axes from north to south. Solar energy is absorbed by a fluid in pipes located along the focal line. The maximum temperature of
the heat transfer fluid does not exceed 450°C, which is insufficient to supply process heat for all steps in a thermochemical cycle. The heliostat solar tower uses arrays of two-axis tracking mirrors to reflect direct insolation onto a receiver/reactor mounted at the top of a centrally located tower. The heliostat solar tower has an important advantage of reaching a large generation capacities in a single unit that concentrates the reflections from thousands of mirrors. The temperature of the heat transfer fluid can reach up to 1000°C. In a parabolic dish system, a point focus collector tracks the sun along two axes, concentrating the isolation onto a receiver located at the focal point of the dish. Temperatures in excess of 1500°C can be achieved. The double concentration system consists of a heliostat field, the reflective tower, and a ground receiver equipped with a secondary concentrator. The receiver/reactor on the ground can achieve temperatures in excess of 1300°C (Kodama and Gokon, 2007; Wang et al., 2011; Ghandehariun et al., 2010).

Figure 2.13: The schematics of large-scale solar concentrating systems: (a) parabolic trough; (b) heliostat power tower; (c) parabolic dish; (d) double concentration (Kodama and Gokon, 2007).

Various heat transfer fluids can be used with those solar systems: water, air and molten salt. Molten salt has an outstanding advantage as the heat transfer medium, since
the solar heat can be stored for tens of hours for use at night, or when sunlight is not available (Wang et al., 2011). A heliostat solar thermal tower working with a molten salt medium is considered in this study.

### 2.2.2 Generation IV SCWR

A Generation IV SCWR nuclear reactor is being designed by AECL to link with a hydrogen plant using the Cu-Cl cycle. This reactor operates at higher temperatures so it can facilitate co-generation of electricity and hydrogen. SCWRs are currently at development stage because of the following main reasons (Naidin et al., 2009):

- The thermal efficiency of nuclear power plants is expected to increase from 30-35% to approximately 45-50%.
- Electrical-energy costs are expected to decrease by reducing capital and operational costs ($1000/kW or even less) (Pioro et al., 2008).
- SCWRs are expected to operate with much higher operating temperatures and pressures compared to conventional nuclear power plants, i.e. steam pressure about 25 MPa and steam outlet temperatures up to 625°C (see Figure 2.14)
- SCWRs are expected to have a simplified flow circuits in which some components are eliminated, such as steam generators, steam dryers, steam separators, etc.

The operating parameters of SCWR of Generation IV plant are presented in Table 2.1. CANDU is the Canada deuterium uranium reactor. Country of origin for ChUWR and KP-SKD is Russia. ChUWR represents the channel-type uranium-graphite water reactor while KP-SKD represents the channel reactor of supercritical pressure. Enriched uranium (4% enrichment) UO$_2$ or Th can be used as fuel in CANDU SCWRs, while 6% enriched uranium is necessary for KP-SKD. ChUWR fast reactors use mixed oxide (MOX) and ChUWR thermal reactors use uranium carbide (UC). Figure 2.14 shows the operating temperature of water for SCWR and some other types of nuclear reactors: pressurized water reactor (PWR), CANDU and boiling water reactor (BWR). SCWRs work at higher temperatures and pressures compared to conventional reactors.
Table 2.1: Modern concepts of pressure-channel SCWRs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CANDU</th>
<th>ChUWR</th>
<th>KP-SKD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Country of origin</td>
<td>Canada</td>
<td>Russia</td>
<td></td>
</tr>
<tr>
<td>Spectrum</td>
<td>Thermal</td>
<td>Thermal</td>
<td>Fast</td>
</tr>
<tr>
<td>Power output (MW)</td>
<td>1220</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Thermal eff. (%)</td>
<td>48</td>
<td>44</td>
<td>43</td>
</tr>
<tr>
<td>Outlet pressure of coolant (MPa)</td>
<td>25</td>
<td>24.5</td>
<td>25</td>
</tr>
<tr>
<td>$T_{\text{inlet}} - T_{\text{exit coolant}}$ (°C)</td>
<td>350 – 625</td>
<td>270 – 545</td>
<td>400 – 550</td>
</tr>
<tr>
<td>Coolant flow rate (kg/s)</td>
<td>1320</td>
<td>1020</td>
<td>–</td>
</tr>
<tr>
<td>Core H/D (m/m)</td>
<td>-4/4</td>
<td>6/12</td>
<td>3.5/11</td>
</tr>
<tr>
<td>Fuel</td>
<td>UO$_2$/Th</td>
<td>UC</td>
<td>MOX</td>
</tr>
<tr>
<td>Enrichment (%)</td>
<td>4</td>
<td>4.4</td>
<td>–</td>
</tr>
<tr>
<td>$T_{\text{max cladding}}$ (°C)</td>
<td>850</td>
<td>630</td>
<td>650</td>
</tr>
<tr>
<td>Moderator</td>
<td>D$_2$O</td>
<td>Graphite</td>
<td>–</td>
</tr>
</tbody>
</table>

Source: Pioro and Duffey (2007).

Figure 2.14: Pressure-Temperature diagram of water for typical operating conditions of SCWRs, PWRs, CANDU-6 reactors and BWRs (Pioro et al., 2008).
CHAPTER 3: LITERATURE REVIEW

3.1 General Studies on Energy Conversion Systems and Hydrogen Production

3.1.1 Energy and Exergy Analyses
Simpson and Lutz (2007) evaluate the performance of hydrogen production via steam methane reforming (SMR) using exergy analysis, with emphasis on exergy flows, destruction, waste, and efficiencies. A steam methane reformer model is developed using a chemical equilibrium model with detailed heat integration. The results show that the majority of the exergy destruction occurs due to the high irreversibility of chemical reactions and heat transfer. A significant amount of exergy is wasted in the exhaust stream.

Energy and exergy analyses are conducted to investigate the thermodynamic-electrochemical characteristics of hydrogen production by a solid oxide steam electrolyzer plant by Ni et al. (2007). The results indicate that the difference between energy efficiency and exergy efficiency is small as the high-temperature thermal energy input is only a small fraction of the total energy input. In addition, the high-temperature waste heat is of high quality and can be recovered. In contrast, for a low-temperature electrolysis plant, the difference between the energy and exergy efficiencies is more apparent because considerable amount of low-temperature waste heat contains little exergy and cannot be recovered effectively.

Rosen (2008) conducts exergy analysis to investigate the thermodynamic performance of the Ispra Mark-10 thermochemical water splitting process for hydrogen production. The analysis shows that the major thermodynamic losses occur in the primary water decomposition reactors and are mainly due to internal irreversibilities associated with chemical reaction and heat transfer across large temperature differences.

Five different commercial or pilot scale gasification systems are considered for the design of a hydrogen production using biomass gasification by Richard et al. (2008). For each of the gasification technique models of two different hydrogen production plants are developed in Cycle-Tempo: one plant with low temperature gas cleaning and the
other with high temperature gas cleaning. The thermal input of all plants is 10 MW of biomass with the same dry composition. An exergy analysis of all processes is conducted to compare their thermodynamic performance.

Yilanci et al. (2011) perform an exergy analysis to a photovoltaic-hydrogen production system and its component using actual data. The average system exergy efficiency is determined to be 3.18%. The major irreversibility occurs in the PVs.

Exergy analysis is used to improve the performance of the hydrogen production from biomass gasification through optimization of the operating parameters and efficiencies by Abuadala et al. (2010). Results show that improvement in hydrogen production from biomass steam gasification depending on the amount of steam and quantity of biomass feeding to the gasifier as well the operating temperature.

3.1.2 Exergoeconomic Analyses

Tsatsaronis and Moran (1997) show how the cost of a thermal system can be minimized using exergy-related variables: the exergetic efficiency, the rates of exergy destruction and exergy loss, an exergy destruction ratio, the cost rates associated with exergy destruction, capital investment and operating and maintenance, a relative cost difference of unit costs and an exergoeconomic factor. Exergy-aided cost minimization method is applied to a simple cogeneration system as a case study.

Kim et al. (1997) develop a general-cost balance equation by combining exergetic and economic analysis which can be applied to any component of a thermal system. The method decomposes the exergy of a material stream into thermal, mechanical and chemical exergy flows and entropy-production flow, and assigns a unit exergy cost to each disaggregated exergy. The monetary evaluations of various exergy (thermal, chemical, etc.) costs, as well as the production cost of electricity of the thermal system are obtained by solving the set of equations. A 1000-kW gas turbine cogeneration system is analyzed as a case study.

The relation between exergy loss and capital cost and those between exergy and environmental impact are investigated.

Lazzaretto and Tsatsaronis (2006) propose a systematic and general methodology for defining and calculating exergetic efficiencies and exergy related costs in thermal systems based on the Specific Exergy Costing (SPECO) approach, in which (i) the fuel and product of a component are defined by taking a systematic record of all exergy additions to and removals from all the exergy streams of the system, and (ii) the costs are calculated by applying basic principles from business administration. The study shows how to conduct an evaluation of cost associated with all the exergy streams, in separate forms (thermal, mechanical, and chemical), entering and exiting a system component.

Colpan and Yesin (2006) perform an exergoeconomic analysis to several configurations of combined cycle cogeneration systems, which are then compared in terms of performance assessment parameters and cost per unit exergy.

Exergoeconomic analysis and optimization of combined heat power production is reviewed by Abusoglu and Kangolu (2009). The concept of exergetic cost and cost accounting methods are discussed and applied to a diesel engine powered cogeneration system.

A biomass-based hydrogen production is investigated through EXCEM exergoeconomic analysis by Kalinci et al. (2012). Hydrogen unit cost is defined and examined how key system parameters affect the unit hydrogen cost. A gasification process with a circulating fluidized bed gasifier for hydrogen production is studied using the actual data taken from the literature. Energy and exergy values of all streams associated with the system, exergy efficiencies of all equipment, and determine the costs of equipment along with their thermodynamic loss rates and ratio of thermodynamic loss rate to capital cost are calculated.

3.1.3 Exergoenvironmental Analyses

Exergoenvironmental assessment of a bioenergy conversion process consisting of a high-temperature solid oxide fuel cell (SOFC) with integrated allothermal biomass gasification is performed by Buchgeister (2010). Their analysis results show that the supply of
Biomass has the highest environmental impact, and that gasifier, heat exchanger and SOFC are the most environmental friendly components of the system.

Benerjee and Tierney (2011) compare the environmental impacts of various candidate energy systems for rural areas in developing countries using five different exergoenvironmental methods. It is found that the method combining a standard environmental impact indicator with exergetic analysis is the most effective because it uses a well-established and continually updated environmental impact metric. According to most of the employed methods, electricity generation from Jatropha oil and heat from biogas have low environmental impacts.

Petrakopolou et al. (2011) use exergoenvironmental analysis to compare three power plants: a plant with chemical looping combustion with 100% CO₂ capture and two advanced zero emission plants with both 100% and 85% CO₂ capture. Results indicate that the plant with the chemical looping combustion is the most environmentally benign option although it results in a higher cost of electricity.

Boyano et al. (2011) apply exergoenvironmental analysis to a steam methane reforming process for hydrogen production. Exergoenvironmental analysis is a combination of exergy analysis and environmental assessment, in which the environmental impacts obtained by LCA or other environmental assessment tools are apportioned to the exergy streams. The results identify the components with the highest environmental impacts and possible improvements, and provide useful information for designing systems with lower overall environmental impacts. Components in which chemical reactions occur are observed to have higher exergy destructions than other components. The overall environmental impact can be reduced by decreasing the exergy destructions within components, which usually requires the use of efficient modern equipment, expensive materials and efficient designs. Boyano et al. (2012) also conduct an advance exergoenvironmental analysis to the steam methane reforming process for hydrogen production considering avoidable and unavoidable parts of exergy destruction.

### 3.1.4 Life Cycle Assessment (LCA)

Life cycle analyses of several H₂ production methods are reported. Spath and Mann presented two reports for the National Renewable Energy Laboratory (NREL) related to
life cycle assessments of hydrogen production via natural gas steam reforming (2001) and via wind/electrolysis (2004). The first report (Spath and Mann, 2001) presents the environmental impacts of hydrogen production via natural gas steam reforming for a hydrogen plant capacity of 1.5 million Nm$^3$/day. The results are given in term of air emissions, GHG and water emissions. The global warming potential (GWP) of the system is found to be 11.8 kg CO$_2$-eq per kg hydrogen produced. The second report (Spath and Mann, 2004) investigates the environmental impacts of hydrogen production based on wind power. Three wind turbines, each with 50 kW capacity, are incorporated to the system which has a hydrogen production capacity of 100 kg per week. The LCA results indicate that GWP of hydrogen production is 0.970 kg CO$_2$-eq and system energy consumption is 9.1 MJ per kg hydrogen produced. Sensitivity analyses are presented in both studies.

Marquevich et al. (2002) conduct a life cycle inventory analysis to assess the environmental load, specifically GWP, associated with H$_2$ production by steam reforming of feedstocks (methane and naphtha) and vegetable oils (rapeseed oil, soybean oil and palm oil). While the GWP of H$_2$ produced from rapeseed oil, palm oil and soybean oil are found to be 6.42, 4.32 and 3.30 kg CO$_2$-eq/kg H$_2$, respectively, the GWPs associated with the production of H$_2$ by steam reforming are 9.71 and 9.46 kg CO$_2$-eq/kg H$_2$. Thus, the GWP may be reduced by up to 60% if natural gas and naphtha are replaced by vegetable oils.

Koroneos et al. (2004) use a comparative LCA to investigate the environmental impacts of natural gas steam reforming and hydrogen production based on renewable energy sources. The fuel systems considered in the analysis are listed as follows:

- Fuels produced from conventional sources:
  - Hydrogen produced from steam reforming of natural gas
- Hydrogen produced from renewable energy sources:
  - From solar energy using photovoltaics for direct conversion
  - From solar thermal energy
  - From wind power
  - From hydro power
  - From biomass

30
Life cycle impact assessment (LCIA), a phase of LCA to classify and quantify environmental impacts of the material and energy flows, is conducted using CML 2001 impact categories and Eco-indicator 95 methods. The total impact scores show that the use of wind, hydropower and solar thermal energy are the most environmentally benign methods. In terms of GWP, hydrogen production using wind power has the lowest environmental impact while hydrogen from steam reforming of natural gas has the highest CO₂-eq emissions.

Utgikar and Thiesen (2006) perform a life cycle assessment of high temperature electrolysis for H₂ production via nuclear energy. High temperature electrolysis is advantageous to low-temperature alkaline electrolysis because of its higher efficiency, which is due to reduced cell potential and consequent electrical energy requirements. The high temperature electrolysis system has a GWP of 2.00 kg CO₂-eq and acidification potential (AP) of 0.15 g H₂ ion equivalent per kg of H₂ produced. A comparison of the environmental impact of the system with natural gas steam reforming and wind, solar photovoltaic, solar thermal, hydroelectric and biomass based electrolysis indicates that emissions of the high temperature water vapour electrolysis process are much lower than those for conventional natural gas steam reforming and comparable with the emissions for H₂ production using renewable based electrolysis.

Utgikar and Ward (2006) present a LCA of a nuclear-assisted ISPRA Mark 9 TWS cycle, a three-step thermochemical cycle involving iron chlorides (Fe-Cl). GWP and AP of the nuclear-based hydrogen production system, per kg hydrogen produced, are found to be 2515 g CO₂-eq and 11.252 g SO₂-eq, respectively.

Solli et al. (2006) present a comparative hybrid life cycle assessment to evaluate and compare environmental impacts of two H₂ production methods: nuclear assisted thermochemical water splitting using the S-I cycle and natural gas steam reforming with CO₂ sequestration. A weighting method is not applied to determine the better option. The results show that thermochemical water splitting has lower environmental impacts in terms of GWP, AP and eutrophication potential (EP), and much higher impacts in terms of radiation (RAD) and human toxicity potential (HTP). While the GWP of natural gas steam reforming is $1.3 \times 10^4$ kg CO₂ eq, the GWP of thermochemical water splitting via
the S-I cycle is $2.9 \times 10^3$ kg CO$_2$ eq for the production of 1 TJ (on the basis of higher heating value (HHV)) of H$_2$.

Koroneos et al. (2008) compare two biomass-to-hydrogen systems: biomass gasification by reforming of the syngas, and gasification followed by electricity generation and electrolysis. Environmental impacts in terms of GWP, AP, and EP are determined, and a weighting using the Eco-indicator 95 method is also applied to compare the overall environmental impacts. While the gasification to electrolysis system has a greater eutrophication effect, biomass gasification by reforming of syngas has higher environmental impacts in terms of GWP and AP. In addition, weighting results show that the biomass-gasification-electricity-electrolysis route has better environmental performance than the process involving reforming of the syngas.

Djomo et al. (2008) propose potato steam peels as a feedstock for producing H$_2$ through fermentation and conduct an LCA for this process. The authors utilized the IMPACT 2002+ method in the LCIA phase. The results show that the two-stage bioreactor, which is used for H$_2$ production, emits 1000-1500 g of CO$_2$ per kg of H$_2$ produced. There are two main sources of CO$_2$ emissions. First, photoheterotrophic bacteria convert all organic acids to H$_2$ and CO$_2$. There is also an electricity requirement for both pre-treatment and fermentation processes in H$_2$ production, and this is another source of greenhouse gas emissions. The study also demonstrates that hydrogen production using potato steam peels offers advantages compared to direct use of peels to feed animals, including reductions in GHGs emissions, non-renewable resource utilization and human health impacts.

Dufour et al. (2009) perform an environmental impact assessment for four H$_2$ production systems: steam reforming of natural gas (the reference system), a coupling of the reference system with CO$_2$ capture, thermal cracking and autocatalytic decomposition of natural gas. The results show that autocatalytic decomposition with a total conversion is the most environmentally benign process. Steam reforming of natural gas with CO$_2$ capture and storage options leads to a lower GWP, but a higher general environmental impact, as calculated with the Eco-indicator method, than conventional steam methane reforming without CO$_2$ capture.
3.1.5 Exergetic Life Cycle Assessment (ExLCA)

The relations between exergy and environmental impact are applied by many researchers. Some of the more significant applications are described in this section. Ayres et al. (1998) discuss exergy, waste accounting, and life-cycle analysis and argued that thermodynamics offers a means of accounting for resource inputs and waste outputs in a systematic and uniform way. The authors further state that exergy is an appropriate measure of resource stocks and flows as well as waste emissions and their potential for environmental harm.

Cornelissen and Hirs (2002) apply exergetic life cycle assessment to different waste wood treatment routes. Waste wood is co-combusted in the first model, while waste wood is used to produce chipboard in model 2. Furthermore, in model 3 and 4 coal for generating electricity is replaced by green wood. Comparing the four models it can be seen that replacing coal by green wood causes more wasting of natural resources, while the depletion of natural resources decreases.

Daniel and Rosen (2002) examine material emissions produced for 13 fuel cycles for automobiles, on mass and exergy bases. Chemical exergies of fuel life cycle emissions are compared with the masses of fuel cycle emissions. For the emissions data used, the chemical exergy results suggest that compressed natural gas use in motor vehicles produces emissions that are the furthest from equilibrium with the natural environment, relative to all other fuel life cycle paths considered. It is also shown that diesel use in grid-independent hybrid electric vehicles has the lowest chemical exergies of emissions for all 13 fuel-vehicle combinations considered, suggesting a lower potential for environmental impact. It is concluded that the exergy methodology presented for assessing the potential for environmental impact may aid the development and design of environmentally benign transportation technologies.

Neelis et al. (2004) analyze a several hydrogen production and storage systems for automotive applications using exergetic life cycle assessment. Eight fuel supply and use chains are analysed. Exergy analysis is shown to provide additional useful information compared to conventional energy analysis based on the heating values of fuels, since exergy can be used for both fuel and non-fuel resources and can play an important role in the quantification of resource depletion in fuel chains. Vehicles with compressed
hydrogen storage are shown to be the most exergy efficient on a normalized (MJ/km) basis.

Granovskii et al. (2007) use exergetic life cycle assessment to evaluate the exergy efficiency, economic effectiveness and environmental impact of producing hydrogen using wind and solar energy in place of fossil fuels. In that work, exergy efficiencies and greenhouse gas and air pollution emissions are evaluated for all process steps, including crude oil and natural gas pipeline transportation, crude oil distillation and natural gas reforming, wind and solar electricity generation, hydrogen production through water electrolysis, and gasoline and hydrogen distribution and utilization. The use of wind power to produce hydrogen via electrolysis, and its application in a fuel cell vehicle, is seen to exhibit the lowest rates of fossil fuel and mineral resource consumption. The authors suggest that “renewable” hydrogen can help address long-term environmental problems.

3.1.6 Multi-generation Systems

Li et al. (2006) perform a thermodynamic, economic and environmental assessment for a trigeneration system which supply heating, cooling and power to an urban residential area in Beijing. System considered consists of a gas turbine, internal combustion engine, absorption chiller and gas boiler. The optimal plant configurations are found with the consideration of system configuration, design and operation under different economic and environmental legislation contexts.

Exergy analysis of a trigeneration plant based on solid oxide fuel cells (SOFC) and an organic Rankine cycle (ORC) is performed by Al-Sulaiman et al. (2010). Other thermodynamic elements of the system are a heat exchanger for the heating process and a single-effect absorption chiller for cooling. The maximum efficiency of the trigeneration plant is calculated to be 74%. The study also investigates the effect of current density and inlet flow temperature on the SOFC cell voltage and voltage loss.

Al-Sulaiman et al. (2011) also use exergy modelling to assess the exergetic performance of a trigeneration system consisting of parabolic solar trough collectors, ORC, and a single effect absorption system. The results show that the main sources of irreversibilities are the solar collectors and ORC evaporators.
Chua et al. (2012) develop a trigeneration system to provide cooling, heating and power needs of a commercial building. The sub-units of the system are photovoltaic-thermal, solar-thermal, fuel cell, microturbine and absorption chiller-water system. The analysis is conducted aiming at (i) operating cost reduction, (ii) energy saving and (iii) minimum environmental impact.

Energy and exergy analyses are performed for a new geothermal based multi-generation system by Coskun et al. (2012). Systems are examined under two distinct main groups for heating and cooling periods. The analysis results show that overall system energy and exergy efficiency are increased by 3.4 and 1.12 times for cooling season and about 4.25 and 1.25 times for heating season, as compared to the single power generating option.

3.2 Cu-Cl Thermochemical Cycle

Many studies are currently available in the literature that analyzes Cu-Cl thermochemical cycle in the light of various approaches and methodologies. These studies are categorized under several titles: advances in nuclear-based hydrogen production, overall system analysis, integrated systems, Aspen Plus simulations, heat recovery, exergy analysis, cost analysis, exergoeconomic analysis, life cycle assessment, exergetic life cycle assessment and exergoenvironmental analysis, studies on individual reactions and other issues. However, it should be noted the aforementioned categories are interconnected and many authors have performed studies that incorporates a number of these categories in their papers. A thorough literature review can be seen below.

3.2.1 Advances in Nuclear-Based Hydrogen Production and the Thermochemical Cu-Cl Cycle

The researchers (e.g., Lewis et al., 2009a; 2009b; Lewis and Masin 2009) have published several studies to re-evaluate thermochemical cycles reported in the literature as having both promising efficiencies and proof-of-concept results. Part I (Lewis et al., 2009a) of this series illustrates the methodology used to recalculate the efficiency and to identify the most critical R&D necessary to further assess the cycles’ potential. Part II (Lewis and
Masin, 2009) contains results of the analyses for all the cycles. A more detailed Level 3 analysis for the Cu-Cl cycle is presented in Part III (Lewis et al., 2009b).

In Part I, the initial screening criteria to eliminate the thermochemical cycles for hydrogen production is described in the literature are the maximum temperature requirement, chemical viability, and thermodynamic feasibility. For example, cycles requiring process heat at temperatures greater than 850°C are eliminated. In the next phase (efficiency calculation), a thermal efficiency equation is used where the numerator is the lower heating value (LHV) of hydrogen, and heat and work are placed in the denominator. A ratio of 0.5 is used in the equation to consider thermal equivalent of different types of work (chemical, electrochemical, mechanical, electrical, separation, etc.). In this study (Lewis et al., 2009a), the efficiency calculations are improved in a systematic manner. Level 1 considers the energy requirements based only on a simplified chemistry of the proposed cycle, whereas Level 2 considers equilibrium issues, such as yields and competing side reactions. If the chemistry is known with available thermodynamic data, various candidate thermochemical cycles can be evaluated relatively easily by only performing Level 1 and 3 analyses. In Level 3, experimental data, as they become available, are used to set more realistic reaction conditions and to determine the actual product distributions. Level 3 also includes developing conceptual designs and Aspen Plus flowsheets of the thermochemical cycles. The energy efficiency of the Cu-Cl cycle is found to be 48%, 39.6% and 41% for Level 1, 2 and 3, respectively.

Part II (Lewis and Masin, 2009) summarizes the results of the down-selection process, which is applied using the methodology explained in Part I to eight promising thermochemical water decomposition cycles: the cerium-chlorine (Ce-Cl), the copper-chlorine (Cu-Cl), the iron-chlorine (Fe-Cl), the vanadium-chlorine (V-Cl), the copper-sulphate (Cu-SO₄), the magnesium-iodine (Mg-I), the hybrid chlorine, and potassium-bismuth (K-Bi). As a result of the down selection process, the Cu-Cl cycle is selected to be the most promising cycle for further R&D because of the following reasons:

- Lower maximum temperature.
- All reactions demonstrated at laboratory scale.
- Hydrogen produced at 300 psi.
- No catalysts needed for thermal reactions.
- International support.
- Preliminary efficiency and hydrogen production costs within DOE targets.

Part III (Lewis et al., 2009b) describes the procedure used to develop the three-step Cu-Cl cycle beyond the relatively simple Level 3 efficiency calculation. The optimization process includes (i) updating the thermodynamic database used in the Aspen Plus simulation, (ii) developing a robust flowsheet and optimizing the energy usage therein, (iii) designing a conceptual process incorporating the Aspen Plus mass and energy flows, and then (iv) estimating the hydrogen production costs. The experimental results for the hydrolysis reactor show that increasing the test temperature increases the conversion of CuCl₂ to Cu₂OCl₂ but also to CuCl. Therefore, it is suggested to have smaller particles and test temperatures near 375°C in order to enhance the conversion of CuCl₂ to Cu₂OCl₂ for the second generation reactor design. It is also concluded that high carrier gas flow rates increase CuCl formation but also improve mass transfer that enhances Cu₂OCl₂ formation. Aspen Plus model for the hydrolysis step also confirm that the maximum yield of Cu₂OCl₂ near 375°C for a steam to Cu ratio of 17. The study also presents the efficiency results of Aspen Plus simulations. Simulations are conducted for 125 MT of hydrogen production per day which requires 210 MW of thermal energy and 87.8 MW of electrical energy. Based on these data and efficiency of converting thermal energy into electrical energy of 40%, the efficiency of the Cu-Cl cycle is found to be 40.4% (LHV basis). The results are based on an assumption that electrolysis reactor operates at a voltage of 0.5 V and a current density of 500 mA/cm². Economic analysis presented in the study of Lewis et al. (2009b) uses the H2A spread sheet developed by DOE. The H2A is a discounted cash flow analysis, which calculates the cost of producing hydrogen if a 10% return on equity is required. Estimates for capital and operating costs are input by the user. Considering the assumptions listed in the paper, the total capital investment for the CuCl plant is found to be $131 million dollars and the estimated cost of hydrogen is $3.30/kg.

Naterer et al. (2009, 2010, 2011a, 2011b) present several studies on advances in nuclear-based hydrogen production using thermochemical water splitting via the Cu-Cl
cycles. Developments of enabling technologies for the Cu-Cl cycle is discussed, particularly the individual reactor designs, thermochemical properties, advanced materials, safety, reliability and linkage between nuclear and hydrogen plants in the first paper (Naterer et al., 2009). Some concluding remarks of this study are (i) the four-step Cu-Cl cycle has an advantage of reducing complexity by eliminating the solid handling and thus less equipment, (ii) spray drying is an efficient method of water removal in drying step of aqueous cupric chloride due to relatively large surface area are available for heat and mass transfer, (iii) high Ni-Cr alloys are identified as the most promising materials to resist corrosion for the copper oxychloride decomposition reactor, and (iv) the electrolysis is economically attractive at low hydrogen production capacities below 10-20 tons/day, but thermochemical plants become more competitive at higher capacities.

The second study (Naterer et al., 2010) presents the advances towards an integrated lab scale Cu-Cl cycle with respect to experimentation, modeling, simulation, advanced materials, thermochemistry, safety, reliability and economics. The study states that low voltage requirement for the electrochemical step is a significant advantage of the Cu-Cl cycle whereas solids handling between processes and corrosive working fluids present unique challenges. The experimental studies on Step 1 (CuCl/HCl electrolysis) show that the rate of the Cu/Cl electrolysis reaction increases with temperature and CuCl concentration. The preferred anolyte concentration is found to be 0.5 molar CuCl in 11 molar HCl, while the preferred catholyte concentration is 11 M HCl. Aspen Plus simulations predict that 100% yield is achievable with steam to a CuCl₂ molar ratio of 17 at 370°C in hydrolysis reactor, which can be lowered by decreasing the pressure (partial vacuum). A predictive model to recover heat from molten CuCl exiting the copper oxychloride decomposer is developed, and results show that full heat recovery can be achieved. Also, it is concluded that the Cu-Cl cycle couples well with various heat sources, such as the SCWR, solar power tower or Na-cooled fast reactor due its relatively low temperature requirement (a 530°C maximum temperature).

Two companion papers by Naterer et al. (2011a, 2011b) present an overview of Canada’s program on the copper-chlorine cycle of thermochemical water splitting and nuclear hydrogen production. It specifically examines and presents recent advances by a Canadian consortium. The first one of two companion papers includes the experimental
unit operations in the Cu-Cl cycle. A promising performance of the CuCl/HCl electrolyzer with stable cell performance at voltages down to 0.477 V have been observed for 10 h. Experimental results for Step 2 (water removal from aqueous Cu(II) chloride) using a Yamota D-41 spray dryer is presented. Method of crystallization experiment is also examined as an alternative water removal process and results are shown. It is stated in the paper that stable operation and production of copper oxychloride from solid feed of Cu(II) chloride is successfully demonstrated in hydrolysis experiments at UOIT. Also, solid feed of copper oxychloride is shown to decompose and produce oxygen gas and molten Cu(I) chloride in a large molten salt reactor. The second of two companion papers focuses on simulations, thermochemical data, advanced materials, safety, reliability and economics of the Cu-Cl thermochemical cycle. The results for exergoeconomic and life cycle assessment applied on the Cu-Cl cycle are presented. Aspen Plus simulations are performed for different system configurations to improve the cycle efficiency. Modelling of the linkage between nuclear and hydrogen plants demonstrates the integration of the Cu-Cl cycle with a Generation IV SCWR. Properties of Cu$_2$OCl$_2$, Cu(I) and Cu(II) chloride species and chemical potentials, solubilities, formation of Cu(I) and Cu(II) complexes are also reported in a study of Naterer et al. (2011b).

### 3.2.2 Overall System Analysis

Dokiya and Kotera (1976) report two-step and three-step copper-chlorine cycles. The cell voltage is found to be 0.6-1.0 V, according to the current density in the preliminary experiment. It is concluded in the study that the cycle merits further investigation as a candidate for water splitting.

Lewis et al. (2003; 2005) report the preliminary experiment results for the Cu-Cl cycle for the six-step (Lewis et al., 2003) and four-step (Option I) (Lewis et al., 2005) Cu-Cl cycles. The results for hydrogen generation reaction, cuprous chloride electrolytic disproportionation, hydrolysis and oxygen generation reactions are presented. The feasibility of the Cu-Cl cycle is demonstrated based on the preliminary experimental results and the thermodynamic studies.

Rosen et al. (2006) study the basics of the nuclear-based hydrogen production with a thermochemical copper-chlorine cycle and presented in Canadian Hydrogen
Association Workshop, 2006. The paper outlines the primary challenges, design issues associated with each step of the five-step Cu-Cl thermochemical cycle. Exergy analysis is proposed as a useful tool to identify efficiencies and thermodynamic losses in the overall process and its steps.

Wang et al. (2008a) examine the heat requirements of each step in the five-step Cu-Cl cycle. The study assumes stoichiometric reactions. Total heat released from the exothermic reactions and cooling processes is calculated as 290.11 kJ/mol H₂. The total heat requirement of the five-step Cu-Cl cycle is also calculated as 451.65 kJ/mol H₂. The heat recovery from oxygen production reactor is also studied which is discussed in Section 2.2.5.

Design issues associated with reactor scale-up in the copper-chlorine cycle are examined by Wang et al. (2008b). A sedimentation cell for copper separation and HCl gas absorption tower are discussed for the thermochemical hydrogen reactor. Scale-up design issues are examined for handling three phases (solid copper oxychloride, liquid CuCl and exiting gas oxygen) within the molten salt reactor. Hydrolysis reactions for two-, three- and five-step Cu-Cl cycles are also discussed.

The advantages and disadvantages of three different copper chlorine cycles, namely the five-step, the four-step (Option I) and the three-step (Option I), are discussed by Wang et al. (2009a). First of all, major advantages and disadvantages in comparison of spray drying and crystallization for drying step of the five-step cycle is discussed. Although 100% drying can be obtained via spray dryer, higher temperatures compared to crystallization is required. Steam to CuCl₂ ratio is defined as 17 to reach a yield higher than 95% in hydrolysis reactor. Maximum recommended temperature for hydrolysis step is 390°C. The excess steam requirement in the hydrolysis step is the primary reason to combine drying and hydrolysis steps, so the four-step (Option I) is formed. The primary advantages of combining these two steps include less steps, less equipment, and less challenges to process solid particles. On the other hand, the major disadvantages are higher heat grade and intensity requirements, more equipment material challenges, and more undesirable side reactions. A three-step cycle with the decomposition reaction being combined into oxychlorination reaction is not recommended for industry due to higher
heat grade requirements (approximately 600°C of maximum temperature) and a very corrosive nature of the system.

Wang et al. (2009b) propose a new six-step Cu-Cl cycle in order to reduce the excess steam requirements. It is found that the steam requirement can decrease by up to ten times, compared the conventional Cu-Cl cycles, and the heat grade of the hydrolysis step in the new cycle is significantly reduced from 375°C to 150°C. However, there are two major challenges associated with the new cycle, (i) the prevention of dehydration of cupric chloride hydrate and (ii) efficient mixing of the reactant particles in the oxygen production step.

An efficiency analysis of the five-step Cu-Cl cycle is presented by Orhan et al. (2009a). It is assumed in the study that stoichiometric reactions take place. Variations of the energy and exergy efficiencies with reaction temperatures and ambient temperature are investigated. Heat loss from the system is assumed to be 30% of the heat input. The energy efficiency of the cycle is found to be 45% and the exergy efficiency 10%. As reaction temperature increases, the input energy needed (the output energy released, in the case of exothermic reaction) to drive the chemical reactions for step 1, 3 and 5 decreases while that for steps 2 and 4 increases. The exergy efficiency decreases with increasing reference environment temperature, while energy efficiency remains constant.

A comparison of copper-chlorine and sulphur-iodine thermochemical hydrogen production cycles is performed by Wang et al. (2010). The required heat quantity and grade, thermal efficiency, engineering challenges and hydrogen production costs are discussed for these two thermochemical cycles. Although the copper-chlorine cycle has the advantage of a lower maximum temperature of 630°C (which is 300°C lower than the maximum temperature of S-I cycle), the heat requirements of these two cycles are similar. The overall energy efficiencies are between 37 and 54% depending on the portion of heat recovery. Total heat requirement of the five-step Cu-Cl cycle is found to be 554.7 kJ/mol H₂, while the total heat release is 232 kJ/mol H₂ (based on stoichiometric reactions). 29.5% of the heat requirement is determined to be low grade heat. The Cu-Cl cycle uses more low grade heat, which means a future potential of utilizing waste heat from thermal power plants. It is also stated that the S-I cycle may have more challenges of equipment material selection and product separation. Finally, the cost assessment
showed that both cycles have similar hydrogen production cost. Details on cost assessment of this study are discussed in Section 2.2.7.

The performance analyses of the three Cu-Cl cycles (the five-step, the four-step Option I and the three-step Option I) are conducted by Orhan et al. (2011a). Each reactors (in the five-step Cu-Cl cycle) energy load are calculated as a function of reaction temperature and for to different yields, 80% and 100% (stoichiometric reaction). The variation of energy and exergy efficiencies with reactor temperatures is also discussed for the five-step Cu-Cl cycle. The results show that decreasing number of steps in the Cu-Cl cycle increases the maximum cycle temperature and exergy efficiency. Moreover, less steps indicates less challenges to process solid particles, less equipment, reduced complexity, better reaction kinetics, and homogenous reaction mixture. Disadvantages of decreasing the number of steps, on the other hand, are higher heat grade, more equipment material challenges, more undesirable side products and lower energy efficiency.

3.2.3 Integrated Systems

Jaber et al. (2010a) investigate natural gas usage as a heat source for integrated SMR and thermochemical hydrogen production technologies. The hydrogen production methods considered are SMR, the thermochemical S-I cycle, the thermochemical Cu-Cl cycle and an integrated Cu-Cl/SMR plant. Results show that integration of SMR with the Cu-Cl cycle is promising since the costs of producing hydrogen decreases, and the overall performance of the plant improves.

Linkage of geothermal sources with thermochemical cycles for hydrogen production is investigated by Balta et al. (2010). Six potential thermochemical and hybrid cycles including the Cu-Cl cycle are compared in terms of operating conditions, temperature ranges, cycle phenomena and performance aspects. It is concluded in the study that the Cu-Cl cycle is the most promising low temperature cycle to produce hydrogen.

Aghahosseini et al. (2011) propose an integrated process model for an integrated gasification combined cycle (IGCC) and the Cu-Cl thermochemical cycle for trigeneration of hydrogen, steam and electricity. The results indicate that the hydrogen content of produced syngas increases about 20% because of the improvement of the
gasification combustion efficiency and reduction of syngas NO\textsubscript{x} emissions, when oxygen output of the Cu-Cl cycle is used instead of air in gasification process. Moreover, it is found that 60\% of heat requirement of the Cu-Cl cycle can be met by the IGCC plant. Hence, integration of the Cu-Cl with IGCC provides a significant improvement in system efficiency.

A solar plant coupled with a Cu-Cl thermochemical plant is analyzed by Ghandehariun et al. (2010) for hydrogen production at three locations across Canada. Parabolic trough solar technology is proposed to supply heat to the oxygen production step. Molten salt, a binary mixture of 60\% NaNO\textsubscript{3} and 40\% KNO\textsubscript{3}, is considered as heat transfer medium. The dimensions of the storage unit are estimated based on the energy requirement of the oxygen reactor and the energy collected by the solar plant.

The operating temperature ranges of various solar thermal energy technologies are analyzed by Wang et al. (2011), with respect to the their compatibility with solar hydrogen production via thermochemical cycles. It is found that heliostat solar thermal tower can provide sufficiently high temperature thermal energy for hydrogen production. Integration of the Cu-Cl thermochemical hydrogen production cycle and a heliostat solar thermal power plant that uses molten salt as a working fluid is examined. The quantity of molten salt and solar plant dimensions for capturing and storing solar heat for an industrial hydrogen production scale are evaluated for 24 h operation per day. The heat losses of molten salt from storage tank and in transport pipelines are also investigated.

Xu and Wiesner (2012) propose a solar receiver-reactor with integrated energy collection and storage. Reactor is designed to supply heat only for the copper oxychloride decomposition (oxygen production) step of the Cu-Cl cycle. There are three parts in the oxygen generating system: the reactor body, the separator and the storage tank. The reactor body consists of three concentric cylinders. The inner one is the reactor, where copper oxychloride particles thermally decompose into CuCl and oxygen. The inner annulus contains the hot molten salt which recycled through a storage tank. The outer annulus is the vacuum cylinder to minimize convective heat losses to the environment. Solar collection is assumed to be accomplished with a compound parabolic trough. The capacity of designed reactor is for 3.6 kg daily hydrogen production. Corresponding
circulation rate of molten salt and storage volume is calculated to be 15 kg/h and 100 m$^3$, respectively.

3.2.4 Aspen Plus Simulations

Chukwu et al. (2008) and Rosen et al. (2012) perform Aspen Plus simulation to examine the energy requirement and corresponding energy efficiency of the five-step Cu-Cl cycle. Stoichiometric reactors are used in the analysis as a preliminary study. The reaction heat for endothermic reactions are found to be 442.1 kJ/mol H$_2$ and total heat from exothermic reactions are evaluated to be 290.1 kJ/mol H$_2$. A heat exchanger effectiveness of 50% is assumed because some of the reactions heat has a low quality and temperature. The electrochemical work is found to be 192.6 kJ (for 50% conversion efficiency and assuming 0.5 V for electrolysis). The work for auxiliary equipment is also assumed to be 38 kJ/mol H$_2$. The corresponding cycle energy efficiency using the higher heating values is 52.6%.

Ferrandon et al. (2008) carry out the three-step Cu-Cl cycle system calculation using Aspen Plus process simulation package. Chemical reactions are examined using the RGibbs reactor model, and the HeatX model of Aspen Plus is used to model the heat exchangers. Equilibrium based reactor types (e.g., RGibbs and REquil) do not take reaction kinetics into account. RGibbs reactor option is quite useful when reactions occurring are not known or are high in number due to many components participating in the reactions. A Gibbs free energy minimization is done to determine the product composition at which the Gibbs free energy of the products is at a minimum. RGibbs is the only Aspen Plus block that deals with solid-liquid-gas phase equilibrium. REquil reactor option computes combined chemical and phase equilibrium by solving reaction equilibrium equations. REquil reactors cannot do a 3-phase flash. However, they are useful when there are many components, a few known reactions, and when relatively few components take part in the reactions. HeatX model is for two-stream heat exchangers, which can perform simplified or rigorous rating calculations. Simplified rating calculations (heat and material balance calculations) can be performed if exchanger geometry is unknown or unimportant. For rigorous heat transfer and pressure drop calculations, the heat exchanger geometry must be specified (Orhan, 2011).
Stoichiometric reactors are used in the study of Ferrandon et al. (2008) as well. Thermal and electrical energy rate requirements of the three-step Cu-Cl cycle are found to be 210 MW and 87.8 MW to produce 125 MT/day hydrogen as also stated in Lewis et al. 2009b). The energy efficiency of the system, hence, is found to be 40.4% (LHV basis).

Orhan et al. (2012) in their recent study develop simulation models for the five-, four- (Option I and Option II), and three-step (Option I and Option II) thermochemical Cu-Cl cycles using Aspen Plus. The study includes a realistic model of the electrolyzer written as a user-defined Fortran model. REquil and RGibbs reactors are used for chemical reactions and the HeatX module is used to design heat exchangers. The thermal efficiency of the five-step Cu-Cl cycle is calculated to be 45%, of the four-step, Option I is 44% and Option II is 40%, of the three-step, Option I is 41% and finally Option II is 40% based on the lower heating value of hydrogen and considering 40% heat to work conversion efficiency. Variation of the cycle energy and exergy efficiencies with heat exchanger effectiveness is also discussed in the study.

### 3.2.5 Heat Recovery

Two types of contact methods (direct and indirect contact) for heat recovery from molten CuCl, a product of copper oxychloride decomposition, are proposed by Wang et al. (2008a). In order to recover heat from molten CuCl by direct contact, a counter-current flow of the molten salt and gas is considered. The molten salt is sprayed downward and gas is flowing upward. The second method (indirect contact) can only be operated at a temperature higher than 430°C, otherwise condensation of CuCl to solid in the pipe plugs the heat exchanger (typically shell and tube heat exchanger).

Daggupati et al. (2008) study heat recovery in the Cu-Cl cycle by utilizing low-grade waste heat for spray drying and vaporizing processes at low temperatures. More detailed results of this study are given in drying section (Section 2.2.11).

A spray column direct heat exchanger model is developed by Jaber et al. (2010b and 2010c) to recover heat from molten CuCl and supply the heat requirements of other steps in the Cu-Cl cycle. Due to two phase change processes that a CuCl droplet passes through, two separate programs are used to analyze the heat transfer process: sensible and latent heat transfer model. The input parameters for the analysis are air inlet temperature,
CuCl exit temperature, CuCl mass flow rate, air mass flow rate, and the heat exchanger’s cross-sectional area. Results show that full heat recovery is achieved with a heat exchanger diameter of 0.13 m, and heights of 0.6 and 0.8 m, for a 1 and 0.5 mm droplet diameter, respectively. The heat exchanger is designed for a CuCl flow that is equivalent to capacity of 3 kg of hydrogen per day in the Cu-Cl cycle. The inlet exit CuCl temperatures are found to be 530 and 70°C, respectively. The air stream has inlet and exit temperatures of 25 and 493°C. It is also concluded in the study that smaller CuCl droplets has lower heat transfer rates than larger droplets.

Ghandehariun et al. (2011) present a review for several heat recovery technologies to recover heat from molten CuCl. Comparison considers heat transfer rate, additional materials in the cycle, energy efficiency, temperature retention, economics, material issues, and design feasibility for the following heat recovery methods: (i) atomization and steam generation with a quench bath, (ii) atomization and steam generation with separate vessel, (iii) atomization and droplet descent in counter-current flow, (iv) atomization and solidification by air or inert gases, (v) rotary/spinning atomization, (vi) casting/extrusion method and (vii) drum flaker. Methods (ii), (v) and (vi) are found to be the most efficient and reliable for heat recovery from molten salt.

Orhan et al. (2011b) analyze heat exchangers in the five-step copper-chlorine cycle to enhance heat recovery and cycle efficiency. The variation of exergy efficiency with heat exchanger effectiveness is studied. It is concluded that both energy and exergy efficiencies of the cycle increase using more effective heat exchangers. Results show that the total heat demand is equal to the recovered heat for the heat exchanger effectiveness of 0.85. However, this analysis does not consider the heat required by endothermic reactions in the Cu-Cl cycle.

### 3.2.6 Exergy Analysis

Energy and exergy analyses of each step of the five-step Cu-Cl cycle are performed by Orhan et al. (2008b; 2008c; 2009b; 2009c and 2009d). Variations of exergy efficiency and exergy destruction due to irreversibilities with parameters like process and reference-environment temperature are quantified and characterized. At a constant reference-environment temperature of 25°C, the exergy destruction of the hydrogen production step
varies between 1000 kJ/kmol H₂ and 7000 kJ/kmol H₂ when the reaction temperature increases from 300°C to 450°C (Orhan et al., 2008b). At a constant reaction temperature of 45°C, the exergy destruction of the copper production step varies between 50 kJ/kmol H₂ and 7000 kJ/kmol H₂ when the reference temperature increases from 0°C to 30°C (Orhan et al., 2008c). At a constant reference-environment temperature of 25°C, the exergy destruction of the oxygen production step varies between 4500 kJ/kmol H₂ and 23000 kJ/kmol H₂ when the reaction temperature increases from 450°C to 1000°C (Orhan et al., 2009b). At a 400°C reaction temperature and 25°C environment temperature, the exergy destruction in the hydrolysis step is 68,000 kJ/kmol H₂ (Orhan et al., 2009c). The exergy analysis of the heat exchangers in the cycle is also performed by Orhan et al. (2011b) as mentioned in the heat recovery section.

3.2.7 Cost Analysis

Orhan et al. (2008a) report an economic analysis of a Cu-Cl pilot plant for hydrogen production. Cost analysis includes various cost components such as the energy costs, operation, maintenance, fixed charges on capital investment and so forth. The total capital investment and total cost of a Cu-Cl pilot plant are estimated by scaling against the corresponding costs of an S-I plant. The fixed capital investment and product cost for the Cu-Cl pilot plant are evaluated to be US $27.5 and US $4.6M for a plant daily capacity of 5 tons of hydrogen. A six-tenths-factor rule, which is a scaling method, is used throughout the analysis. The sensitivity of cost with plant capacity, capacity factor and percentages of each cost component are also assessed.

Ferrandon et al. (2008) carry out a cost analysis using the hydrogen analysis (H2A) methodology. Capcost software is used to estimate capital and operating costs of the hydrogen production plant. Cost analysis is assessed assuming a daily hydrogen plant capacity of 125 tons. The capital investment in the electrolyzer is calculated to be $69.7 M, and total capital investment is $131 M. Considering other factors affecting cost (e.g. labor cost), the estimated cost of hydrogen is $3.30/kg.

Naterer et al. (2008a) present cost comparison of different hydrogen production methods namely off-peak electrolysis, steam methane reforming and thermochemical copper-chlorine plant. Scaling factor of 0.66 is used to estimate the cost of hydrogen.
produced using the Cu-Cl thermochemical cycle for various production capacities (2, 10, 50 and 200 tons/day). The results indicate that the cost of hydrogen is $2.00/kg for a capacity of 200 tons per day, and $2.24, $2.71, $3.49/ kg hydrogen for daily plant capacity of 50, 10 and 2 tons, respectively.

### 3.2.8 Exergoeconomic Analysis

Orhan et al. (2010a) investigated how exergy-related parameters can be used to reduce the cost of a copper-chlorine (Cu-Cl) thermochemical cycle for hydrogen production. Specific exergy cost (SPECO) method is used in the study to conduct exergoeconomic analysis. The results showed that the effect of exergy efficiency on the cost of hydrogen is very high in the efficiency range of 5-30% and very low in the efficiency range of 30-60%. The hydrogen cost approaches its lowest and becomes roughly constant above an exergy efficiency of 60%.

An exergoeconomic assessment of the Cu-Cl thermochemical cycle using exergy-cost-energy-mass (EXCEM) analysis is described by Orhan et al. (2010b). Exergetic cost allocations and various exergoeconomic performance parameters are determined for the overall cycle and its components. Exergy and cost are the only EXCEM quantities that are not subject to conservation laws. Exergy enters at the inlet at the rate of 0.151 GW and exit at the rate of 0.068 GW, since the remaining exergy is destroyed in the cycle and/or lost to the environment. The situation is reversed for cost. The cost flow rate at the inlet of the cycle is 0.893 $/kg while it is 2.24 $/kg at the outlet of the cycle, because 1.347 $/kg is generated within the cycle.

Exergoeconomic analysis is performed to four-step Cu-Cl cycle linked with geothermal energy using EXCEM method by Balta et al. (2011). The energy and exergy efficiencies are calculated to be 49% and 54%, respectively. The cost flow rates at the inlet and exit of the cycle are 0.51 $/kg and 2.046 $/kg, respectively. Because, 1.54 $/kg cost is generated within the cycle. The ratio of thermodynamic loss rate to capital cost varies between 0.004 and 0.012 (GJ/$) for the various hydrogen production capacities.

### 3.2.9 Life Cycle Assessment

Lubis et al. (2010) present a preliminary LCA for hydrogen production using nuclear energy, based on the Cu-Cl thermochemical cycle. The results are presented in terms of
CML 2001 impact categories and show that the GWP of the system over its lifetime is 0.0025 g CO$_2$ eq, and that major contributors to the GWP are construction of nuclear and hydrogen plants.

Ozbilen et al. (2011a) conduct a preliminary environmental impact assessment using LCA for the five-step Cu-Cl cycle and compared with other hydrogen production methods: the sulphur-iodine (S-I) thermochemical cycle, high temperature water electrolysis, steam reforming of natural gas and electrolysis using renewable sources. The results, which are presented with respect to GWP, AP and Eco-indicator weighting factor, indicate that the thermochemical cycles have lower environmental impacts while steam reforming of natural gas has the highest.

The variations of environmental impacts with lifetime and production capacity are reported for nuclear based hydrogen production plants using the three-, four- and five-step (copper-chlorine) Cu-Cl thermochemical water decomposition cycles by Ozbilen et al. (2011b). The LCA is performed using GaBi 4 environmental impact assessment software. The parametric studies show that increasing plant hydrogen production capacity and lifetime does not significantly affect the values of the impact categories per kg hydrogen production, if the capacities and lifetimes are sufficiently great. The parametric studies also indicate that APs and GWPs for the four-step Cu-Cl can be reduced from 0.0031 to 0.0028 kg SO$_2$-eq and from 0.63 to 0.55 kg CO$_2$-eq, if the lifetime increases from 10 years to 100 years.

The environmental impacts of nuclear based hydrogen production via thermochemical water splitting using the Cu-Cl cycle are quantified and described using life cycle analysis by Ozbilen et al. (2012b). The LCAs for the three-, four- and five-step Cu-Cl cycles consider four scenarios, which relate to electrical power distribution. Multiple scenarios are considered to account for possible future Cu-Cl cycle designs using GaBi 4 LCA software. The results are presented in seven impact categories defined by CML, including global warming potential, and show that negative impacts can be associated with hydrogen production, depending on its source, even though hydrogen is a clean energy carrier. The four-step Cu-Cl cycle linked with a Generation IV SCWR, which supplies all electricity requirements for the production processes, is seen to have the lowest environmental impact due to its lower thermal energy requirement. If electrical
energy output of the nuclear plant is used for all processes in nuclear-based hydrogen production, the GWP can be decreased from an initial value 15.8 kg to 0.56 kg CO₂-eq. The four-step Cu-Cl thermochemical water splitting cycle exhibits lower environmental impacts compared to the three- and five-step cycles. The primary contributors to environmental impact categories are observed to be fuel processing, especially mining and conversion due to the fossil fuel use in these processes, and nuclear plant utilization.

### 3.2.10 Exergetic Life Cycle Assessment

ExLCA is applied with life cycle assessment (LCA) to the five-step Cu-Cl hydrogen production process by Ozbilen et al. (2012c). LCA, which is an analytical tool to identify, quantify and decrease the overall environmental impact of a system or a product, is extended to ExLCA. Exergy efficiencies and air pollution emissions are evaluated for all process steps, including the uranium processing, nuclear and hydrogen production plants. LCA results for one megajoule exergy of produced hydrogen are presented in four categories: acidification potential, eutrophication potential, global warming potential and ozone depletion potential. A parametric study is performed for various plant lifetimes. Variation of environmental impacts (GWP and AP) with exergy efficiency of the five-step Cu-Cl cycle is also investigated. The ExLCA results indicate that the greatest irreversibility is caused by uranium processing. The primary contributor of the life cycle irreversibility of the nuclear-based hydrogen production process is fuel (uranium) processing, for which the exergy efficiency is 26.7% and the exergy destruction is 2916.3 MJ/ kg hydrogen. The lowest global warming potential per megajoule exergy of hydrogen is 5.65 g CO₂-eq achieved a plant capacity of 125,000 kg H₂/day. The corresponding value for a plant capacity of 62,500 kg H₂/day is 5.75 g CO₂-eq.

### 3.2.11 Exergoenvironmental Analysis

Currently, the only study that relates thermodynamics to environmental impacts for the Cu-Cl cycle is reported by Ozbilen et al. (2012c) through an exergetic life cycle assessment (ExLCA). There is no study in the literature that performs an exergoenvironmental analysis to the Cu-Cl cycle.
3.2.12 Studies on Individual Reactions

This section presents studies on individual reactions of the Cu-Cl cycle: hydrolysis, copper oxychloride decomposition, drying of cupric chloride and hydrogen reaction.

Hydrolysis

Ferrandon et al. (2008) model the hydrolysis reactor with Aspen Plus with a feed of 100 kmol/hr of CuCl$_2$ and various amounts of water. A steam-to-copper ratio of 17 is needed in order to achieve maximum yield of 50 mol of Cu$_2$OCl$_2$ below 400°C. It is concluded that during the hydrolysis, high yields of Cu$_2$OCl$_2$ can be achieved, up to 89wt%, however at high steam/Cu ratio and at the expense of undesired CuCl formation. The formation of undesired CuCl is reduced less than 1% at a low steam/Cu ratio of 10 when using ball milled CuCl$_2$•2H$_2$O at low flow total flow rate for a reaction temperature of 375°C and a reaction time of 30 min. However, at that condition, the amount of Cu$_2$OCl$_2$ appears to be very low. A reactor system that sprays a fine mist of a CuCl$_2$ solution into a hot zone, followed by rapid quenching is suggested to improve mass transfer between steam and CuCl$_2$ while inhibiting the decomposition into CuCl.

Haseli et al. (2008) focus on the transport phenomena for the hydrolysis reaction. Volumetric model (VM) and shrinking core model (SCM) are considered as limiting cases due to lack of experimental data regarding hydrodynamics and chemistry of the reaction to define the kinetics of the particle reaction. The results indicate that for both VM and SCM cases, the conversion of steam decreases with superficial velocity, whereas the conversion of solid particles increases. Moreover, a higher bed inventory leads to higher conversion of both reactants.

The Argonne National Laboratory designs a spray reactor where an aqueous solution of CuCl$_2$ is atomized into a heated zone, into which steam/Ar are injected in co- or counter-current flow (Ferrandon et al., 2010a). Investigation includes two types of atomizers: a pneumatic nebulizer and an ultrasonic nozzle. With a pneumatic nebulizer, the counter-current flow design gave high yields of Cu$_2$OCl$_2$ compared to co-current design, some CuCl$_2$, however, remained unreacted in both designs. High yields of Cu$_2$OCl$_2$, up to 95% with a small amount of CuCl is achieved using steam/Cu ratio of 24
with ultrasonic nozzle and co-current flow. The desired HCl is achieved at a reaction temperature of 390°C while no Cl₂ is detected until the bed temperature is above 400°C.

Ferrandon et al. (2010b) report the favourable effect of reduced pressure in the hydrolysis reaction. An experimental setup is modified to allow CuCl₂ hydrolysis in the pressure range of 0.4-1 atm. The experiment results show that a decrease in the reactor pressure results in less formation of CuCl and shifts the maximum formation of Cu₂OCl₂ from a steam to copper molar ration of from near 20 (for 1 atm) to approximately 15 (for 0.4-0.7 atm). The reduced ratio allows a decrease in excess steam without an increase in undesired CuCl concentration; the lower amount of water needed for the hydrolysis reaction decreases the amount of energy input to the Cu-Cl cycle.

**Copper Oxychloride Decomposition**

Serban et al. (2004) study the reaction kinetics for the oxygen production step for the four-step Cu-Cl cycle (Option I). The results show that the yield to O₂ is 85% at 500°C and the reaction is virtually complete at 530°C. The XRD of the solid product indicates that the solid phase is pure CuCl.

Naterer et al. (2008b) study the oxygen production reactor with respect to several issues: thermal design, supply of copper oxy chloride particles, processing of molten salt from the reactor, processing of other byproducts. The equipment design is analyzed to scale-up past work in small proof-of-principle test tubes, up to larger capacities of oxygen production with engineering lab-scale equipment.

**Drying of Cupric Chloride**

Daggupati et al. (2008) study evaporative spray drying of cupric chloride. It is stated in the study that the droplet evaporation and drying time depend on the droplet size, air velocity, air temperature, air humidity and operating pressure. In the analysis, the following ranges of variables are examined: Droplet size: 10-5000 μm, inlet air humidity: 0.0025-0.015 kg water/kg dry air, air temperature: 35-70°C, air velocity: 0.5-4 m/s, operating pressure: 0.5-1 atm. The results show that the drying time rises with an increase in droplet size, inlet air humidity and operating pressure, while it decreases with an increase in air temperature and air velocity.
Naterer et al. (2008c) examine the evaporative spray drying and conclude that benefits of flashing the solution to enhance drying are relatively minor, compared to rate of evaporative drying in the process. The volume of the dryer decreases rapidly at higher temperatures due to increased convective heat transfer rate. The inlet temperature must be as high as possible and the temperature difference between inlet and outlet air must as small as possible in order to minimize moisture content of the final product. Finally, the evaporative drying is possible down to low temperatures (as low as 35°C) at low operating pressures of 0.5 atm, although such low-temperature drying may limit the product quality and throughput.

**Hydrogen Reaction**
Serban et al. (2004) study the reaction kinetics also for the hydrogen production reactions for the four-step Cu-Cl cycle (Option I). It is stated that the reaction proceeds rapidly at 230°C, the temperature at which 93% of HCl is decomposed, but no hydrogen is detected at this temperature. Hydrogen starts to be produced in significant amounts at temperatures above 350°C. Furthermore, the kinetics of the reaction are accelerated at temperatures higher than 430°C, the temperature at which CuCl melts, facilitating the interaction between HCl and Cu. The experiment results also indicate that the conversion of HCl to hydrogen is a function of Cu particles. The hydrogen yields are 65% and 100% for the copper particle sizes of 100-μm and 3-μm, respectively.

The reaction kinetics of the hydrogen production step is analyzed by Zamfirescu et al. (2010a). The effects of particle size, temperature and molar ratios on reaction kinetics are investigated. The results show that (i) the residence time of copper particles varies between 10 and 100s, depending on the operating condition, (ii) the hydrogen conversion at equilibrium varies between 55 and 85%, depending on the reaction temperature. The particle temperature can increase by up to 200°C during the exothermic reaction.

**3.2.13 Other Issues**
Various conceptual steam-cycle arrangements of pressure-channel SCWRs operating at higher temperatures are discussed with major parameters of the copper-chlorine cycle for the cogeneration of hydrogen by Naidin et al. (2009). Thermal efficiencies for the SCWR
are calculated to be 46, 48 and 49% for no-reheat, single-reheat and the double-reheat cycles respectively.

Zhang et al. (2008a and 2008b) discuss potential safety and reliability issues associated with the hydrogen plant using Cu-Cl cycle. Using a flowsheet of the hydrogen plant created by an Aspen Plus simulation by ANL, four fault-trees are constructed for potential risk scenarios. Based on the results from the fault tree analyses, the risk levels of the hydrogen generation plant under different accident scenarios can be calculated. Potential problems encountered in Cu-Cl cycle are identified based on the results and possible solutions are recommended for future improvements.

Thermodynamic properties of the Cu-Cl compounds at elevated temperatures, including the specific heat, enthalpy and thermal conductivity were examined by Avsec and Naterer (2008). Changes in the thermodynamic properties of cupric chloride during its phase changes (solid-solid and solid-liquid) are discussed. Analytical models are also developed to determine the thermophysical properties of CuCl and HCl in the liquid and gas regions.

The study of Zamfirescu et al. (2010b) identifies the available experimental data for the properties of copper compounds relevant to the Cu-Cl cycle analysis and design. The properties are evaluated at 1 atm and a range of temperatures from ambient to 675-1000 K which are consistent with the operating conditions of the cycle. Chemical exergies for Cu₂OCl₂, CuO, CuCl₂ and CuCl are updated as 21.08, 6.268, 82.474 and 75.0 kJ/mol, respectively. The estimated viscosity for the molten CuCl is evaluated to be 1.7 to 2.6 mPas.

3.3 Main Gaps in the Literature
This section explains the main gaps in the present state of knowledge and how this research addresses these shortcomings. The first main gap is identified as a realistic simulation of the four-step Cu-Cl cycle. Previous Aspen Plus models in the literature use stoichiometric reactions either for all main reactors (hydrolysis, copper oxychloride decomposition, electrolysis, dryer) or at least one of them (Chukwu, 2008), or are for other multi-step Cu-Cl cycles (three-step and five-step Cu-Cl cycles) (Ferrandon et al., 2008; Orhan et al., 2012), or have very high steam to copper molar ratio (>20) in
hydrolysis step (Orhan 2011, Orhan et al., 2012). In this regard, a novel Cu-Cl design with reduced excess steam requirement modelled using Aspen Plus is proposed in this thesis.

Second, a component level exergoeconomic analysis, which combines exergy analysis and economic principles and designs and/or operates a cost-effective system, of the four-step Cu-Cl cycle is not performed. Previous exergoeconomic studies on the Cu-Cl cycle examine different configurations of the Cu-Cl cycle, use data based on the stoichiometric reactions and perform an overall system analysis (A black box approach) rather than a component level analysis (Balta et al., 2010; Orhan et al. 2010a; Orhan et al., 2010b). Hence, a component level exergoeconomic analysis is performed and multi-objective optimization with respect to exergy and cost is conducted in this research.

There is also no study in the literature that analyzes the Cu-Cl cycle with respect to exergy and environment via an exergoenvironmental analysis. Therefore, an exergoenvironmental analysis is conducted for the four-step Cu-Cl cycle, which is the optimized with respect to exergy and environmental impact.

Last, there are limited studies on the integration of the Cu-Cl cycle with other thermodynamic systems (Jaber et al., 2010a; Balta et al., 2010; Aghahosseini et al., 2011; Ghandehariun et al., 2010; Wang et al., 2011). In this regard, Cu-Cl based multi-generation systems are developed and analyzed in order to increase overall efficiency while reducing wastes and associated environmental impacts.
CHAPTER 4: SYSTEM DESCRIPTION AND DEVELOPMENT

Hydrogen production via thermochemical water splitting using the Cu-Cl cycle is a promising alternative to conventional hydrogen production methods. Multi-generation systems are often attractive due to their higher energy and exergy efficiencies compared to individual cycles (e.g. steam or gas turbine cycles). An increase in efficiency often allows, for the same output, less resources (or exergy) to be used. This, in return, reduces the extraction from the environment of energy resources (e.g., fossil fuels), and decreases the associated environmental impacts. This chapter presents the description of the four-step Cu-Cl cycle and three novel Cu-Cl based integrated systems and their sub-units. Each system produces hydrogen using the Cu-Cl thermochemical cycle, stores it and converts it to electricity when needed. Energy management using energy storage is very important considering the increased number of renewable plants with intermittent characteristics.

4.1 The Four-Step Cu-Cl Cycle

This research focuses on the four-step Cu-Cl thermochemical cycle, which is currently under experimental investigation in the Clean Energy Research Lab at UOIT. The four-step Cu-Cl cycle (Figure 4.1) consists of four main sections: hydrolysis, copper oxychloride decomposition, electrolysis and dryer as follows:

- Step 1 (Hydrolysis step at 370-400°C):
  \[ \text{CuCl}_2 (s) + \text{H}_2\text{O} (g) \rightarrow \text{Cu}_2\text{OCl}_2 (s) + 2\text{HCl} (g) \]  
  (4.1)

- Step 2 (Copper oxychloride decomposition at 500-550°C):
  \[ \text{Cu}_2\text{OCl}_2 (s) \rightarrow 2\text{CuCl} (s) + \frac{1}{2} \text{O}_2 (g) \]  
  (4.2)

- Step 3 (Hydrogen production step at 25-100°C):
  \[ 2\text{HCl} (aq) + 2\text{CuCl} (aq) \rightarrow \text{H}_2 (g) + \text{CuCl}_2 (aq) \]  
  (4.3)

- Step 4 (Drying step at 80-100°C):
  \[ \text{CuCl}_2 (aq) \rightarrow \text{H}_2\text{O} (g) + \text{CuCl}_2 (s) \]  
  (4.4)
The water splitting process begins in the hydrolysis reactor where steam reacts with solid cupric chloride particles to form solid copper oxychloride and hydrochloric gas. The exiting copper oxychloride then decomposes into oxygen gas and molten cuprous chloride in the decomposition reactor. Solidified cuprous chloride is dissolved in the condensed hydrochloric gas from the hydrolysis reactor to release hydrogen gas in the CuCl/HCl electrolyzer. The exiting aqueous cupric chloride is then transferred to the drying section to form solid particles for the hydrolysis reactor. Figures 4.2-4.6 demonstrate the process in the individual reactors.

**Figure 4.1: Conceptual schematic of the four-step Cu-Cl cycle.**

In the hydrolysis reactor (Figure 4.2), heated CuCl$_2$ stream is sprayed into the superheated steam environment, where it forms a free jet. The free jet spray expands the CuCl$_2$ and aspirates the superheated steam into the jet, which results in high mass and heat transfer between the CuCl$_2$ in the jet and the steam, producing HCl and Cu$_2$OCl$_2$. HCl and the excess steam exit the reactor in order to be cooled and fed into the electrolysis reactor. Solid Cu$_2$OCl$_2$ particles accumulated at the bottom of the reactor, flow by gravity to the copper oxchloride decomposition reactor (Figure 4.3). Cu$_2$OCl$_2$ particles are heated first to the reactor temperature (500-550°C), where it decomposes to
molten CuCl and oxygen. The oxygen leaves the reactor as a gas, and molten CuCl is fed to the electrolyzer.

![Diagram](image)

**Figure 4.2: Hydrolysis reactor of the four-step Cu-Cl cycle (Adapted from Ferrandon et al., 2008).**

The electrolysis of CuCl/HCl is shown in Figure 4.4. The molten CuCl from the copper oxyclore decomposition reactor changes phase to a solid c phase when it is cooled down to electrolysis temperature. The feed water with solid CuCl is then pumped to the electrolyzer pressure and fed to the anode section of the electrolyzer. The aqueous HCl is also pumped to electrolyzer pressure. The chloride ions migrate from cathode to anode, where it reacts with CuCl and forms CuCl₂. The H⁺ ion is reduced to H₂ at the cathode. CuCl₂ and water is then transferred to the dryer. Figure 4.5 demonstrates the fourth main process of the four-step Cu-Cl cycle, in which the aqueous CuCl₂ is dried to CuCl₂.2W (CuCl₂ + 2H₂O). The spray drying involves evaporation of moisture from an atomized feed by mixing the spray and the drying medium.
Figure 4.3: Copper oxychloride decomposition reactor of the four-step Cu-Cl cycle (Adapted from Ferrandon et al., 2008).

Figure 4.4: Electrolyzer of the four-step Cu-Cl cycle (Adapted from Ferrandon et al., 2008).
4.2 Cu-Cl Based Multi-generation Systems

All three systems discussed in this chapter produce hydrogen as the main output. Product hydrogen is considered to be exported as a commodity for industry and/or as a fuel. All systems also have the capability of hydrogen storage for energy management. Thus, the produced hydrogen is always a product; and when energy management is needed, a part of it is stored and converted to electricity using fuel cells. Oxygen as a product of the Cu-Cl cycle is also treated as a byproduct which is sufficiently pure for use or sale (Naterer et al., 2008a). All the systems also have the capability of generating electricity and providing cooling, hot water and drying air.

LiBr-H$_2$O absorption cooling system is considered in the study for all three systems which uses the excess energy of solar/nuclear heat transfer fluid to obtain the cooling effect. The absorption cooling system (ACS) is used instead of a conventional compression cooling system to utilize surplus heat. Hot water at 42°C is supplied to the community by the integrated system. Also, drying air is obtained by heating ambient air to drying temperature (50°C) using excess heat of the exhaust gases. Drying air can be used in many applications, mainly drying fruits and vegetables.
4.2.1 System I – Cu-Cl Based Multi-generation System Using Solar Energy

Solar thermal energy, concentrated using heliostat solar tower, is the energy source of the System I (Figure 4.6). Molten salt is considered as a heat transfer fluid (HTF) to supply heat to the Cu-Cl cycle. Molten salt has an advantage in that the solar heat can be stored for tens of hours for use at night, or when sunlight is not available (Wang et al., 2011). Initially, heat is supplied to the copper oxychloride (Cu₂OCl₂) to increase the temperature from 390°C to 530°C. Then, the heat is transferred to the decomposition step (step 2) which has the highest temperature heat requirement (530°C) in the cycle. Finally, heat is supplied to the cupric chloride (CuCl₂). Heat requirement of hydrolysis and drying step is managed via thermal management within the cycle (further details on thermal management are available in Section 6.1.3). The temperature of the molten salt in a low temperature storage tank is higher than 250°C which is about 30°C higher than the melting point of the molten salt. A hydrogen storage tank and fuel cell unit is also integrated to the Cu-Cl cycle for energy management. Energy management with hydrogen storage option is promising, since hydrogen can be converted to electricity efficiently via fuel cells during peak hours.

System I also comprises of a steam turbine cycle, which has a low pressure and a high pressure steam turbine, and a LiBr-H₂O ACS. The steam turbine cycle and absorption system utilize the solar energy. Figure 4.6 shows the system diagram, and Table 4.1 presents the flows in the system. The water streams in Table 4.1 are differentiated in terms of their use as follows:

- 13-30: H₂O is working fluid of the STC.
- 37-40: H₂O is working fluid of the ACS.
- 41-44: H₂O is for heat rejection from ACS.
- 47-49: H₂O is used in hot water production.
- 50: H₂O is feed to the Cu-Cl cycle.
Figure 4.6: Schematic diagram of System I.

Table 4.1: Material flows in System I.

<table>
<thead>
<tr>
<th>Sub-unit</th>
<th>Solar tower</th>
<th>Steam Turbine Cycle (STC)</th>
<th>Absorption Cooling system (ACS)</th>
<th>Drying air</th>
<th>Hot water</th>
<th>Cu-Cl cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream number</td>
<td>1-12</td>
<td>13-30</td>
<td>31-36</td>
<td>37-40</td>
<td>41-44</td>
<td>45-46</td>
</tr>
<tr>
<td>Stream material</td>
<td>Molten salt</td>
<td>H₂O</td>
<td>LiBr-H₂O</td>
<td>H₂O</td>
<td>H₂O</td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂O</td>
<td>H₂O</td>
<td>O₂</td>
</tr>
</tbody>
</table>
4.2.2 System II – Cu-Cl Based Multi-generation System Using Nuclear Energy

The second Cu-Cl based integrated system considered here utilizes nuclear power. As mentioned earlier, the SCWR is a suitable match for the Cu-Cl cycle. The HTF can be both water and molten salt in this case. Unlike solar based systems, nuclear power does not have intermittent characteristics. Nuclear plant can continuously supply heat to the Cu-Cl cycle using water as the HTF. Thus, molten salt is not a must for 24h per day hydrogen production using the Cu-Cl thermochemical cycle which is linked with nuclear power plants. The coolant (water) inlet and exit temperatures are defined as 350 and 625°C, respectively. Also, the coolant pressure and mass flow rate are 25 MPa and 1320 kg/s (Pioro and Duffey, 2007). The LiBr-H₂O ACS is also introduced to provide cooling, therefore, there are multiple outputs in System II. A hydrogen storage and fuel cell unit are also used in System II. Figure 4.2 shows the system diagram, and Table 4.2 presents the flows in the system. Similarly, the water streams in Table 4.2 are differentiated in terms of their use as follows:

- 1-6: H₂O is heat transfer fluid.
- 13-16: H₂O is working fluid of the ACS.
- 17-20: H₂O is for heat rejection from ACS.
- 23-25: H₂O is used in hot water production.
- 26: H₂O is feed to the Cu-Cl cycle.

Table 4.2: Material flows in System II.

<table>
<thead>
<tr>
<th>Sub-unit</th>
<th>Nuclear HTF</th>
<th>Absorption cooling system (ACS)</th>
<th>Drying air</th>
<th>Hot water</th>
<th>Cu-Cl cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream number</td>
<td>1-6</td>
<td>7-12</td>
<td>13-16</td>
<td>17-20</td>
<td>21-22</td>
</tr>
<tr>
<td>Stream material</td>
<td>H₂O</td>
<td>LiBr-H₂O</td>
<td>H₂O</td>
<td>H₂O</td>
<td>Air</td>
</tr>
</tbody>
</table>
Figure 4.7: Schematic diagram of System II.

4.2.3 System III – Cu-Cl Based Multi-generation System Using Solar Energy and Natural Gas

The third system considered here is developed to produce electricity, hydrogen, and cooling. Hot water, drying air and oxygen are also by-products of the system. The main sub-units of the system are the Cu-Cl cycle, heliostat solar thermal tower, steam turbine cycle, gas turbine cycle and LiBr-H₂O absorption cooling system. Fossil fuel is added to System III for the use in the combustion chamber of the gas turbine unit. Fossil fuel usage differentiates System III from other systems considered in this chapter. Although it is a disadvantage from an environmental point of view, the purpose of adding fossil fuel is to integrate the gas turbine cycle into the system and to investigate the change in energy and exergy efficiencies.

The steam turbine cycle considered here is a dual turbine system (i.e. high pressure and low pressure). Thermal energy of the exhaust gas from the gas turbine cycle
is utilized to run the steam turbine cycle. In this integrated system, portion of electricity produced is transferred to the Cu-Cl cycle for its electrical work requirement.

The gas turbine unit (GTU) considered here has two compressors, one intercooler unit, preheating unit combustion chamber and turbine. Fuel (i.e. natural gas) is supplied to the combustion chamber of the gas turbine cycle; thermal energy of molten salt is also utilized in the regenerator of the GTU. Figure 4.8 shows the system diagram, and Table 4.3 presents the flows in the system. The water streams in Table 4.1 are differentiated in terms of their use as follows:

- 13-30: \( \text{H}_2\text{O} \) is working fluid of the STC.
- 37-40: \( \text{H}_2\text{O} \) is working fluid of the ACS.
- 41-44: \( \text{H}_2\text{O} \) is for heat rejection from ACS.
- 47-51: \( \text{H}_2\text{O} \) is used in hot water production.
- 62: \( \text{H}_2\text{O} \) is feed to the Cu-Cl cycle.
Table 4.3: Material flows in System III.

<table>
<thead>
<tr>
<th>Sub-unit</th>
<th>Solar tower</th>
<th>STC</th>
<th>ACS</th>
<th>Drying air</th>
<th>Hot water</th>
<th>GTC</th>
<th>Cu-Cl cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream number</td>
<td>1-12</td>
<td>13-30</td>
<td>31-36</td>
<td>37-40</td>
<td>41-44</td>
<td>45-46</td>
<td>47-51</td>
</tr>
<tr>
<td>Stream material</td>
<td>Molten salt</td>
<td>H₂O</td>
<td>LiBr-H₂O</td>
<td>H₂O</td>
<td>H₂O</td>
<td>Air</td>
<td>H₂O</td>
</tr>
</tbody>
</table>

Figure 4.8: Schematic diagram of System III.
CHAPTER 5: SIMULATION FRAMEWORK AND METHODOLOGY

The Cu-Cl thermochemical water splitting cycle is modelled in Aspen Plus software initially in order to perform energy, environmental and economic analyses using exergy, life cycle assessment, exergetic life cycle assessment, exerгоenvironmental analysis and exergoeconomic analysis tools. Thermodynamic analysis of the integrated systems is conducted based on the energy requirements of the Cu-Cl cycle, which is evaluated using Aspen Plus.

Aspen Plus is a process simulator that predicts the behaviour of chemical reactions and steps using standard engineering relationships, such as mass, energy and entropy balances, rate correlations, as well as phase and chemical equilibrium data. By choosing the appropriate unit operations and thermodynamic models, reliable thermodynamic data and realistic operating conditions, Aspen Plus uses mathematical models to predict the performance of the cycle and simulated plant behaviour. A successful simulation can be carried out performing the following steps in Aspen Plus (Chukwu, 2008; Orhan, 2011):

- Selecting and defining unit operation models for the simulation and placing them onto the flow sheet. This includes labeling the unit blocks from the Aspen Plus library, including user defined blocks.

- Linking the unit operations together using labeled streams. All material and energy streams must be identified, including the input and output streams.

- Specifying the global setup. This includes units of measurement, run type, input, mode, flow conditions, and so forth.

- Specifying all components that are involved in the process. This can be performed from the Aspen Plus component database, and non-database components.
• Specifying thermodynamic models for all unit blocks to represent the physical properties of the components and mixtures in the process, including properties that are not given in the Aspen Plus database.

• Specifying flow rate and thermodynamic conditions of all feed streams.

• Specifying the operating conditions of all unit operations.

• Performing the simulation; normal, automatic, troubleshooting, or on-demand case.

• Performing model analyses, flowsheeting options, or calculator blocks for sensitivity analyses.

Component modeling and system modeling are two levels of modeling. In the first stage, a detailed modeling of individual components in the Cu-Cl cycle is presented. A detailed comparative literature review is carried out to find most suitable and reliable models for the components. Second, thermal model of the overall Cu-Cl cycle is developed.

Using Aspen Plus, a new design for the Cu-Cl cycle is analyzed and discussed. Then, for selected configuration, exergy analysis is applied to calculate the exergy destructions within the system and exergy losses to the environment. Performance assessment parameters related to energy and exergy analyses are calculated. Numerical simulations are performed to determine whether steam requirement can be reduced by operating the hydrolysis reactor at partial pressure and/or by partial condensation of the effluent steam. The system level design continues with exergoeconomic and exergoenvironmental analyses. Hence, according to the results of system level design, conclusions are drawn for the most feasible configuration.

5.1 Simulation Framework

This section provides information regarding the unit operation models and the property methods used in Aspen Plus for simulation of the Cu-Cl cycle. Detailed explanations on those are presented in Appendix A. The definitions and explanations presented in Section
5.1 are adopted from the following sources: Aspen Tech (2010); Chukwu (2008); Nyoni (2011) and Orhan (2011).

5.1.1 Unit Operation Model Types
In the Aspen Plus simulation package, unit operation models are used to represent actual pieces of equipment, such as heat exchangers, pumps and distillation columns. These unit operation models perform specific functions based on feed input, thermodynamic models and operating conditions. Blocks used in the simulation are described below.

5.1.1.1 Reactors
Balanced based, equilibrium based and kinetics based reactors are three main group of reactor blocks in the Aspen Plus. Balanced based reactors are RYield (yield reactor) and RStoic (stoichiometric reactor), equilibrium based reactors are REquil (equilibrium reactor) and RGibbs (Gibbs reactor), and kinetics based reactors are RCSTR (continuous stirred tank reactor), RPlug (plug flow reactor) and RBatch (batch reactor). RGibbs and RStoic reactors are used in the simulation.

The RGibbs model uses Gibbs free energy minimization, and useful when reactions occurring are not known. This model does not require reaction stoichiometry. RGibbs can determine phase equilibrium without chemical reaction. It is the only reactor that deals with solid-liquid-gas phase equilibrium.

The RStoic model requires both an atom and mass balance. It is used in situations where both the equilibrium data and the kinetics are either unknown or unimportant. It can specify or calculate heat of reaction at a reference temperature and pressure. Details regarding remaining reactors are given in Appendix A.

5.1.1.2 Heat Exchangers
Heat exchangers determine the thermal and phase conditions of a mixture with one or more inlet streams. The heat exchanger models simulate the performance of heaters or two or multi stream heat exchangers. Heater (heater or cooler), HeatX (two-stream heat exchanger), MHeatX (multistream heat exchanger) and HXFlux (heat transfer calculations block) are the heat exchangers blocks available.
Heater can be used to represent heaters, coolers, valves, pumps and compressors (when work-related results are not required). The heater block mixes any number of inlet streams to produce a single outlet stream. Heat duty of the block is calculated when the outlet stream conditions are specified. Details regarding other heat exchanger blocks are given in Appendix A.

5.1.1.2 Pressure Changers
These unit operation models are used to change pressure of streams. Pump (pump or hydraulic turbine), Compr (compressor or turbine), MCompr (multi-stage compressor turbine), Valve (control valve), Pipe (single-segment pipe) and Pipeline (multi-segment pipe) are the blocks in this section.

The Pump block is used to simulate pumps and hydraulic turbines. Power requirement is either calculated or inputted. Pump is designed to handle a single liquid phase.

The Compr block is used to simulate a polytropic compressor, polytropic positive displacement compressor, isentropic compressor, and isentropic turbine. Compr calculates either the power requirement given an outlet pressure specification, or the outlet pressure given a power specification. Details regarding remaining pressure changers are given in Appendix A.

5.1.1.3 Mixers and Splitters
Mixer (stream mixer), FSplit (stream splitter) and SSplit (Substream splitter) are the blocks in this section. Mixer combines material, heat or work streams into a single stream. A single mixer block, however, cannot mix streams of different kinds (such as material and heat). Details of splitters are given in Appendix A.

5.1.1.4 Separators
Flash models, separator models and decanter are the separator blocks. Flash2 (two-outlet flash) and Flash 3 (three outlet flash) are the flash models. Sep (multi-outlet component separator) and Sep2 (two-outlet component separator) are separator type blocks. Decanter block is a liquid-liquid decanter.
Sep and Sep2 combine feed streams and then split the resulting stream, based on user defined specifications. Flash2 performs rigorous 2 or 3 phase equilibrium calculations; produces one vapor outlet stream, one liquid outlet stream and optional water decant stream. Flash2 can be used to model flashes, evaporators, knock-out drums, and any other single-stage separators, with sufficient vapor disengagement space. A percentage of the liquid phase can also be specified to be entrained in the vapor stream.

5.1.2 Property Methods
The physical property methods in the Aspen Plus package are categorized into (i) equation of state, (ii) activity coefficient models, and (iii) special models.

5.1.2.1 Equation of State Method
Equations of state describe a relationship between pressure, volume, and temperature of pure components and/or mixtures. Equations of state are good for vapor phase modelling and liquids of low polarity, limited in ability to represent non-ideal liquids, and consistent in the critical region. Peng Robinson and Redlich-Kwong are available methods in Aspen Plus.

5.1.2.2 Activity Coefficient Method
Activity coefficient models are good for liquid phase modelling and can represent highly non-ideal liquids but they are inconsistent in the critical region. Wilson, NRTL and ELECNRTL are some examples of the activity coefficient methods.

ELECNRTL model is the most flexible electrolyte property method. It involves the description of the ionic interactions along with pure component and pair-wise parameters for the ionic and non-ionic components. It can handle a wide range of concentrations of aqueous and mixed solvent systems with a single pair of binary systems.

ELECNRTL method has proved to be very successful in representing thermodynamic properties of electrolyte solutions. The ELECNRTL model is fully in agreement with the NRTL for liquid phase property calculation and uses the Redlich Kwong property method for vapor phase calculations.
5.1.2.3 Special Methods
AMIINES (Kent-Eisenberg amines model), STEAM-TA (ASME steam table correlations) and STEAMNBS (NBS/NRC steam table equation of state) are some examples of the property methods for special systems.

5.1.2.3 Property Method Selection for the Simulation
It is important to select a proper property method for a system because each property method is suitable for a certain group of components and a range of conditions, and a poor choice of a property method can lead to unreliable simulation results (Seader et al., 2006).

The Cu-Cl thermochemical cycle chemical species include strong acid (HCl) that dissociate hence an electrolytic model is essential for accurate and reliable modelling. ELECNRTL physical property method, hence, is selected to represent the Cu-Cl cycle by Aspen Plus. STEAMNBS property method is selected for the process with steam as stream material, such as steam turbine cycle.

5.2 Methodology for Analyses
5.2.1 Energy and Exergy Analyses
Exergy is a quantity that stems from the second law of thermodynamics, and helps in analyzing energy and other systems and processes. The exergy of a system is defined as the maximum shaft work that can be attained when it is in a reference environment that is assumed to be infinite, in equilibrium, and to enclose all other systems. Exergy is not a thermodynamic property, but rather is a property of both a system and the reference environment (Dincer and Rosen, 2007). The reference environment is typically defined by specifying its temperature, pressure and chemical composition.

Exergy analysis is an assessment tool based on exergy in which exergy flows, balances, destructions and efficiencies are determined for an overall process or system and its subparts. Exergy analysis permits many of the shortcomings of energy analysis to be overcome. Exergy analysis is based on the second law of thermodynamics, and is useful in identifying the causes, locations and magnitudes of process inefficiencies. Exergy analysis acknowledges that, although energy cannot be created or destroyed, it
can be degraded in quality, eventually reaching a state in which it is in complete
equilibrium with the surroundings and hence of no further use for performing tasks
(Dincer and Rosen, 2007).

The mass, energy, entropy and exergy balances are required in the first step of the
exergy analysis to determine the heat input/output, entropy generation rate, exergy
destruc\-\ons, and energy and exergy efficiencies. The mass and energy balance equations
for a steady-state condition, which is the case for the Cu-Cl cycle, are defined as follows:
\[
m_{in} = m_{out} \quad (5.1)
\]
\[
E_{in} = E_{out} \quad (5.2)
\]

where \(m\) and \(E\) are associated with mass flow and energy transfer rate, and show
that the respective total rates in/out across the boundary are conserved. The heat transfer
for the chemical processes in the Cu-Cl cycle involving no work interaction \(W\) is
determined from Equation 5.2, and the energy balance reduces to
\[
Q = H_p - H_R = \sum n_p (h_f + h) - \sum n_R (h_f + h) \quad (5.3)
\]

The entropy and exergy balance equations can be written as follows:
\[
\dot{S}_{in} + \dot{S}_{gen} = \dot{S}_{out} \quad (5.4)
\]

where \(\dot{S}_{in}\) and \(\dot{S}_{out}\) are the entropy flow rate of input and output streams, and \(\dot{S}_{gen}\) is the
entropy generation rate. The amount of entropy transferred out of the boundary exceeds
the amount of input entropy due to entropy generation associated with irreversibilities.
\[
\dot{E}_{x_{in}} = \dot{E}_{x_{out}} + \dot{E}_{x_{dest}} \quad (5.5)
\]

where
\[
\dot{E}_{x_{dest}} = T_0 \dot{S}_{gen} \quad (5.6)
\]

Here, \(\dot{E}_{x}\) represents the exergy flow or destruction rate. The amount of exergy transferred
out of the boundary must be less than the input exergy due to exergy destruction within
the process/system. Exergy of a matter flow can be expressed in terms of physical, kinetic
and potential and chemical components.
\[
Ex_{flow} = Ex_{ph} + Ex_{kin} + Ex_{pot} + Ex_{ch} \quad (5.7)
\]
For a chemical process, kinetic and potential term can be neglected, and Equation 5.7 reduces to
\[ \overline{e x} = (\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + \overline{e x}^{ch} \] (5.8)

### 5.2.2 Exergoeconomic Analysis

Exergoeconomic analysis is a crucial tool which combines exergy analysis and economic principles and designs and/or operates a cost-effective system, which is always not possible through a conventional energy and cost analyses (Tsatsoronis and Moran, 1997).

In the analysis and design of energy systems, techniques that combine scientific disciplines (mainly thermodynamics) with economic disciplines (mainly cost accounting) are often used to achieve optimum designs. Conventionally, unit costs based on energy have been considered for cost accounting of energy conversion devices. However, costs are better distributed among outputs based on thermodynamic quantity exergy, which is a more consistent measure of an economic value than energy. In addition, there exist exergy-based economic analysis methodologies such as thermoeconomics and exergoeconomics. Moreover, since the ratio of thermodynamic loss rate to capital cost is one of the most important criteria for analyzing the systems based on a thermoeconomic approach, the correlation between specific second-law based thermodynamic losses (total and internal exergy losses) and capital cost is examined through an exergoeconomic analysis to provide an optimization between the scientific and economic disciplines (Dincer and Rosen, 2007).

A comprehensive exergoeconomic analysis of the Cu-Cl cycle includes (i) a thermodynamic (exergy) analysis, (ii) an economic (cost) analysis, (iii) exergy costing, and (iv) an exergoeconomic evaluation and optimization. The exergy of all streams, exergy destruction rates, and the exergy efficiencies are evaluated for each plant component in the exergy analysis. In an economic analysis, on the other hand, the annual values of carrying charges, fuel costs, raw water costs, and operating and maintenance expenses \( \dot{Z} \) supplied to the overall system are the cost components. Annualized values for all cost components are typically used in the economic analyses, since cost components are subject to change over their economic lives (Orhan et al., 2010a).
Exergoeconomic analysis of the Cu-Cl cycle is conducted with SPECO method. The methodology consists of three main steps (Lazzeretto and Tsatsaronis, 2006):

- Identification of exergy streams: An initial decision must be made with respect to whether the analysis of the components should be performed using total exergy or separate forms of the total exergy of a material system, such as thermal, mechanical and chemical exergies. Then, all exergy flows within the system are identified and the exergy values are calculated.

- Definition of fuel and product: The fuel and product of the system and corresponding exergy values must be well-defined for the analysis.

- Cost equations: Exergoeconomic rests on the notion that exergy is the only rational basis for assigning costs. Hence, the exergy streams are the basis of the cost equations.

The cost rate \( \dot{C} \) is used for the exergoeconomic analysis. With exergy costing, each of the cost rates is evaluated in terms of the associated rate of exergy transfer and a unit cost. Hence, cost rate can be defined for an entering or exiting stream, as follows:

\[
\dot{C} = c \dot{E}x
\]  

(5.9)

where \( c \) denotes the cost per unit of exergy and \( \dot{E}x \) is the associated exergy transfer rate. In exergy costing, a cost is associated with each exergy stream. Exergy cost rates associated with matter, work and heat flows may be written respectively as

\[
\dot{C}_{\text{matter}} = (c \dot{E}x)_{\text{matter}}
\]  

(5.10)

\[
\dot{C}_w = (c \dot{E}x)_w = c_w \dot{W}
\]  

(5.11)

\[
\dot{C}_q = (c \dot{E}x)_q = c_q \dot{Q}(1 - \frac{\theta_0}{\theta})
\]  

(5.12)

Here, the component related cost is shown as \( \dot{Z} \), which includes life cycle phases of construction, operating and maintenance and disposal. The general cost rate balance can be written as

\[
\dot{C}_p = \dot{C}_f + \dot{Z}
\]  

(5.13)
The cost rate of exergy destruction \( \dot{C}_{dest} \) identifies the environmental impact due to exergy destruction.

\[
\dot{C}_{dest} = c_f E x_{dest}
\]  

(5.14)

The steady state form of the control volume cost balance can be written as follows:

\[
\sum_e (c_e E x_e)_k + c_{w,k} E x_{w,k} = c_{q,k} E x_{q,k} + \sum_i (c_i E x_i)_k + \dot{Z}_k
\]

(5.15)

Here, the total cost of the exiting streams equals to the total expenditure to obtain them (Lazzaretto and Tsatsaronis, 2006). In general, there are “\( n_e \)” exergy stream exiting the component, “\( n_e \)” unknowns and only one cost balance equation. This leads to a necessity for “\( n_e - 1 \)” auxiliary equations that are formulated using fuel (F) and product (P) rules.

The F rule (fuel rule) refers to the removal of exergy from an exergy stream within the considered component when exergy differences between the inlet and outlet are considered in the fuel definition for this stream. Thus, this rule states that the specific cost (cost per exergy unit) associated with this fuel stream exergy removal must be equal to the average specific cost at which the removed exergy was supplied to the same stream in upstream components. This provides an auxiliary equation for each removal of exergy, which equals the number of exiting exergy streams and “\( n_{e,f} \)” that are associated with the definition of the fuel for each component. The P rule (product rule) refers to the supply of exergy to an exergy stream within the component and states that each exergy unit is applied to any stream associated with the product at the same average cost. Since this corresponds to an exiting stream, the number of auxiliary equations provided by this rule always equals \( n_{e,p} - 1 \), where \( n_{e,p} \) is the number of exiting exergy streams that are included in the product definition. Thus, since each exiting stream is defined as either fuel or product, the total number of exiting streams is equal to “\( n_{e,f} + n_{e,p} \)”, which provides “\( n_e - 1 \)” auxiliary equations (Lazzaretto and Tsatsaronis, 2006).

To identify the most important components from the viewpoint of formation of cost, the sum of costs \( \dot{Z} + \dot{C}_{dest} \) is used.

When the SPECO method is applied, the performance of a component can be defined and the cost flow rates through components associated with the exergy loss are
calculated using the cost history of the plant. This is provided by the exergoeconomic factor $f$ and defined as

$$f = \frac{z}{z + cf\dot{E}_{dest}}$$  \hspace{1cm} (5.16)$$

The relative cost difference ($RCD$) is another useful variable for evaluating and optimizing a system component in thermoeconomic evaluations, which measures the relative increase in the average cost per exergy unit between fuel and product of the component. The relative cost difference for the cycle can be written as

$$RCD = \frac{c_p - cf}{cf}$$  \hspace{1cm} (5.17)$$

where $c_p$ is the unit exergetic cost of the product of the system and $cf$ is the unit exergetic cost of the required fuel used.

Once the exergoeconomic analysis is conducted to a system, the SPECO method can also be used in an exploratory approach aimed at improving the cost effectiveness of a thermal system by applying the following steps (Tsatsaronis and Moran, 1997):

- Rank the components in descending order of cost importance using the sum ($\dot{Z} + \dot{C}_{dest}$).
- Consider design changes initially for components for which the value of this sum is high.
- Pay particular attention to components with a high relative cost difference ($RCD$), especially when the cost rates $\dot{Z}$ and $\dot{C}_{dest}$ are high.
- Use the exergoeconomic factor $f$ to identify the major cost source (capital investment or cost of exergy destruction):
  - if $f$ is high, investigate whether it is cost effective to reduce the capital investment for the $k$th component at the expense of component efficiency; and
  - if $f$ is low, try to improve the component efficiency by increasing the capital investment.
- Eliminate any subprocesses that increase the exergy destruction or exergy loss without contributing to the reduction of capital investment or of fuel costs for other components.
Consider improving the exergy efficiency of a component if it has relatively low exergy efficiency or relatively large values of exergy destruction, exergy destruction ratio, or exergy loss ratio.

When applying this methodology, it is important to recognize that the values of all thermo-economic variables depend on the component types: heat exchanger, turbine, pump and so forth. Therefore, whether a particular value is judged to be high or low can be determined only with reference to a particular class of components.

**Estimation of Purchased Equipment Costs**

Five generally accepted classifications of capital cost estimates that are most likely to be encountered in the process industries are:

- Detailed estimate
- Definitive estimate
- Preliminary estimate
- Study estimate
- Order-of magnitude estimate (Turton et al., 2009).

The study estimate utilizes a list of major equipment found in the process. This includes all pumps, compressors and turbines, columns and vessels, fired heaters, and exchangers. In this research, study estimate is used since the purchased costs of the major equipments are required for the exergoeconomic analysis. Detailed explanations on capital cost estimation categories are given in Appendix B.

The effect of capacity and time are two important factors for estimation purchased equipment cost. The most common relationship between the purchased cost attribute of the equipment related to units of capacity is given by

\[
\frac{C_a}{C_b} = \left(\frac{A_a}{A_b}\right)^{0.6}
\]

(5.18)

where \(A\) is equipment cost attribute, \(C\) is the purchased cost. Subscript \(a\) refers to the equipment with the required attribute and \(b\) refers to equipment with the base attribute. The relation shown in Equation 5.18 is also referred to as the “six-tenths rule”. The
equipment cost attribute is the equipment parameter that is used to correlate capital cost. The equipment cost attribute is most often related unit capacity (Turton et al., 2009).

It is also essential to be able to update purchased costs to take changing economic factors. This can be achieved using the following expression:

\[ C_1 = C_2 \left( \frac{CEPCI_1}{CEPCI_2} \right) \]  

(5.19)

where \( C \) is the purchased cost, CEPCI is the Chemical Engineering Plant Cost Index. Subscript 1 refers to base time when cost is known, and 2 refers to time when cost is desired. CEPCI is one of the most generally accepted cost indices and is used to convert purchased equipment cost to the present time (November, 2012). CEPCI values are available in Chemical Engineering journal, and are presented from 2001 to 2012 in Table 5.1.

Table 5.1: The values for the Chemical Engineering Plant Cost Index from 2001 to 2012.

<table>
<thead>
<tr>
<th>Year</th>
<th>Chemical Engineering Plant Cost Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>394</td>
</tr>
<tr>
<td>2002</td>
<td>396</td>
</tr>
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<td>402</td>
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<tr>
<td>2010</td>
<td>551</td>
</tr>
<tr>
<td>2011</td>
<td>586</td>
</tr>
<tr>
<td>2012</td>
<td>571</td>
</tr>
</tbody>
</table>


5.2.3 Exergoenvironmental Analysis

Exergoenvironmental analysis is a combination of an exergy analysis with a comprehensive environmental assessment. Exergoenvironmental analysis includes three steps, (i) exergy analysis, (ii) life cycle assessment of each relevant system component and all relevant input streams to the overall system (iii) exergoenvironmental impact assessment. In the last step, the environmental impact obtained from the LCA is assigned
to the exergy streams in the system: exergoenvironmental variables are calculated and an exergoenvironmental evaluation is carried out. The most important components with the highest environmental impact can be identified with the aid of system evaluation (Meyer et al., 2009; Buchgeister, 2010). Exergoenvironmental analysis is very similar to exergoeconomic analysis; instead of cost analysis in the exergoeconomic analysis a life cycle assessment is performed.

The method considered in this thesis for exergoenvironmental analysis is developed by (Meyers et al., 2009) and is performed in analogy to the assignment of costs to exergy streams in exergoeconomics (SPECO method). An environmental impact rate $\dot{B}$ is the environmental impact expressed in Eco-indicator points per time unit (Pts/s or mPts/s). Eco-indicator is weighting method used in life cycle impact assessment phase, which converts overall environmental impacts of a system to a single value, and permits users to observe the environmental impacts of design alternatives. $\dot{B}$, for an entering or exiting stream, can be defined as follows:

$$\dot{B} = b \dot{E}x$$  \hspace{1cm} (5.20)

where $b$ is environmental impact per unit exergy. It may be useful to distinguish between physical and chemical exergy depending on the system or component being analyzed. $\dot{B}$, when a chemical reaction occurs, is

$$\dot{B} = \dot{B}^{ch} + \dot{B}^{ph} = b^{ch} \dot{E}x^{ch} + b^{ph} \dot{E}x^{ph} = b \dot{E}x$$  \hspace{1cm} (5.21)

Here, the exergy flow rate has two components as

$$\dot{E}x = \dot{E}x^{ch} + \dot{E}x^{ph}$$  \hspace{1cm} (5.22)

The environmental impact rates associated with matter, electricity and heat flows may be written respectively as

$$\dot{B}_{\text{matter}} = (b \dot{E}x)_{\text{matter}}$$  \hspace{1cm} (5.23)

$$\dot{B}_{\text{electricity}} = (b \dot{E}x)_{\text{electricity}} = (b \dot{E})_{\text{electricity}}$$  \hspace{1cm} (5.24)

$$\dot{B}_{\text{heat}} = (b \dot{E}x)_{\text{heat}} = b \dot{Q}(1 - \frac{T_0}{T})$$  \hspace{1cm} (5.25)

The component related environmental impact is shown as $\dot{Y}$ (analogous to $\dot{Z}$ in exergoeconomic analysis), which includes life cycle phases of construction, operating
and maintenance and disposal. To account for pollutant formation, a new variable should be defined, $\dot{B}^{PF}$. Pollutant formation term can be neglected if no pollutants formed within the process, i.e. for process without a chemical reaction (Meyer et al., 2009; Boyano et al., 2011). The value of $\dot{B}^{PF}$, for the components where chemical reaction occurs, is

$$\dot{B}^{PF} = \sum_i b_i(\dot{m}_{out} - \dot{m}_{in})$$  \hspace{1cm} (5.26)

where only pollutant streams which finally will be emitted to the environment are taking into account: CO, CO$_2$, CH$_4$, N$_2$O, NO$_x$ and SO$_x$.

The environmental impact rate balance can be written as

$$\dot{B}_p = \dot{B}_f + (\dot{Y} + \dot{B}^{PF})$$  \hspace{1cm} (5.27)

If $\dot{B}^{PF}$ is not taken into account, the balance equation reduces to

$$\dot{B}_p = \dot{B}_f + \dot{Y}$$  \hspace{1cm} (5.28)

The environmental impact of exergy destruction $\dot{B}_{dest}$ identifies the environmental impact due to exergy destruction.

$$\dot{B}_{dest} = b_f \dot{E}_x_{dest}$$  \hspace{1cm} (5.29)

To identify the most important components from the viewpoint of formation of environmental impacts, the sum of environmental impacts ($\dot{Y} + \dot{B}^{PF} + \dot{B}_{dest}$) is used.

The exergoenvironmental factor $f_b$ is defined as

$$f_b = \frac{\dot{Y}}{\dot{Y} + b_f \dot{E}_x_{dest}}$$  \hspace{1cm} (5.30)

The relative difference of specific environmental impact $r_b$ is an indicator of the potential for reducing the environmental impact associated with a component. $r_b$ is defined as

$$r_b = \frac{b_p - b_f}{b_f}$$  \hspace{1cm} (5.31)

### 5.3 Methodology for Life Cycle Assessment (LCA)

LCA is a method used to help engineers, scientists, policy makers and others to assess and compare energy and material use, emissions and wastes, and environmental impacts for a product or process. The method can be used to evaluate the total environmental
impact of a product or process. Overall environmental impact cannot be assessed by examining only operation, but must consider all life stages from resource extraction to disposal during the lifetime of a product. LCA can also be conducted to compare impacts for competing products or processes. In addition, LCA can identify critical phases where process changes could significantly decrease impacts. This section presents detailed background information related to LCA.

5.3.1 Life Cycle Assessment (LCA)

Life cycle assessment consists of four main phases (see Figure 5.1), which are explained further in the following sections. The arrows in Figure 5.1 indicate that all phases of LCA are linked to each other. In this regard, a life cycle interpretation is also linked to all phases, since the phases of LCA should be reviewed and necessary modifications should be done according to results of the LCA study.

5.3.1.1 Goal and Scope Definition

The first phase of LCA is goal and scope definition. The LCA step is critical for clarifying the main objectives of an assessment and breadth of system considered. The goal and scope must be clearly defined and consistent with the intended application. The insights of interest from the LCA must be iterated clearly in this phase, and the intended audience and reasons for the study must be identified. In defining the scope of an LCA, a system boundary is normally drawn, which indicates the breadth and detail of the inventory analysis. Further information on this LCA step is available elsewhere, e.g. (ISO, 1997).

5.3.1.2 Life Cycle Inventory Analysis

The second phase of LCA is life cycle inventory analysis (LCI). All process steps within system boundary and the corresponding inputs/outputs of all flows are identified in as the first step of LCA. Consequently, LCI analysis includes data collection and calculation procedures to quantify relevant inputs and outputs of the system. Inputs associated with the system may be material or energy, while outputs may be releases to air, water and land (ISO, 1997). Several methods exist for data collection, often including the collection of process-specific data directly by measurements, obtaining data reported in the
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literature or by relevant organizations, or calculating data by process modelling. A combination of these techniques is generally required to obtain the required set of inputs and outputs for LCI. Solli (2004) indicates that LCA-databases that contain life cycle data are available for a number of generic processes (e.g., steel production and electricity generation, sometimes broken down by source, country or other factors).

Figure 5.1: Life cycle assessment framework.

5.3.1.3 Life Cycle Impact Assessment

Life cycle impact assessment is the third phase of LCA. The purpose of LCIA is to evaluate environmental impacts of the material and energy flows identified in the inventory analysis. The goal and scope definition affects the level of details, impact categories and evaluation methodologies in LCIA. ISO-14042 (ISO, 2000) divides LCIA into the following steps:
• Classification: In the first step of LCIA, impact categories are determined which are consistent with the goal and scope of the study. Then, inventory data (i.e., the flows in the analysis) are assigned to the impact categories, such as GWP and AP.

• Characterization: Characterization is defined as modelling of inventory data within impact categories. Once the inventory data are matched with impact categories, their contributions to these impact categories needs to be quantified. Hence, the impacts of different environmental flows are assessed using a common indicator unit in each impact category. This step is often done using previously developed characterization factors (Solli, 2004).

• Normalization and weighting: In this optional step, all environmental impacts are combined and reduced into a single score.

A number of impact assessment methods exist, such as CML 2001, Eco-indicator 95 & 99, EPS 2000, IMPACT 2002+, IPCC 200 and TRACI. The CML 2001 method is used in the present analysis.

5.3.1.4 Improvement Analysis
Improvement analysis, the final phase of LCA, the results of LCI and LCIA are combined and assessed, so as to allow conclusions to be drawn and recommendations to be made. These typically relate to the goal and scope of the study. This phase can help decision makers identify environmental beneficial options and inform the decision process, which is also affected by other factors, such as technical performance, economics and social concerns.

5.3.2 Exergetic Life Cycle Assessment (ExLCA)
The framework and flow diagrams of ExLCA (see Figure 5.2) and LCA are similar. The main steps of ExLCA, and their similarities and differences from the main steps of LCA, are as follows:

5.3.2.1 Goal and Scope Definition
The first step for ExLCA is identical with that for LCA, and involves clarifying the system and the audience considered.
5.3.2.2 Inventory Analysis

The inventory analysis of ExLCA is more detailed than that for LCA. A complete flow diagram for the mass and energy flows involved in each of the life cycle stages is required in ExLCA. Therefore, all inputs and outputs must be identified and quantified. The material and energy balances have to be closed, which is not always the case in LCA (Cornelissen, 1997). Sometimes, a more simplified black box approach is preferred for ExLCA, in which only the inputs and outputs of the life cycle steps are taken into account.

5.3.2.3 Impact Assessment

ExLCA impact analysis focuses on the determination of the exergies of flows, and the exergy destructions and exergy efficiencies of the overall process and its subprocesses.
Determination of exergy contents of flows is often a combination of utilizing data reported in the literature or by relevant organizations and calculating data with exergy analysis. A limited impact classification phase is included in ExLCA.

5.3.2.4 Improvement Analysis

The improvement analysis in ExLCA is intended to reduce its life cycle irreversibilities (Cornelissen, 1997). The summation of all exergy destructions in the life cycle, which are calculated using exergy analysis, identifies the life cycle irreversibility of the product or the process. The results of ExLCA are interpreted to develop conclusions and recommendations that relate to the goal and scope of the study, that can help decision makers identify and choose an appropriately environmentally benign alternative, bearing in mind that the decision process is also affected by technical, economic, social and other factors.

5.4 Multi-objective Optimization

Multi-objective optimization is necessary in order to compensate shortcomings of traditional single objective approaches (namely single objective exergy, exergoeconomic and exergoenvironmental optimizations) by allowing a larger perspective and determining a more complete spectrum of solutions that optimize the design according to more than one objective at a time. In most practical decision making problems, the objectives are conflicting in nature and a unique optimal solution cannot be identified. Thus, Pareto optimality is introduced to determine whether a solution is really one of the best possible trade-offs (Hamut, 2012; Lazzaretto and Toffolo 2004; Sayyaadi and Babaelahi, 2011).

5.4.1 Objective Functions

A multi-objective optimization problem requires the simultaneous satisfaction of a number of different and usually conflicting objectives characterized by distinct measure of performance. It should be noted that multi-objective optimization problems generally show a possible uncountable set of solutions which represents the best possible trade-offs in the objective function space and that no combination of decision variable values can
minimize/maximize all the components of functions simultaneously (Sayyaadi and Babaelahi, 2011).

5.4.2 Genetic Algorithm

There are many search techniques that are used to deal with multi-objective optimization problems. These include, but are not limited to, generic algorithm, simulated annealing, tabu and scatter search, ant system, particle swarm and fuzzy programming. Among these, there is no technique that provides the optimum results for all problems and thus the best method should be selected with respect to the current system (Hamut, 2012). In this research, a generic algorithm (GA) is used since it requires no initial conditions, works with multiple design variables, finds global optima (as opposed to local optima), utilizes populations (as opposed to individuals) and uses objective function formation (as opposed to derivatives).

In the last decades, genetic algorithms (GAs) have been extensively used as search and optimization tools in various problem domains due to their broad applicability, ease of use and global perspective (Goldberg, 1989). The concept of GAs was first conceived by Holland in 1970s in order to simulate growth and decay of living organisms in a natural environment and various improvements were conducted ever since. GAs today apply an iterative and stochastic search strategy to drive its search towards an optimal solution through mimicking nature’s evolutionary principles and have received increasing attention by the research community as well as the industry to be used in optimization procedures.

Based on the inspired evolutionary process, the weak and unfit species are faced with extinction while the strong ones have greater opportunity to pass their genes to future generation via reproduction. Throughout this process, given long enough time line, the species carrying the suitable combination in their genes become the dominant population.

In the analysis, the GA terminology adopted by Konak et al. (2006) is used. Based on this terminology, a solution vector is called an individual or a chromosome, which consists of discrete units called genes. Each gene controls one or more features of the chromosome, which corresponds to a unique solution in the solution space. Moreover, the
collection of these chromosomes are called a population, which are initialized randomly at first and includes solutions with increasing fitness as the search evolves until converging to a single solution. Furthermore, operators called crossover and mutation are used to generate new solutions from existing ones. Crossover is one of the key operators where two chromosomes, called parents, are combined together to form new chromosomes called offspring. Due to the having preference towards fitness, these offspring will inherit good genes from the parents and through the iterative process, and therefore the good genes are expected to appear more frequently in the population, where they eventually converge to an overall good solution.

The mutation operator on the other hand introduces random changes into the characteristics of the chromosomes at the gene level. Usually the mutation rate (probability of changing properties of a gene) is very small and therefore the new chromosome produced will not be very different than the original one. The key here is that, while the crossover leads the population to converge (by making the chromosome in the population alike) the mutation reintroduces genetic diversity and assists to the escape from local optima (Konak et al., 2006). Reproduction involves selection of chromosomes for the next generation, where the fitness of an individual usually determined the probability of its survival. The selection procedures can vary depending on how the fitness values are used (such as proportional selection, ranking and tournament). The basic schematic for the evolutionary algorithm for the case used in the study is given in Figure 5.3.

The GA has major advantages since constraints of any type can be easily implemented and that they can find more than one near-optimal point in the optimization space, which enables users to pick the most applicable solution for the specific optimization problem and therefore are widely used for various multi-objective optimization approaches (Ghaffarizadeh, 2006; Ahmadi and Dincer, 2010; Ahmadi et al., 2011). Even though maximizing/minimizing a criterion would be beneficial, many real-world problems involve multiple measures of performance, or objectives, which should be optimized simultaneously. Objectives that are optimized individually can provide optimal results with respect to their own criteria while providing very low performance in other objective functions. Thus, a trade-off is needed among the different dimensions in

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order to obtain a family of optimal “acceptable” solutions for the problem (Fonseca and Fleming, 1995). This ability along with not requiring the user to prioritize, scale or weigh objectives makes them unique in solving multi-objective optimization problems.

Figure 5.3: Sample schematic for the evolutionary algorithm used.

One of the most prominent differences of classical search and optimization algorithms is that EAs use population of solutions in each iteration (instead of single solutions), which produces a final outcome of a population of multiple non-dominated solutions (that are in parallel) by taking advantage of similarities in the family of possible solutions. Since usually, EAs usually do not converge in a single solution (due to conflicting criteria), EA captures multiple optimum solutions in its final population. These solutions are called “Pareto optimal”, where no other feasible solution can reduce some objective function without causing a simultaneous increase in at least no other objection function. The objective function values corresponding to these feasible non-dominating solutions are called “Pareto frontier” (Sayyaadi and Nejatolahi, 2011; Hamut, 2011). The general concept of Pareto frontier is illustrated in Figure 5.4.
Figure 5.4: Sample schematic for the evolutionary algorithm used.
CHAPTER 6: ASPEN SIMULATIONS AND ANALYSIS

6.1 Aspen Simulations

Aspen simulations include Aspen Plus modeling and simulations and the use of Aspen Energy Analyzer to build and analyze the heat exchanger network. This section describes the development of an Aspen Plus flowsheet for the four-step Cu-Cl cycle (second option) since it is under experimental investigation at UOIT. The energy and mass balances, stream flows and properties, the heat exchanger duties and shaft works are calculated. An integrated heat exchanger network is designed via Aspen Energy Analyzer to utilize the heat from the process streams efficiently and reduce the external heat demand.

The main objective is to build a new Aspen Plus model for the four-step Cu-Cl cycle to provide a more realistic model. Previous Aspen Plus models in the literature:

- use stoichiometric reactions either for all the main reactors (hydrolysis, copper oxychloride decomposition, electrolysis, dryer) or at least one of them (Chukwu, 2008), or
- are for other multi-step Cu-Cl cycles (three-step and five-step Cu-Cl cycles) (Ferrandon et al., 2008; Orhan et al., 2012), or
- have very high steam to copper molar ratio (>20) in the hydrolysis step (Orhan 2011, Orhan et al., 2012).

In this regard, a novel Cu-Cl design with reduced excess steam requirement (modelled using Aspen Plus) is proposed in this thesis. Details about the modelling are given in the following subsections.

6.1.1 Modelling of Individual Reactors using Aspen Plus

In this section, modelling of the hydrolysis reactor, copper oxy chloride decomposition reactor, electrolyzer and dryer are described.

Hydrolysis Reactor

The hydrolysis reactor is modelled using equilibrium reactors: REquil and RGibbs (Figure 6.1). The REquil reactor is first used for the modelling. The steam to copper ratio
for 100% yield of Cu₂OCl₂ is simulated to be 2.5. Both experimental and simulation results in the literature, however, states that the steam to copper molar ratio in the hydrolysis reactor is approximately 17-20 at 390°C and 1 atm (Naterer et al., 2010; Ferrandon et al., 2010b). Therefore, the RGibbs reactor is used since it is the only reactor of Aspen Plus that deals with solid-liquid-gas phase equilibrium. A steam to copper ratio of 16 is achieved under the same conditions. Hence, RGibbs is determined to be used. Pressure of the hydrolysis reactor is then reduced to vacuum pressure (0.4 atm) to reduce excess steam requirements. The steam to copper molar ratio is reduced to 10 under this condition. The results are provided in Chapter 7.

**Copper Oxychloride Decomposition Reactor**
The RGibbs reactor is also used for the second step: copper oxychloride decomposition (Ferrandon et al., 2008, Orhan et al, 2012). The reaction takes place at 1 atm and 530°C, and 100% decomposition of Cu₂OCl₂ is achieved. Figure 6.2 represents the Aspen Plus simulation block for the copper oxychloride decomposition reactor.

**Electrolysis**
A realistic Aspen Plus model of the Cu-Cl electrolyzer is done by Orhan, 2011. In the prior simulations a simple stoichiometric model is used for the electrolyzer, which unfortunately cannot determine the electrical work input. This study also presents a realistic model of the electrolyzer that calculates the work input using the block and stream parameters: gibbs free energy of the reaction, electrolyzer temperature and pressure. A Fortran code is written for the work input using the calculator block option of Aspen Plus.

Figure 6.3 shows the electrolyzer block. The work input of the electrolyzer that is required to produce 1 mol of hydrogen is

\[ W_{elec} = n_e \cdot F \cdot E \]  

(6.1)
Figure 6.1: Aspen Plus block for hydrolysis using (a) REquil and (b) RGibbs.

The thermodynamic voltage associated with reaction is calculated as follows:

\[ E = E^0 + \frac{RT_{elec}}{n_e F} \ln \left( \frac{P_{H_2} Y_{CuCl}}{Y_{CuCl} Y_{HCl}} \right) \]  

(6.2)

where \( R = 8.314 \), the universal gas constant, \( \gamma \) is the activity coefficient. However, activity coefficients of the copper compounds are not available in the literature and the equation above can be changed to (Liu et al., 2012):

\[ E = E^0 + \frac{3RT_{elec}}{2n_e F} \ln(P_{elec}) \]  

(6.3)
Here, $T_{elec}$ and $P_{elec}$ are the electrolyzer temperature and pressure, respectively. And,

$$E^0 = \Delta H^0 - T_{elec} \cdot \Delta S^0$$

(6.4)

where $n_e = 2$, the number of electrons exchanged during the electrochemical splitting; $F = 96,485 \, \text{C/mol}$ and $E$ is thermodynamic voltage associated with reaction.

**Dryer**

For the dryer step of the four-step Cu-Cl cycle, the Flash 2 separator block is used. The drying temperature is selected to be 80°C. As explained in Section 4.1, aqueous CuCl$_2$ is dried to solid particles. One should note that the solid CuCl$_2$ particles also have water content, 2 mol H$_2$O/ mol CuCl$_2$. The heat required to evaporate the remaining water content of the input aqueous CuCl$_2$ is also calculated at dryer block. The dryer block of Aspen Plus is shown in Figure 6.4.

**6.1.2 Integration of the Cu-Cl Cycle using Aspen Plus**

Four main reactors of the four-step Cu-Cl cycle are integrated using Aspen Plus. Heat exchangers, pumps, separators and mixers are also used wherever necessary. The Aspen Plus flowsheet of the Cu-Cl cycle is presented in Figure 6.5.

To integrate the main steps of the Cu-Cl cycle, pumps, separators, mixers, expansion valve and heat exchangers are used. In Figure 6.5, pumps (denoted by P1 and P2) are used to increase stream pressure to the electrolyzer pressure. Separators are used
to separate streams from the reactors. An expansion valve is used to decrease the pressure of stream from the electrolyzer pressure to atmospheric pressure. Stream 11 is for the oxygen, stream 25 is for the hydrogen produced; whereas stream 18 is the feed water.

Figure 6.3: Aspen Plus block for electrolyzer.

Figure 6.4: Aspen Plus block for spray dryer.
Figure 6.5: Aspen Plus flowsheet of the four-step Cu-Cl cycle.
Aspen Plus cannot work with loops, an input to the system is necessary. There are two main loops in the Aspen Plus flowsheet above, one is for the CuCl as the electrolyzer input, one is for the whole system. The electrolyzer loop is for conversion efficiency of the CuCl. Since not all of CuCl is converted into CuCl\(_2\) in the electrolyzer, a conversion efficiency of 0.8 is selected. In order to solve this problem and simulate a steady-state operation of the cycle, material properties (mass flow rate of each material, stream temperature and pressure) of streams 26-1 and 26-2 are set to be the same using the calculator block of Aspen Plus. Similar block operation is applied for the streams 28-1 and 28-2.

A hierarchy block is also used for CuCl cooling, since molten CuCl undergoes two transformations: liquid-solid and solid-solid. Molten CuCl remains in a liquid phase down to 423°C, and it then changes phase to solid β phase. Further cooling down of CuCl, there happens another transformation at 412°C, and changes to another solid form (c solid). In this phase, CuCl is still solid, but has a different microstructure and different thermophysical properties. These transformations are demonstrated using stoichiometric reactors (H4 and H6, in Figure 6.6).

![Figure 6.6 Aspen Plus hierarchy block for CuCl.](image)

The heater blocks are used for heating and cooling of the streams, and to determine heat duties of the heat exchangers. Using the simulation results for the heat exchangers, a heat exchanger network is built using Aspen Energy Analyzer.

### 6.1.3 Development of New Designs for Heat Exchanger Network

Aspen Energy Analyzer is designed for creating, analyzing and improving heat exchanger networks. The simulation results of the four-step Cu-Cl cycle using Aspen Plus are transferred to the Aspen Energy Analyzer to build an effective heat exchanger network. The simulation results transferred are the mass flow rate of streams, heat loads or specific heats, inlet and exit temperatures. Physical properties are also extracted from the simulation to be used in Aspen Energy analyzer, which help us calculate overall heat transfer coefficients and heat exchanger areas. Segmentation for the streams is also
applied when the specific heat changes significantly over its temperature range, or whenever there is a phase change. Segmentation example for water is presented in Figure 6.7 which shows the segmentation of water viscosity over a temperature range of 390 to 70°C.

![Figure 6.7: Variation of water viscosity with temperature as a segmentation example.](image)

As mentioned earlier, the stoichiometric steam to copper molar ratio in the hydrolysis reaction is 0.5, however experiments and simulation results show that it is 16-20 in real conditions. The ratio is ten for the vacuum pressure in the hydrolysis reactor, meaning 9 mol excess steam is required for 1 mol of CuCl₂. Evaporation of the excess H₂O and increasing its temperature to the hydrolysis reactor temperature are energy intensive processes for a high steam to copper molar ratio. The thermal energy required by this energy-intensive processes is supplied by the condensation of aqueous HCl.

However, the first attempt to build an effective heat exchanger network was not successful. The reason is related to the condensation temperature of the aqueous HCl (86-88°C) at reduced pressure. Reducing the pressure of the hydrolysis reactor leads to low pressure gas products (HCl and steam). A composite curve for this attempt is presented in Figure 6.8, which shows that the heat loads and temperatures of hot streams (red line) and cold streams (blue line) are not properly matched.
The heat exchanger network for the composite curve in Figure 6.8 has two main disadvantages: (i) thermal energy requirement for the H$_2$O evaporation and heating, and (ii) cold utility need to cool down the aqueous HCl. In this regard, the resulting heat exchanger network is not desirable from both a thermodynamic and an economic point of view. Therefore, the integrated Cu-Cl cycle design has been changed and a compressor that increases the pressure of aqueous HCl is added (Figure 6.20). Addition of the compressor increases the work input of the Cu-Cl cycle, but dramatically decreases the thermal energy and cold utility need. Figure 6.9 shows the composite curves for the new design.

A pinch analysis is developed for an integrated heat exchanger network to enable an effective heat recovery within the Cu-Cl cycle. The first step is to determine the optimum $\Delta T_{\text{min}}$, minimum temperature difference between hot and cold streams. Figure 6.10 shows the variation of total cost index with $\Delta T_{\text{min}}$. The cost index has two components: operating cost index and capital cost index (Figure 6.11). Those indexes are calculated using Aspen Energy analyzer. The capital cost is associated with purchase equipment costs of the heat exchangers, while operating cost covers the operation of the hot and cold utility streams. A dramatic change in total cost at 11°C temperature difference is seen. Since heat loads of aqueous HCl and steam are not matched for a temperature difference greater than 10°C, a minimum temperature difference of 10°C is picked for the design.
Figure 6.9: Composite curves of the final heat exchanger network.

The eight different heat exchanger design options are studied (Figures 6.12-6.19) for better thermal management within the system. The option with minimum number of heat exchangers and minimum cost is selected to be the final heat exchanger network.

Figure 6.10: Variation of total cost index with $\Delta T_{\text{min}}$.

An overview of the proposed heat exchanger network designs is given in Table 6.1. It should be noted that Design 8 is selected as the heat exchanger network for the Cu-Cl cycle. It has the lowest total cost index and number of units calculated by Aspen Energy Analyzer.
Figure 6.11: Variations of capital and operating cost index with $\Delta T_{\text{min}}$.

Figure 6.19 shows the heat exchanger network selected for the Cu-Cl cycle. Blue and red lines in Figure 6.19 are for the cold and hot streams, respectively. Abbreviation CU is used for the cold utility and HU is used for the hot utility. The heat recovered by the hot streams is not only transferred to the cold streams, but also to the dryer and the hydrolysis reactors.

Figure 6.12: A schematic diagram of Design 1 for heat exchanger network.
Figure 6.13: A schematic diagram of Design 2 for heat exchanger network.

Figure 6.14: A schematic diagram of Design 3 for heat exchanger network.

Figure 6.15: A schematic diagram of Design 4 for heat exchanger network.
Figure 6.16: A schematic diagram of Design 5 for heat exchanger network.

Figure 6.17: A schematic diagram of Design 6 for heat exchanger network.

Figure 6.18: A schematic diagram of Design 7 for heat exchanger network.
Table 6.1: Evaluation of the recommended heat exchanger designs.

<table>
<thead>
<tr>
<th>Design Number</th>
<th>Total Cost Index</th>
<th>Heating (MW)</th>
<th>Cooling (MW)</th>
<th>Units</th>
<th>Shells</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.828</td>
<td>74.00</td>
<td>41.03</td>
<td>20</td>
<td>639</td>
</tr>
<tr>
<td>6</td>
<td>0.827</td>
<td>81.80</td>
<td>41.22</td>
<td>22</td>
<td>620</td>
</tr>
<tr>
<td>1</td>
<td>0.811</td>
<td>50.79</td>
<td>41.22</td>
<td>20</td>
<td>686</td>
</tr>
<tr>
<td>5</td>
<td>0.810</td>
<td>74.36</td>
<td>41.22</td>
<td>22</td>
<td>624</td>
</tr>
<tr>
<td>7</td>
<td>0.795</td>
<td>50.79</td>
<td>41.22</td>
<td>20</td>
<td>598</td>
</tr>
<tr>
<td>2</td>
<td>0.751</td>
<td>81.40</td>
<td>41.03</td>
<td>19</td>
<td>609</td>
</tr>
<tr>
<td>4</td>
<td>0.745</td>
<td>81.40</td>
<td>41.03</td>
<td>19</td>
<td>609</td>
</tr>
<tr>
<td>8*</td>
<td>0.741</td>
<td>64.92</td>
<td>36.38</td>
<td>17</td>
<td>620</td>
</tr>
</tbody>
</table>

*Selected heat exchanger design.

6.1.4 Final Design of the Cu-Cl cycle in Aspen Plus

Figure 6.20 presents the final design of the four-step Cu-Cl cycle. The previous design (Figure 6.5) is updated with the design changes after building the heat exchanger network. Simulation results are presented in Chapter 7.

Heat exchanger networks for O₂, HCl (aq), CuCl, H₂O and CuCl₂ streams are shown in hierarchy blocks in Figure 6.20. Those are presented in Figures 6.21-6.25.

Figure 6.22 shows the heat exchanger network for the HCl stream. Condensation of HCl and steam mixture occurs between streams 5-3 and 5-4, hence the heat requirements of HEX6C, HEX8C and the dryer are supplied by a single heat exchanger (HEX6, 8 and dry).

Figure 6.19: Heat exchanger network for the four-step Cu-Cl cycle.
Figure 6.20: Final design for the four-step Cu-Cl.

Figure 6.21: Heat exchanger network for oxygen stream.

Figure 6.22: Heat exchanger network for aqueous HCl stream.
6.2 Energy and Exergy Analyses for the Cu-Cl cycle

Mass, energy, entropy and exergy balances are needed to be written in order to determine heat input, rate of entropy generation and exergy destructions as well as the energy and exergy efficiencies.

In this study; mass, energy and entropy balances are developed first to conduct exergy analysis. Thermochemical properties, such as enthalpy, entropy and exergy, of the flows are obtained from the simulation results. The enthalpy and entropy data for the copper compounds are validated with the study of Zamfirescu et al. (2010b); and the property results for HCl and steam are validated with Schomate equations (NIST, 2012). Exergy balance equations for components in the Cu-Cl cycle are as given in Table 6.2.
Table 6.2: Exergy balance equations for the four-step Cu-Cl cycle.

<table>
<thead>
<tr>
<th>Component</th>
<th>Exergy Balance Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>$(\dot{E}x_1 + \dot{E}x_2) + (\dot{E}x_5 - \dot{E}x_{5-1}) = (\dot{E}x_4 + \dot{E}x_8) + \dot{E}x_{d, s1}$</td>
</tr>
<tr>
<td>Copper oxychloride decomposition</td>
<td>$\dot{E}x_9 + \dot{E}x_{Q,step\ 2} = (\dot{E}x_{11} + \dot{E}x_{13}) + \dot{E}x_{d, s2}$</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>$\dot{W}<em>{elec} + (\dot{E}x</em>{21} + \dot{E}x_7) = (\dot{E}x_{24} + \dot{E}x_{27}) + \dot{E}x_{d, s3}$</td>
</tr>
<tr>
<td>Drying, HEX 6 and HEX 8</td>
<td>$\dot{E}x_{5-3} - \dot{E}x_{5-4} = (\dot{E}x_{30} + \dot{E}x_{31-1}) - \dot{E}x_{28} + \dot{E}x_{d, HEX\ 6-8-dry}$</td>
</tr>
<tr>
<td>HEX 1</td>
<td>$\dot{E}x_{11-1} - \dot{E}x_{11-2} = \dot{E}x_{30-1} - \dot{E}x_{30} + \dot{E}x_{d, HEX1}$</td>
</tr>
<tr>
<td>HEX 2</td>
<td>$\dot{E}x_{14} - \dot{E}x_{15} = \dot{E}x_{30-2} - \dot{E}x_{30-1} + \dot{E}x_{d, HEX2}$</td>
</tr>
<tr>
<td>HEX 3</td>
<td>$\dot{E}x_{5-2} - \dot{E}x_{5-3} = \dot{E}x_{30-3} - \dot{E}x_{30-2} + \dot{E}x_{d, HEX3}$</td>
</tr>
<tr>
<td>HEX 4</td>
<td>$\dot{E}x_{11} - \dot{E}x_{11-1} = \dot{E}x_{30-4} - \dot{E}x_{30-3} + \dot{E}x_{d, HEX4}$</td>
</tr>
<tr>
<td>HEX 5</td>
<td>$\dot{E}x_{13} - \dot{E}x_{14} = \dot{E}x_{2} - \dot{E}x_{30-4} + \dot{E}x_{d, HEX5}$</td>
</tr>
<tr>
<td>HEX 7</td>
<td>$\dot{E}x_{5-1} - \dot{E}x_{5-2} = \dot{E}x_{31-2} - \dot{E}x_{31-1} + \dot{E}x_{d, HEX7}$</td>
</tr>
<tr>
<td>HEX 9</td>
<td>$\dot{E}x_{15} - \dot{E}x_{16} = \dot{E}x_{19} - \dot{E}x_{18} + \dot{E}x_{d, HEX9}$</td>
</tr>
<tr>
<td>HEX H1</td>
<td>$\dot{E}x_{Q,HU1} = \dot{E}x_9 - \dot{E}x_8 + \dot{E}x_{d, HEX-HU1}$</td>
</tr>
<tr>
<td>HEX H2</td>
<td>$\dot{E}x_{Q,HU2} = \dot{E}x_1 - \dot{E}x_{31-2} + \dot{E}x_{d, HEX-HU2}$</td>
</tr>
<tr>
<td>HEX C1</td>
<td>$\dot{E}x_{Q,CU1} = \dot{E}x_{5-4} - \dot{E}x_6 + \dot{E}x_{d, HEX-CU1}$</td>
</tr>
<tr>
<td>HEX C2</td>
<td>$\dot{E}x_{Q,CU2} = \dot{E}x_6 - \dot{E}x_{17} + \dot{E}x_{d, HEX-CU2}$</td>
</tr>
<tr>
<td>HEX C3</td>
<td>$\dot{E}x_{Q,CU3} = \dot{E}x_{11-2} - \dot{E}x_{12} + \dot{E}x_{d, HEX-CU3}$</td>
</tr>
<tr>
<td>HEX C4</td>
<td>$\dot{E}x_{Q,CU4} = \dot{E}x_{24} - \dot{E}x_{25} + \dot{E}x_{d, HEX-CU4}$</td>
</tr>
<tr>
<td>Compressor</td>
<td>$\dot{E}x_4 + \dot{W}<em>{comp} = \dot{E}x_5 + \dot{E}x</em>{d, comp}$</td>
</tr>
<tr>
<td>Expansion valve</td>
<td>$\dot{E}x_{27} = \dot{E}x_{28} + \dot{E}x_{d, ev}$</td>
</tr>
<tr>
<td>Pump - 1</td>
<td>$\dot{E}x_5 + \dot{W}<em>{pump, 1} = \dot{E}x_6 + \dot{E}x</em>{d, pump 1}$</td>
</tr>
<tr>
<td>Pump - 2</td>
<td>$\dot{W}<em>{pump, 2} + \dot{E}x</em>{20} = \dot{E}x_{21} + \dot{E}x_{d, pump 2}$</td>
</tr>
</tbody>
</table>

The energy and exergy efficiencies for the Cu-Cl cycle can be defined as follows:

$$\eta_{en} = \frac{\dot{m} \times LHV_{H_2}}{\dot{W} + \dot{Q}} \quad (6.5)$$

and

$$\eta_{ex} = \frac{\dot{E}x_{H_2}}{\dot{E}x_0 + \dot{W}} \quad (6.6)$$

where $LHV$ is lower heating value, and $\dot{W}$ and $\dot{Q}$ are rate of electrical work and rate of heat input to the cycle. $\dot{E}x_{H_2}$ is chemical exergy of hydrogen multiplied by mass flow rate of product hydrogen, and $\dot{E}x_Q$ associated with a thermal energy rate $\dot{Q}$ is as follows:

$$\dot{E}x_Q = \sum_{i=1}^{n} \dot{Q}_i \times \left(1 - \frac{T_0}{T_i}\right) \quad (6.7)$$

where $T_i$ and $T_0$ are system and reference environment temperatures, respectively.
6.3 Exergoeconomic Analysis for the Cu-Cl cycle

Exergoeconomic analysis described in Section 5.2.2 is applied to the four-step Cu-Cl cycle. Cost balance equations and purchase equipment cost correlations are used for each component of the cycle. Unit costs of each stream are found via cost accounting, and exergoeconomic evaluation is performed.

6.3.1 Cost Balance Equations

The cost flow rate $\dot{\mathcal{C}} (\$/s)$, is defined for each flow in a system, and a cost balance for each component is written in order to conduct an exergoeconomic analysis. Prior to analysis, however, the fuel and product exergies for each component are needed to be defined. The fuel exergy is defined as the resources consumed in generating the product, while the product exergy is the cost of owning and operating a component under consideration (Bejan et al., 1986). The fuel and product exergies for each component of the Cu-Cl cycle can be seen in Table 6.3.

The cost balance equations (CBE) with auxiliary equations for the Cu-Cl cycle are given below. The definitions of the F (Fuel) and P (Product) rules used for auxiliary equations are given in Section 5.2.2.

**Hydrolysis reactor (reactor 1)**

\[
\dot{c}_5 - \dot{c}_{5-1} + \dot{Z}_{R1} = (\dot{c}_4 + \dot{c}_8) - (\dot{c}_1 + \dot{c}_2) \quad (6.8)
\]

$c_5 = c_{5-1}$ (F rule)

$c_4 = c_8$ (P rule)

**Copper oxychloride decomposition reactor (reactor 2)**

\[
\dot{c}_{\text{thermal}} \dot{E}x_{Q,\text{step}2} + \dot{Z}_{R2} = (\dot{c}_{11} + \dot{c}_{13}) - \dot{c}_9 \quad (6.9)
\]

$c_{11} = c_{13}$ (P rule)

**Electrolysis**

\[
c_{\text{electricity}} W_{\text{elec}} + \dot{Z}_{\text{elec}} = (\dot{c}_{24} + \dot{c}_{27}) - (\dot{c}_{21} + \dot{c}_7) \quad (6.10)
\]

$c_{24} = c_{27}$ (P rule)
Table 6.3: Fuel and product definitions with respect to the Cu-Cl cycle.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fuel</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>$\dot{E} x_5 - \dot{E} x_{5-1}$</td>
<td>$(\dot{E} x_4 + \dot{E} x_8) - (\dot{E} x_1 + \dot{E} x_2)$</td>
</tr>
<tr>
<td>Copper oxychloride decomposition</td>
<td>$E x_{Q, step , 2}$</td>
<td>$(\dot{E} x_{11} + \dot{E} x_{13}) - \dot{E} x_9$</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>$W_{elec}$</td>
<td>$(\dot{E} x_{24} + \dot{E} x_{27}) - (\dot{E} x_{21} + \dot{E} x_7)$</td>
</tr>
<tr>
<td>Drying, HEX 6 and HEX 8</td>
<td>$\dot{E} x_{5-3} - \dot{E} x_{5-4}$</td>
<td>$(\dot{E} x_{30} + \dot{E} x_{31-1}) - \dot{E} x_{28}$</td>
</tr>
<tr>
<td>HEX 1</td>
<td>$\dot{E} x_{11-1} - \dot{E} x_{11-2}$</td>
<td>$\dot{E} x_{30-1} - \dot{E} x_{30}$</td>
</tr>
<tr>
<td>HEX 2</td>
<td>$\dot{E} x_{14} - \dot{E} x_{15}$</td>
<td>$\dot{E} x_{30-2} - \dot{E} x_{30-1}$</td>
</tr>
<tr>
<td>HEX 3</td>
<td>$\dot{E} x_{5-2} - \dot{E} x_{5-3}$</td>
<td>$\dot{E} x_{30-3} - \dot{E} x_{30-2}$</td>
</tr>
<tr>
<td>HEX 4</td>
<td>$\dot{E} x_{11} - \dot{E} x_{11-1}$</td>
<td>$\dot{E} x_{30-4} - \dot{E} x_{30-3}$</td>
</tr>
<tr>
<td>HEX 5</td>
<td>$\dot{E} x_{13} - \dot{E} x_{14}$</td>
<td>$\dot{E} x_{2} - \dot{E} x_{30-4}$</td>
</tr>
<tr>
<td>HEX 7</td>
<td>$\dot{E} x_{5-1} - \dot{E} x_{5-2}$</td>
<td>$\dot{E} x_{31-2} - \dot{E} x_{31-1}$</td>
</tr>
<tr>
<td>HEX 9</td>
<td>$\dot{E} x_{15} - \dot{E} x_{16}$</td>
<td>$\dot{E} x_{19} - \dot{E} x_{18}$</td>
</tr>
<tr>
<td>HEX HU1</td>
<td>$\dot{E} x_{Q,HU1}$</td>
<td>$\dot{E} x_6 - \dot{E} x_8$</td>
</tr>
<tr>
<td>HEX HU2</td>
<td>$\dot{E} x_{Q,HU2}$</td>
<td>$\dot{E} x_1 - \dot{E} x_{31-2}$</td>
</tr>
<tr>
<td>HEX CU1</td>
<td>$\dot{E} x_{Q,CU1}$</td>
<td>$\dot{E} x_{5-4} - \dot{E} x_6$</td>
</tr>
<tr>
<td>HEX CU2</td>
<td>$\dot{E} x_{Q,CU2}$</td>
<td>$\dot{E} x_{16} - \dot{E} x_{17}$</td>
</tr>
<tr>
<td>HEX CU3</td>
<td>$\dot{E} x_{Q,CU3}$</td>
<td>$\dot{E} x_{11-2} - \dot{E} x_{12}$</td>
</tr>
<tr>
<td>HEX CU4</td>
<td>$\dot{E} x_{Q,CU4}$</td>
<td>$\dot{E} x_{24} - \dot{E} x_{25}$</td>
</tr>
<tr>
<td>Compressor</td>
<td>$W_{comp}$</td>
<td>$\dot{E} x_5 - \dot{E} x_4$</td>
</tr>
<tr>
<td>Expansion valve</td>
<td>$\dot{E} x_{27}$</td>
<td>$\dot{E} x_{28}$</td>
</tr>
<tr>
<td>Pump - 1</td>
<td>$W_{pump,1}$</td>
<td>$\dot{E} x_6 - \dot{E} x_5$</td>
</tr>
<tr>
<td>Pump - 2</td>
<td>$W_{pump,2}$</td>
<td>$\dot{E} x_{21} - \dot{E} x_{20}$</td>
</tr>
<tr>
<td>Mixer -1</td>
<td>$\dot{E} x_{19} + \dot{E} x_{17}$</td>
<td>$\dot{E} x_{20}$</td>
</tr>
</tbody>
</table>

Drying, Hex 6 and Hex 8

$$\dot{c}_{5-3} - \dot{c}_{5-4} + \dot{z}_{Hex\, 6, 8, dry} = (\dot{c}_{30} + \dot{c}_{31-1}) - \dot{c}_{28} \quad (6.11)$$

c_{5-4} = c_{5-3} \quad (F \, rule)

c_{30} = c_{31} \quad (P \, rule)

$$\frac{(\dot{c}_{31-1} - \dot{c}_{31})}{(\dot{E} x_{31-1} - \dot{E} x_{31})} = \frac{(\dot{c}_{29} - \dot{c}_{28})}{(\dot{E} x_{29} - \dot{E} x_{28})} \quad (P \, rule)$$

$$\frac{(\dot{c}_{29} - \dot{c}_{28})}{(\dot{E} x_{29} - \dot{E} x_{28})} = \frac{(\dot{c}_{30} + \dot{c}_{31-1} - \dot{c}_{20})}{(\dot{E} x_{30} + \dot{E} x_{31-1} - \dot{E} x_{20})} \quad (P \, rule)$$

Hex 1

$$\dot{c}_{11-1} - \dot{c}_{11-2} + \dot{z}_{Hex\, 1} = \dot{c}_{30-1} - \dot{c}_{30} \quad (6.12)$$

c_{11-1} = c_{11-2} \quad (F \, rule)
Hex 2
\[
\dot{c}_{14} - \dot{c}_{15} + \dot{z}_{HEX2} = \dot{c}_{30-2} - \dot{c}_{30-1}
\] (6.13)
c_{14} = c_{15} \text{ (F rule)}

Hex 3
\[
\dot{c}_{52} - \dot{c}_{53} + \dot{z}_{HEX3} = \dot{c}_{30-3} - \dot{c}_{30-2}
\] (6.14)
c_{52} = c_{53} \text{ (F rule)}

Hex 4
\[
\dot{c}_{11} - \dot{c}_{11-1} + \dot{z}_{HEX4} = \dot{c}_{30-4} - \dot{c}_{30-3}
\] (6.15)
c_{11} = c_{11-1} \text{ (F rule)}

Hex 5
\[
\dot{c}_{13} - \dot{c}_{14} + \dot{z}_{HEX5} = \dot{c}_{2} - \dot{c}_{30-4}
\] (6.16)
c_{13} = c_{14} \text{ (F rule)}

Hex 7
\[
\dot{c}_{13} - \dot{c}_{14} + \dot{z}_{HEX5} = \dot{c}_{2} - \dot{c}_{30-4}
\] (6.17)
c_{13} = c_{14} \text{ (F rule)}

Hex 9
\[
\dot{c}_{13} - \dot{c}_{14} + \dot{z}_{HEX5} = \dot{c}_{2} - \dot{c}_{30-4}
\] (6.18)
c_{13} = c_{14} \text{ (F rule)}

Hex HU1
\[
c_{thermal} \dot{E}_{X, HU1} + \dot{z}_{HEXHU1} = \dot{c}_{9} - \dot{c}_{8}
\] (6.19)

Hex HU2
\[
c_{thermal} \dot{E}_{X, HU2} + \dot{z}_{HEXHU2} = \dot{c}_{1} - \dot{c}_{31-2}
\] (6.20)

Hex CU1
\[
c_{cw} \dot{E}_{X, CU1} + \dot{z}_{HEXCU1} = \dot{c}_{5-4} - \dot{c}_{6}
\] (6.21)

Hex CU2
\[
c_{cw} \dot{E}_{X, CU2} + \dot{z}_{HEXCU2} = \dot{c}_{16} - \dot{c}_{17}
\] (6.22)
\textbf{Hex CU3}
\[ c_{cw} \dot{E}_{x,\text{CU3}} + \dot{Z}_{\text{HEXCU3}} = \dot{C}_{11-2} - \dot{C}_{12} \quad (6.23) \]

\textbf{Hex CU4}
\[ c_{cw} \dot{E}_{x,\text{CU4}} + \dot{Z}_{\text{HEXCU4}} = \dot{C}_{24} - \dot{C}_{25} \quad (6.24) \]

\textbf{Compressor}
\[ c_{electricity} W_{\text{Comp}} + \dot{Z}_{\text{Comp}} = \dot{C}_{5} - \dot{C}_{4} \quad (6.25) \]

\textbf{Expansion Valve}
\[ \dot{C}_{27} + \dot{Z}_{\text{ev}} = \dot{C}_{28} \quad (6.26) \]

\textbf{Pump 1}
\[ c_{electricity} W_{\text{Pump1}} + \dot{Z}_{\text{Pump1}} = \dot{C}_{6} - \dot{C}_{5} \quad (6.27) \]

\textbf{Pump 2}
\[ c_{electricity} W_{\text{Pump2}} + \dot{Z}_{\text{Pump2}} = \dot{C}_{21} - \dot{C}_{20} \quad (6.28) \]

\textbf{Mixer}
\[ \dot{C}_{19} + \dot{C}_{17} = \dot{C}_{20} \quad (6.29) \]

\section*{6.3.2 Purchased Equipment Cost Correlations}

The capital investment rate can be calculated using the purchase cost of equipment and capital recovery, as well as the maintenance factor over the number of operation hours per year as given as follows:

\[ \dot{Z}_k = \frac{Z_k \cdot CRF \cdot \phi}{N} \cdot F_m \quad (6.30) \]

where \( N \) is the annual number of operation hours for the unit and \( \phi \) is the maintenance factor, generally taken as 1.06 (Bejan et al., 1996). \( F_m \) is the material factor. The capital recovery factor, \( CRF \), depends on the interest rate \( "i" \), and equipment life-time in years \( (n) \) as

\[ CRF = \frac{i \cdot (1 + i)^n}{(1 + i)^n - 1} \quad (6.31) \]
where $Z_k$ is the purchase equipment cost of the system components which should be written in terms of design parameters (Valero, 1994). The correlations for each component are given below.

**Hydrolysis Reactor**

The vertical process vessels are considered for the hydrolysis reactor, with a diameter of 4 m and height of 24 m. The number of hydrolysis reactors is determined based on steam residence time. In order to keep the number of hydrolysis reactors at a reasonable number, a short residence time of steam (5 s) had to be assumed. However, a short residence time is desirable to prevent the formation of CuO and CuCl (Ferrandon et al., 2008).

The purchased equipment cost of each reactor is determined by the following equation (Turton et al., 2009):

$$\text{# of reactors} = \frac{\text{volumetric flow rate of steam} \cdot \text{residence time}}{\text{volume of one reactor}}$$

(6.32)

The purchased equipment cost of each reactor is determined by the following equation (Turton et al., 2009):

$$\log_{10}Z_{R1} = 3.4974 + 0.4485 \cdot \log_{10}(V_{R1}) + 0.1074 \cdot [\log_{10}(V_{R1})]^2$$

(6.33)

where $V_{R1}$ is the volume of one reactor. The cost correlation is given for the year 2001, but is normalized for the year 2012 in the analysis.

**Copper Oxychloride Reactor**

A vertical process vessel is also used for the copper oxychloride reactor, which is sized for a residence time of 60 min for $\text{Cu}_2\text{OCl}_2$ to allow plenty of time for decomposition. For the residence time given, a reactor with a diameter of 3 m and height of 9.56 m is required.

The purchased equipment cost of copper oxychloride decomposition reactor is determined as follows (Turton et al., 2009):

$$\log_{10}Z_{R2} = 3.4974 + 0.4485 \cdot \log_{10}(V_{R2}) + 0.1074 \cdot [\log_{10}(V_{R2})]^2$$

(6.34)

where $V_{R2}$ is the volume of the reactor. The cost correlation is given for the year 2001, but it is normalized for the year 2012 in the analysis.
Electrolyzer

Electrolysis cell capital cost for a thermochemical cycle is given by Gorensek et al. (2009). The cost components are listed in Table 6.4.

Table 6.4: Electrolysis cell capital cost.

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
<th>Cost Basis</th>
<th>$/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Nafion® 117 or equiv</td>
<td>$300/m²</td>
<td>300</td>
</tr>
<tr>
<td>Gas diffusion layers</td>
<td>Porous carbon</td>
<td>$75/m² (2 layers req’d)</td>
<td>150</td>
</tr>
<tr>
<td>Electrocatalyst</td>
<td>1 mg/cm² Pt (total)</td>
<td>$1500/troy oz</td>
<td>480</td>
</tr>
<tr>
<td>Bipolar plates</td>
<td>3/8-in graphite</td>
<td>$200/m²</td>
<td>200</td>
</tr>
<tr>
<td>Seals, gaskets, etc.</td>
<td>PEEK or equiv</td>
<td>$50/m²</td>
<td>50</td>
</tr>
<tr>
<td>Cell assembly</td>
<td>Automated</td>
<td>1 man-hr @$50/man-hr</td>
<td></td>
</tr>
</tbody>
</table>

Single cell cost 1,230

Source: Gorensek et al. (2009).

Hence, cost correlation for

\[ Z_{\text{elec}} = 1230 \cdot \frac{s}{m^2} \cdot A_{\text{cell}} \]

(6.35)

where \(A_{\text{cell}}\) is the active cell area. The cost correlation is for 2009, and it is normalized to 2012 for the analysis.

Dryer

The residence time of aqueous cupric chloride is set to be 5 min (Ferrandon et al., 2008). A single dryer has 2 m diameter and height of 9.55 m. The number of dryers is selected in a similar fashion to the way the number of hydrolysis reactors is chosen:

\[ \# \text{ of dryers} = \frac{\text{volumetric flow rate of CuCl}_2(aq) \cdot \text{residence time}}{\text{volume of one reactor}} \]

(6.36)

The purchased equipment cost correlation for one dryer is as follows (Turton et al., 2009):

\[ \log_{10} Z_{\text{dry}} = 4.5097 - 0.8269 \cdot \log_{10}(V_{R4}) + 0.1344 \cdot [\log_{10}(V_{R4})]^2 \]

(6.37)

where \(V_{R4}\) is the volume of one dryer. The cost correlation is given for the year 2001, but it is normalized for the year 2012 in the analysis.
Heat Exchangers

The equipment cost attribute for the heat exchangers is area. Area of the heat exchangers is determined using the logarithmic mean temperature difference (LMTD) method as follows:

\[
A = \frac{\dot{Q}}{U \cdot \Delta T_{lm}} \tag{6.38}
\]

where \( \dot{Q} \) is the rate of heat transfer, \( U \) is the overall heat transfer coefficient value and is obtained from Aspen Energy Analyzer as explained in Section 6.1. \( \Delta T_{lm} \) is the logarithmic mean temperature difference and defined as

\[
\Delta T_{lm} = \frac{(T_{H,i} - T_{C,o}) - (T_{H,o} - T_{C,i})}{\ln \left( \frac{T_{H,i} - T_{C,o}}{T_{H,o} - T_{C,i}} \right)} \tag{6.39}
\]

where the subscripts \( H \) and \( C \) represent hot and cold streams and \( i \) and \( o \) refer to “in” and “out”.

The shell and tube type heat exchangers are selected for all heat exchangers except HEX-HU1, where Cu₂OCl₂ solid particles are heated using a thermal source in a Bayonet type heat exchanger (Ferrandon et al., 2008, Turton et al., 2009). Cost correlation for the shell and tube heat exchanger is as follows:

\[
\log_{10}Z_{HEX,s&t} = 4.3247 - 0.3030 \cdot \log_{10}(A) + 0.1634 \cdot [\log_{10}(A)]^2 \tag{6.40}
\]

The cost correlation for the bayonet type heat exchanger is given as follows:

\[
\log_{10}Z_{HEX,bayonet} = 4.2768 - 0.0495 \cdot \log_{10}(A) + 0.1431 \cdot [\log_{10}(A)]^2 \tag{6.41}
\]

where \( A \) is the area of heat exchangers. The cost correlations for heat exchangers are also given for the year 2001, but they are normalized for the year 2012 in the analysis.

Compressor, Pumps and Expansion Valve

Cost correlations for compressors and pumps are given as (Turton et al., 2009):

\[
\log_{10}Z_{compressor} = 2.2897 + 1.3604 \cdot \log_{10}(W_{comp}) - 0.1027 \cdot [\log_{10}(W_{comp})]^2 \tag{6.42}
\]

\[
\log_{10}Z_{pump} = 3.8696 - 0.3161 \cdot \log_{10}(W_{comp}) + 0.1220 \cdot [\log_{10}(W_{comp})]^2 \tag{6.43}
\]
The cost correlation of the expansion valve is normalized from the study of Hamut (2012). The equipment cost attribute is the mass flow rate.

\[ Z_{ev} = 12.36 \cdot \dot{m}_{28} \] (6.44)

### 6.3.3 Cost Accounting

Cost balances for each component are needed to be solved in order to estimate the cost rate of exergy destruction in each component. Implementing a cost equation for each component together with the auxiliary equations form a system of linear equations as follows:

\[
[\dot{E}x_k] \times [c_k] = [\dot{Z}_k]
\] (6.45)

where the equation entails matrices of exergy rate (from exergy analysis), exergetic cost vector (to be evaluated) and the vector of \([\dot{Z}_k]\) factors (from economic analysis) respectively (Ahmedi et al., 2011). The size of the exergy rate matrix is 43 × 43, created using cost balance equations in Section 6.3.1. By solving these equations simultaneously, the cost rate of each flow is calculated, which is used to determine the cost rate of exergy destruction in each system component.

### 6.3.4 Exergoeconomic Evaluation

Exergoeconomic evaluation is performed by means of exergoeconomic factor and relative cost difference (Equations 5.13 and 5.14). Also, the total cost rate provides the component with the highest priority from exergoeconomic viewpoint and is the combination of the cost rate of exergy destruction and the investment cost rates.

\[
\dot{C}_{tot,k} = \dot{C}_{D,k} + \dot{Y}_k
\] (6.46)

Here, the exergoeconomic evaluation is performed and results are presented in Chapter 7.

### 6.4 Exergoenvironmental Analysis for the Cu-Cl cycle

Exergoenvironmental analysis reveals the environmental impact associated with each system component and the real sources of the impact by combining exergy analysis with a comprehensive environmental assessment method.
In the environmental analysis, LCA is carried out in order to obtain the environmental impact of each relevant system components and input streams. It consists of goal definition, inventory analysis and interpretation of results, which incorporates the supply of the input streams (especially fuel) and full life cycle of components. The quantification of environmental impact with respect to depletion and emissions of a natural resource can be conducted using different methodologies. In this study, impact analysis using Eco-indicator 99 points along with previously determined impact analyses in the literature are used. For the LCA analysis, various damage categories are covered and the results are weighted and expressed in terms of Ecoindicator points (mPts) (Petrakopoulou et al., 2011) by using SimaPro 7.1 (SimaPro, 2007).

SimaPro is a life cycle assessment software package that has the capability of collecting, analyzing and monitoring the environmental performance of products and services and can model and evaluate complex life cycles in a systematic and transparent way following the ISO 14040 series recommendations. The software is integrated with an ecoinvent database that is used for a variety of applications including carbon footprint calculations, product design/ecodesign as well as assessing the environmental impact with respect to various parameters. The software can define non-linear relationships in the model, conduct analysis of complex waste treatment and recycling scenarios and allocate multiple output processes. Thus, it provides significant value in conducting LCA for the system components (SimaPro, 2007).

6.4.1 Environmental Impact Balance Equations
The environmental impact flow rate $\dot{B}$ (Pt/s), is defined for each flow in a system, and an environmental impact balance for each component is written in order to conduct an exergoenvironmental analysis. Environmental impact balance equations (EIBE) with auxiliary equations (analogous to exergoeconomic equations) for the Cu-Cl cycle are given below:

**Hydrolysis reactor (reactor 1)**

$$
\dot{b}_5 - \dot{b}_{5-1} + \dot{y}_{R1} = (\dot{b}_4 + \dot{b}_8) - (\dot{b}_1 + \dot{b}_2)
$$

(6.47)

$b_5 = b_{5-1}$ (F rule)

$b_4 = b_8$ (P rule)
Copper oxychloride decomposition reactor (reactor 2)

\[ b_{\text{thermal}} \dot{E}_{XQ,\text{step} \ 2} + \dot{Y}_{R2} = (\dot{B}_{11} + \dot{B}_{13}) - \dot{B}_{9} \]  
\[ b_{11} = b_{13} \ (\text{P rule}) \]

Electrolysis

\[ b_{\text{electricity}} \dot{W}_{\text{elec}} + \dot{Y}_{\text{elec}} = (\dot{B}_{24} + \dot{B}_{27}) - (\dot{B}_{21} + \dot{B}_{7}) \]  
\[ b_{24} = b_{27} \ (\text{P rule}) \]

Drying, Hex 6 and Hex 8

\[ \dot{B}_{5-3} - \dot{B}_{5-4} + \dot{Y}_{\text{HEX6,8,dry}} = (\dot{B}_{30} + \dot{B}_{31-1}) - \dot{B}_{28} \]  
\[ b_{5-4} = b_{5-3} \ (\text{F rule}) \]
\[ b_{30} = b_{31} \ (\text{P rule}) \]
\[ \frac{(\dot{B}_{31-1} - \dot{B}_{31})}{(E_{31-1} - E_{31})} = \frac{(\dot{B}_{29} - \dot{B}_{28})}{(E_{29} - E_{28})} \ (\text{P rule}) \]
\[ \frac{\dot{B}_{29} - \dot{B}_{28}}{E_{29} - E_{28}} = \frac{\dot{B}_{30} + \dot{B}_{31-1} - \dot{B}_{29}}{(E_{30} + E_{31-1} - E_{29})} \ (\text{P rule}) \]

Hex 1

\[ \dot{B}_{11-1} - \dot{B}_{11-2} + \dot{Y}_{\text{HEX1}} = \dot{B}_{30-1} - \dot{B}_{30} \]  
\[ b_{11-1} = b_{11-2} \ (\text{F rule}) \]

Hex 2

\[ \dot{B}_{14} - \dot{B}_{15} + \dot{Y}_{\text{HEX2}} = \dot{B}_{30-2} - \dot{B}_{30-1} \]  
\[ b_{14} = b_{15} \ (\text{F rule}) \]

Hex 3

\[ \dot{B}_{52} - \dot{B}_{53} + \dot{Y}_{\text{HEX3}} = \dot{B}_{30-3} - \dot{B}_{30-2} \]  
\[ b_{52} = b_{53} \ (\text{F rule}) \]

Hex 4

\[ \dot{B}_{11} - \dot{B}_{11-1} + \dot{Y}_{\text{HEX4}} = \dot{B}_{30-4} - \dot{B}_{30-3} \]  
\[ b_{11} = b_{11-1} \ (\text{F rule}) \]

Hex 5

\[ \dot{B}_{13} - \dot{B}_{14} + \dot{Y}_{\text{HEX5}} = \dot{B}_{2} - \dot{B}_{30-4} \]  
\[ b_{13} = b_{14} \ (\text{F rule}) \]
Hex 7
\[ \dot{B}_{13} - \dot{B}_{14} + \dot{Y}_{\text{HEX5}} = \dot{B}_2 - \dot{B}_{30-4} \] (6.56)
\[ b_{13} = b_{14} \text{ (F rule)} \]

Hex 9
\[ \dot{B}_{13} - \dot{B}_{14} + \dot{Y}_{\text{HEX5}} = \dot{B}_2 - \dot{B}_{30-4} \] (6.57)
\[ b_{13} = b_{14} \text{ (F rule)} \]

Hex HU1
\[ b_{\text{thermal}} \dot{E}_{Q,HU1} + \dot{Y}_{\text{HEXHU1}} = \dot{B}_9 - \dot{B}_8 \] (6.58)

Hex HU2
\[ b_{\text{thermal}} \dot{E}_{Q,HU2} + \dot{Y}_{\text{HEXHU2}} = \dot{B}_1 - \dot{B}_{31-2} \] (6.59)

Hex CU1
\[ b_{cw} \dot{E}_{Q,CU1} + \dot{Y}_{\text{HEXCU1}} = \dot{B}_{5-4} - \dot{B}_6 \] (6.60)

Hex CU2
\[ b_{cw} \dot{E}_{Q,CU2} + \dot{Y}_{\text{HEXCU2}} = \dot{B}_{16} - \dot{B}_{17} \] (6.61)

Hex CU3
\[ b_{cw} \dot{E}_{Q,CU3} + \dot{Y}_{\text{HEXCU3}} = \dot{B}_{11-2} - \dot{B}_{12} \] (6.62)

Hex CU4
\[ b_{cw} \dot{E}_{Q,CU4} + \dot{Y}_{\text{HEXCU4}} = \dot{B}_{24} - \dot{B}_{25} \] (6.63)

Compressor
\[ b_{\text{electricity}} \dot{W}_{\text{comp}} + \dot{Y}_{\text{comp}} = \dot{B}_5 - \dot{B}_4 \] (6.64)

Expansion Valve
\[ \dot{B}_{27} + \dot{Y}_{ev} = \dot{B}_{28} \] (6.65)

Pump 1
\[ b_{\text{electricity}} \dot{W}_{\text{Pump1}} + \dot{Y}_{\text{Pump1}} = \dot{B}_6 - \dot{B}_5 \] (6.66)

Pump 2
\[ b_{\text{electricity}} \dot{W}_{\text{Pump2}} + \dot{Y}_{\text{Pump2}} = \dot{B}_{21} - \dot{B}_{20} \] (6.67)
6.4.2 Environmental Impact Correlations

In order to be able to solve the environmental balance equations, the environmental impacts associated with each component are determined with respect to Eco-indicator 99 points, which enable a fair comparison among different components. These impact points are approximated with respect to a combination of correlations developed from numerous studies conducted in literature, available data as well as the LCA developed for this study.

Environmental impacts of hydrolysis and copper oxychloride decomposition reactors are calculated based on material input during its production. Dimensions for those reactors are given in Section 6.3.2. Wall thickness of the reactors is selected to be 4 cm (Nyoni, 2011). A correction factor of 1.06 is used for the porcelain coating (Ferrandon et al., 2008). The Eco-indicator point associated with the spray dryer is given by Ciesielski and Zbicinski, 2010, which is normalized for the Cu-Cl cycle needs. The mass flow rate of the steam is the environmental impact attribute for the dryer. Data for the electrolyzer material is obtained from Gorensek et al., 2009, and an LCA is conducted using SimaPro 7 software. The power input of the electrolyzer given by Gorensek et al., 2009 is 7.5 MW. Therefore, the environmental impact results are normalized for the Cu-Cl electrolyzer.

The environmental impact correlations for the compressor and pumps are normalized from Eco-invent database (Ecoinvent, 2012) and the study of Buyano et al. (2011). The expansion valve environmental impact is obtained from Hamut, 2012 and normalized. The criterion to assess the environmental impact of the pumps and compressor is work input, whereas mass flow rate is used as a criterion for the expansion valve. SimaPro 7 flowsheet of a sample electrolyzer and a sample compressor used for the environmental impact correlations are presented in Figure 6.26, 6.27. The results shown in Figures 6.26 and 6.27 are normalized for the four-step cycle system capacity.

The eco-indicator points are rough estimations, based on area for the heat exchangers, and are calculated by normalizing various case studies performed in the literature (Buyano et al., 2011; Meyer et al., 2009). The component related heat exchanger environmental impacts associated with the non-heat exchanging areas are neglected due to their relatively small size and unavailability of the data.
Figure 6.26: Life cycle assessment of an air compressor using SimaPro 7.

Figure 6.27: Life cycle assessment of electrolyzer using SimaPro 7.
The environmental impact rate of a component can be calculated with respect to the environmental impacts associated with its production and operational time. 

\[ \dot{Y}_k = \frac{Y_k}{N \cdot n} \]  \hspace{1cm} (6.68)

where \( N \) is the annual number of operation hours for the unit, and \( n \) is the equipment lifetime. Impact points for the major components of the Cu-Cl cycle are listed in Table 6.5.

**Table 6.5: Environmental impact correlations (Eco-indicator 99) developed.**

<table>
<thead>
<tr>
<th>Component</th>
<th>( \dot{Y} ) (mPts/h)</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>0.387</td>
<td>( m_{steam} )</td>
</tr>
<tr>
<td>Copper oxychloride</td>
<td>0.00675</td>
<td>( m_{Cu_2OCl_2} )</td>
</tr>
<tr>
<td>decomposition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrolysis</td>
<td>0.456</td>
<td>( W_{elec} )</td>
</tr>
<tr>
<td>Spray dryer</td>
<td>0.0240</td>
<td>( m_{CuCl_2(aq)} )</td>
</tr>
<tr>
<td>HEX 1</td>
<td>0.000537</td>
<td>( A_{HEX1} )</td>
</tr>
<tr>
<td>HEX 2</td>
<td>0.00693</td>
<td>( A_{HEX2} )</td>
</tr>
<tr>
<td>HEX 3</td>
<td>0.0645</td>
<td>( A_{HEX3} )</td>
</tr>
<tr>
<td>HEX 4</td>
<td>0.000895</td>
<td>( A_{HEX4} )</td>
</tr>
<tr>
<td>HEX 5</td>
<td>0.0138</td>
<td>( A_{HEX5} )</td>
</tr>
<tr>
<td>HEX 6</td>
<td>0.0803</td>
<td>( A_{HEX6} )</td>
</tr>
<tr>
<td>HEX 7</td>
<td>0.0127</td>
<td>( A_{HEX7} )</td>
</tr>
<tr>
<td>HEX 8</td>
<td>0.00136</td>
<td>( A_{HEX8} )</td>
</tr>
<tr>
<td>HEX 9</td>
<td>0.000552</td>
<td>( A_{HEX9} )</td>
</tr>
<tr>
<td>HEX HU1</td>
<td>0.000808</td>
<td>( A_{HEXHU1} )</td>
</tr>
<tr>
<td>HEX HU2</td>
<td>0.0159</td>
<td>( A_{HEXHU2} )</td>
</tr>
<tr>
<td>HEX CU1</td>
<td>0.00631</td>
<td>( A_{HEXCU1} )</td>
</tr>
<tr>
<td>HEX CU2</td>
<td>0.000803</td>
<td>( A_{HEXCU2} )</td>
</tr>
<tr>
<td>HEX CU3</td>
<td>0.000261</td>
<td>( A_{HEXCU3} )</td>
</tr>
<tr>
<td>HEX CU4</td>
<td>0.000674</td>
<td>( A_{HEXCU4} )</td>
</tr>
<tr>
<td>Compressor</td>
<td>0.0492</td>
<td>( W_{comp} )</td>
</tr>
<tr>
<td>Expansion valve</td>
<td>(8.69 \times 10^{-7})</td>
<td>( m_{CuCl_2(aq)} )</td>
</tr>
<tr>
<td>Pump - 1</td>
<td>0.000168</td>
<td>( W_{Pump1} )</td>
</tr>
<tr>
<td>Pump - 2</td>
<td>0.000103</td>
<td>( W_{Pump2} )</td>
</tr>
</tbody>
</table>

6.4.3 Environmental Impact Accounting

Environmental impact balances for each component are needed to be solved in order to estimate the environmental impact rate of exergy destruction in each component. Implementing environmental impact balance equations for each component, together with the auxiliary equations, form a system of linear equations as follows:
\[ [\dot{E}x_k] \times [b_k] = [\dot{Y}_k] \]  

6.4.4 Exergoenvironmental Evaluation

Exergoeconomic evaluation is performed by means of the exergoeconomic factor and relative cost difference (Equations 5.16 and 5.17). Also, the total cost rate provides the component with the highest priority from an exergoeconomic viewpoint and is the combination of the cost rate of exergy destruction and the investment cost rates.

\[ \dot{C}_{tot,k} = \dot{C}_{D,k} + \dot{Y}_k \]

6.5 Optimization for the Cu-Cl cycle

The optimization of an energy system consists of modifying the system structure and component design parameters according to one or more specified design objectives. Multiple objectives are generally involved in a design process: thermodynamic (e.g. maximum efficiency, minimum fuel consumption), economic (e.g. maximum profit, minimum cost) and environmental (e.g. minimum GHGs emission). Multi-objective optimization is used to find the optimal set of design variables that satisfies the pre-set objectives (Toffolo and Lazzaretto, 2002; Ahmadi et al., 2011).

6.5.1 Objective Functions

Three objective functions considered in this study for multi-objective optimization are exergy efficiency (to be maximized), the total cost rate of product (to be minimized) and the total environmental impact rate (to be minimized), and are compared against single-objective optimizations of these objectives. Consequently, the objective functions in the
A four-step Cu-Cl cycle can be expressed through Equations 6.71-6.73. Even though each objective function varies in terms of the objective it is optimizing, they all have the same underlying parameters which are affected by the changes in the selected decision variables. It should be noted that all the objectives in the multi-objective optimization are assumed to be equally important, and therefore no additional weighting criteria are assigned to the objectives in order to minimize subjectivity in the analysis. Instead, the LINMAP (linear programming technique for multidimensional analysis of preference) method is used, where the point on the Pareto frontier closest to an ideal unreachable point (where all selected objectives are optimized) is selected as the single best optimization point.

**Objective Function 1: Exergy Efficiency**

\[
\eta_{ex} = \frac{\dot{m}_{H_2} \times \text{ex}_{ch,H_2}}{\dot{W}_{total} + \dot{Ex}_{Qtotal}} \tag{6.71}
\]

where the inputs are power inputs (electrolyzer, compressor and pumps), and heat input (HEX-HU1, HEX-HU2 and copper oxychloride decomposition reactor) (refer to Section 6.2 and 7.2).

**Objective Function 2: Total Cost Rate**

\[
\dot{C}_{total} = \dot{Z} + \dot{C}_{dest} \tag{6.72}
\]

where the total cost rates of the system consists of the total investment cost and cost of exergy destruction, respectively (refer to Section 6.3).

**Objective Function 3: Total Environmental Impact Rate**

\[
\dot{B}_{total} = \dot{Y} + \dot{B}_{dest} \tag{6.73}
\]

where the total environmental impact of the system consists of the component related environmental impact and the impact associated with exergy destruction, respectively (refer to Section 5.4). The environmental impact points are determined from LCA conducted using SimaPro 7 along with various correlations developed from the data available in the literature.

### 6.5.2 Decision Variables and Constraints

In this study, the following five decision variables are chosen for the analysis:
• the hydrolysis reactor (Step 1) temperature ($T_{S1}$)
• the copper oxychloride reactor (Step 2) temperature ($T_{S2}$)
• the electrolyzer (Step 3) temperature ($T_{S3}$)
• the spray dryer (Step 4) temperature ($T_{S4}$)
• the electrolyzer pressure ($P_{S3}$)

Note that in the field of engineering, optimization constraints on the trade-off decision variables that arise from appropriate feasibility, commercial availability and engineering constraints (Sayyaadi and Nejatolahi, 2011). The limitations on the minimum and maximum ranges of decision variables are given in Table 6.6.

Table 6.6: Constraints associated with the decision variables selected for the Cu-Cl cycle.

<table>
<thead>
<tr>
<th>Constraints</th>
</tr>
</thead>
<tbody>
<tr>
<td>370 °C ≤ $T_{S1}$ ≤ 410 °C</td>
</tr>
<tr>
<td>510 °C ≤ $T_{S2}$ ≤ 550 °C</td>
</tr>
<tr>
<td>65 °C ≤ $T_{S3}$ ≤ $T_{S4}$</td>
</tr>
<tr>
<td>$T_{S3}$ ≤ $T_{S4}$ ≤ 85 °C</td>
</tr>
<tr>
<td>2000 kPa ≤ $P_{S3}$ ≤ 2500 kPa</td>
</tr>
</tbody>
</table>

The constraints for the temperatures are due to design of the heat exchanger network, as well as reaction temperatures. The pressure of the electrolyzer is selected to be in the range of 20-25 atm, since the cell voltage is more stable at high pressure (Figure 6.28). The disadvantage of raising the pressure is to increase the work input to the electrolyzer.

6.5.3 Artificial Neural Network (ANN)

Decision variables are correlated with the objective functions using artificial neural network. The training function selected is the Levenberg-Marquardt algorithm and sigmoid transfer function as suggested elsewhere (Priddy and Keller, 2005) for networks with a few hundred datasets or less. The neural network toolbox in the MATLAB software is used to develop the ANN structure. The number of datasets used to develop the ANN is 216, and these are obtained using Aspen Plus and EES software. 80% of these patterns are used for training, while 5% and 15% are used for validation and testing, respectively.
The training of the network is accomplished by adjusting the weights and is carried out through training sets and training cycles (epochs). The goal of the learning procedure is to find the optimal set of weights, which in an ideal case produce the proper output for any input. The output of the network is compared with a desired response to produce an error. The performance of the network is measured in terms of a desired signal and the criterion for convergence. For one sample, the absolute fraction of variance ($R^2$) is determined as follows (Akdağ et al., 2009):

$$ R^2 = 1 - \frac{\sum_i (t_i - o_i)^2}{\sum_i (o_i)^2} $$

where $t$ is the target value and $o$ is the output value.

### 6.6 Energy and Exergy Analyses of the Cu-Cl Based Integrated Systems

Mass, energy, entropy and exergy balances are needed to be written in order to determine heat input, rate of entropy generation and exergy destructions as well as the energy and exergy efficiencies of the integrated systems.
In this study, mass, energy and entropy balances are developed for each component of the integrated systems first to conduct an exergy analysis. Aspen Plus simulation results are used for energy requirements of the four-step Cu-Cl cycle.

The energy and exergy efficiencies of the integrated System I are defined as follows:

\[
\eta_{en} = \frac{m_{H_2} \times LHV_{H_2} + \dot{W}_{net} + \dot{Q}_{cooling} + \dot{m}_{air} \times (h_{air} - h_{air,0}) + \dot{m}_{hotwater} \times (h_{hotwater} - h_{water,0})}{m_{htf} \times (h_1 - h_{12})} \quad (6.75)
\]

\[
\eta_{ex} = \frac{E_{xH_2} + \dot{W}_{net} + \dot{E}_{xQ_{cooling}} + \dot{m}_{air} \times (ex_{air} - ex_{air,0}) + \dot{m}_{hotwater} \times (ex_{hotwater} - ex_{water,0})}{m_{htf} \times (ex_1 - ex_{12})} \quad (6.76)
\]

where \( \dot{W}_{net} = \dot{W}_{net,STC} - \dot{W}_{in,CuCl} \)

The energy and exergy efficiencies of the integrated System II are defined as follows:

\[
\eta_{en} = \frac{m_{H_2} \times LHV_{H_2} + \dot{Q}_{cooling} + \dot{m}_{air} \times (h_{air} - h_{air,0}) + \dot{m}_{hotwater} \times (h_{hotwater} - h_{water,0})}{m_{htf} \times (h_1 - h_{12}) + \dot{W}_{in,CuCl}} \quad (6.77)
\]

\[
\eta_{ex} = \frac{E_{xH_2} + \dot{E}_{xQ_{cooling}} + \dot{m}_{air} \times (ex_{air} - ex_{air,0}) + \dot{m}_{hotwater} \times (ex_{hotwater} - ex_{water,0})}{m_{htf} \times (ex_1 - ex_{12}) + \dot{W}_{in,CuCl}} \quad (6.78)
\]

The energy and exergy efficiencies of the integrated System III are defined as follows:

\[
\eta_{en} = \frac{m_{H_2} \times LHV_{H_2} + \dot{W}_{net} + \dot{Q}_{cooling} + \dot{m}_{air} \times (h_{air} - h_{air,0}) + \dot{m}_{hotwater} \times (h_{hotwater} - h_{water,0})}{m_{htf} \times (h_1 - h_{12})} \quad (6.79)
\]

\[
\eta_{ex} = \frac{E_{xH_2} + \dot{E}_{xQ_{cooling}} + \dot{m}_{air} \times (ex_{air} - ex_{air,0}) + \dot{m}_{hotwater} \times (ex_{hotwater} - ex_{water,0})}{m_{htf} \times (ex_1 - ex_{12})} \quad (6.80)
\]

where \( \dot{W}_{net} = \dot{W}_{net,STC} + \dot{W}_{net,GTC} - \dot{W}_{in,CuCl} \)

6.7 Exergoeconomic Analysis for the Integrated Systems

Exergoeconomic analysis described in Section 5.2.2 is applied to the Cu-Cl based integrated systems. Cost balance equations are used for each subsystem. Unit costs of the main streams of the integrated systems are found via cost accounting, and exergoeconomic evaluation is performed. State points in Tables 6.6, 6.7 and 6.8, and also in equations 6.75-6.82 are consistent with the points in Figures 4.6, 4.7 and 4.8.
6.7.1 Exergoeconomic analysis of System I

The fuel and product exergies for subsystems of the integrated System I can be seen in Table 6.7.

Table 6.7: Fuel and product definitions with respect to the System I.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fuel</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam turbine cycle</td>
<td>( \dot{E}x_3 - \dot{E}x_4 )</td>
<td>( \dot{W}<em>{stc} + (\dot{E}x</em>{20} - \dot{E}x_{21}) )</td>
</tr>
<tr>
<td>Four-step Cu-Cl cycle</td>
<td>( \dot{E}x_5 - \dot{E}x_8 )</td>
<td>( \dot{m}<em>{52} \cdot ex</em>{ch,H_2} + (\dot{m}<em>{51} \cdot ex</em>{ch,O_2}) )</td>
</tr>
<tr>
<td>Absorption cooling system</td>
<td>( \dot{E}x_0 - \dot{E}x_{10} )</td>
<td>( \dot{E}x_{41} - \dot{E}x_{42} )</td>
</tr>
<tr>
<td>Drying air</td>
<td>( \dot{E}x_{37} - \dot{E}x_{38} )</td>
<td>( \dot{E}x_{46} - \dot{E}x_{45} )</td>
</tr>
<tr>
<td>Water heating</td>
<td>( \dot{E}x_{20} - \dot{E}x_{21} )</td>
<td>( \dot{E}x_{48} - \dot{E}x_{47} )</td>
</tr>
</tbody>
</table>

The cost balance equations for the integrated System I are written as follows:

For the steam turbine cycle and water heating

\[
\dot{c}_3 - \dot{c}_4 + \dot{Z}_{stc} = (\dot{c}_{48} - \dot{c}_{47}) + c_{stc} \cdot \dot{W}_{stc} \tag{6.81}
\]

\[
c_3 = c_4 \quad \text{(F rule)}
\]

\[
\frac{\dot{c}_{48} - \dot{c}_{47}}{(\dot{E}x_{48} - \dot{E}x_{47})} = c_{stc} \quad \text{(P rule)}
\]

For the four-step Cu-Cl cycle

\[
\dot{c}_5 - \dot{c}_8 + \dot{Z}_{Cu-Cl} = (c_{H_2} \cdot \dot{m}_{52} \cdot ex_{ch,H_2}) + (c_{O_2} \cdot \dot{m}_{51} \cdot ex_{ch,H_2}) \tag{6.82}
\]

\[
c_5 = c_8 \quad \text{(F rule)}
\]

\[
\frac{\dot{c}_{H_2}}{\dot{E}x_{H_2}} = \frac{\dot{c}_{O_2}}{\dot{E}x_{O_2}} \quad \text{(P rule)}
\]

For the absorption cooling system and drying air

\[
\dot{c}_9 - \dot{c}_{10} + \dot{Z}_{ACS} = (\dot{c}_{41} - \dot{c}_{42}) + (\dot{c}_{46} - \dot{c}_{45}) \tag{6.83}
\]

\[
c_9 = c_{10} \quad \text{(F rule)}
\]

\[
\frac{(\dot{c}_{42} - \dot{c}_{41})}{(\dot{E}x_{42} - \dot{E}x_{41})} = \frac{(\dot{c}_{46} - \dot{c}_{45})}{(\dot{E}x_{46} - \dot{E}x_{45})} \quad \text{(P rule)}
\]

6.7.2 Exergoeconomic analysis of System II

The fuel and product exergies for subsystems of the integrated System II can be seen in Table 6.8.
Table 6.8: Fuel and product definitions with respect to the System II.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fuel</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>The four-step Cu-Cl cycle</td>
<td>$(\dot{E}x_1 - \dot{E}x_4)$</td>
<td>$(\dot{m}<em>{28} \cdot ex</em>{ch,H_2}) + (\dot{m}<em>{27} \cdot ex</em>{ch,O_2})$</td>
</tr>
<tr>
<td>Absorption cooling system</td>
<td>$(\dot{E}x_4 - \dot{E}x_5)$</td>
<td>$(\dot{E}x_{17} - \dot{E}x_{18})$</td>
</tr>
<tr>
<td>Drying air</td>
<td>$(\dot{E}x_{13} - \dot{E}x_{14})$</td>
<td>$(\dot{E}x_{22} - \dot{E}x_{21})$</td>
</tr>
<tr>
<td>Water heating</td>
<td>$(\dot{E}x_5 - \dot{E}x_6)$</td>
<td>$(\dot{E}x_{23} - \dot{E}x_{24})$</td>
</tr>
</tbody>
</table>

The cost balance equations for the integrated System II are written as follows:

**For the four-step Cu-Cl cycle**

$$\dot{C}_1 - \dot{C}_4 + \dot{Z}_{Cu-Cl} = (\dot{C}_{H_2} \cdot \dot{m}_{28} \cdot ex_{ch,H_2}) + \dot{C}_{O_2} \cdot \dot{m}_{27} \cdot ex_{ch,H_2}$$  \hspace{1cm} (6.84)

$$c_5 = c_8 \text{ (F rule)}$$

$$\frac{\dot{C}_{H_2}}{Ex_{H_2}} = \frac{\dot{C}_{O_2}}{Ex_{O_2}} \text{ (P rule)}$$

**For absorption cooling system and drying air**

$$\dot{C}_4 - \dot{C}_5 + \dot{Z}_{ACS} = (\dot{C}_{18} - \dot{C}_{17}) + (\dot{C}_{22} - \dot{C}_{21})$$  \hspace{1cm} (6.85)

$$c_4 = c_5 \text{ (F rule)}$$

$$\frac{(\dot{C}_{18} - \dot{C}_{17})}{(Ex_{18} - Ex_{17})} = \frac{(\dot{C}_{22} - \dot{C}_{21})}{(Ex_{22} - Ex_{21})} \text{ (P rule)}$$

**For water heating**

$$\dot{C}_5 - \dot{C}_6 + \dot{Z}_{WH} = \dot{C}_{24} - \dot{C}_{23}$$  \hspace{1cm} (6.86)

$$c_5 = c_6 \text{ (F rule)}$$

**6.7.3 Exergoeconomic analysis of System III**

The fuel and product exergies for subsystems of the integrated System III are presented in Table 6.9. The cost balance equations for the integrated System I are given as follows:

**For the four-step Cu-Cl cycle**

$$\dot{C}_3 - \dot{C}_6 + \dot{Z}_{Cu-Cl} = (\dot{C}_{H_2} \cdot \dot{m}_{52} \cdot ex_{ch,H_2}) + \dot{C}_{O_2} \cdot \dot{m}_{51} \cdot ex_{ch,H_2}$$  \hspace{1cm} (6.87)

$$c_5 = c_8 \text{ (F rule)}$$

$$\frac{\dot{C}_{H_2}}{Ex_{H_2}} = \frac{\dot{C}_{O_2}}{Ex_{O_2}} \text{ (P rule)}$$
Table 6.9: Fuel and product definitions with respect to the System III.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fuel</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>The four-step Cu-Cl cycle</td>
<td>$(\dot{E}x_3 - \dot{E}x_6)$</td>
<td>$(\dot{m}<em>{64} \cdot ex</em>{ch,H_2}) + (\dot{m}<em>{63} \cdot ex</em>{ch,O_2})$</td>
</tr>
<tr>
<td>Gas turbine unit</td>
<td>$(\dot{E}x_7 - \dot{E}x_8)$ + $\dot{m}<em>{64} \cdot ex</em>{ch,CH_4}$</td>
<td>$W_{gtu} + (\dot{E}x_{58} - \dot{E}x_{59}) + (\dot{E}x_{59} - \dot{E}x_{60})$</td>
</tr>
<tr>
<td>Steam turbine cycle</td>
<td>$(\dot{E}x_{58} - \dot{E}x_{59})$</td>
<td>$W_{stc} + (\dot{E}x_{20} - \dot{E}x_{21})$</td>
</tr>
<tr>
<td>Absorption cooling system</td>
<td>$(\dot{E}x_9 - \dot{E}x_{10})$</td>
<td>$(\dot{E}x_{41} - \dot{E}x_{42})$</td>
</tr>
<tr>
<td>Drying air</td>
<td>$(\dot{E}x_{37} - \dot{E}x_{38})$</td>
<td>$(\dot{E}x_{46} - \dot{E}x_{45})$</td>
</tr>
<tr>
<td>Water heating</td>
<td>$(\dot{E}x_{59} - \dot{E}x_{60}) + (\dot{E}x_{20} - \dot{E}x_{21})$</td>
<td>$(\dot{E}x_{50} - \dot{E}x_{49}) + (\dot{E}x_{48} - \dot{E}x_{47})$</td>
</tr>
</tbody>
</table>

For gas turbine unit, HRSG and water heating

$$\dot{c}_7 - \dot{c}_8 + (c_{CH_4} \cdot \dot{m}_{61} \cdot ex_{ch,CH_4}) + Z_{GTU} = (\dot{c}_{58} - \dot{c}_{59}) + (\dot{c}_{59} - \dot{c}_{60}) + c_{gtu} \cdot W_{GTU}$$  \(6.88\)

c_7 = c_8 (F rule)

$$\frac{(\dot{c}_{58} - \dot{c}_{59})}{(\dot{E}x_{58} - \dot{E}x_{59})} = c_{stc} \ (P \ rule)$$

$$\frac{(\dot{c}_{59} - \dot{c}_{60})}{(\dot{E}x_{59} - \dot{E}x_{60})} = c_{stc} \ (P \ rule)$$

For steam turbine cycle and water heating

$$\dot{c}_{58} - \dot{c}_{59} + Z_{STC} = (\dot{c}_{48} - \dot{c}_{47}) + c_{stc} \cdot W_{STC}$$ \(6.89\)

c_{58} = c_{59} (F rule)

$$\frac{(\dot{c}_{48} - \dot{c}_{47})}{(\dot{E}x_{48} - \dot{E}x_{47})} = c_{stc} \ (P \ rule)$$

For absorption cooling system and drying air

$$\dot{c}_9 - \dot{c}_{10} + Z_{ACS} = (\dot{c}_{41} - \dot{c}_{42}) + (\dot{c}_{46} - \dot{c}_{45})$$ \(6.90\)

c_9 = c_{10} (F rule)

$$\frac{(\dot{c}_{42} - \dot{c}_{41})}{(\dot{E}x_{42} - \dot{E}x_{41})} = \frac{(\dot{c}_{46} - \dot{c}_{45})}{(\dot{E}x_{46} - \dot{E}x_{45})} \ (P \ rule)$$

6.8 Optimization of the Cu-Cl Based Integrated Systems

Multi-objective optimization of the integrated systems (System I, II and III) is performed with the help of genetic algorithms. The main subsystem, i.e. the four-step Cu-Cl cycle, has been already optimized (Section 7.5). For the remaining subsystems, which are steam
turbine cycle, absorption cooling system and gas turbine unit; optimized decision variables are obtained from the literature. Exergoeconomic optimization of the LiBr-H₂O absorption cooling system is performed by Misra et al. (2005). Optimized decision variables are given in Table 6.10. The third column “multi-objective exergoeconomic” shows the decision variables when multi-objective optimization with respect to total cost rate and exergy efficiency is conducted.

Table 6.10: Optimized values for the LiBr-H₂O absorption cooling system.

<table>
<thead>
<tr>
<th>Decision Variable</th>
<th>Base Case Design</th>
<th>Multi-Objective Exergoeconomic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condenser Temperature (°C)</td>
<td>35</td>
<td>34.8</td>
</tr>
<tr>
<td>Evaporator Temperature (°C)</td>
<td>7</td>
<td>8.8</td>
</tr>
<tr>
<td>Generator Temperature (°C)</td>
<td>80</td>
<td>88.8</td>
</tr>
<tr>
<td>Absorber Temperature (°C)</td>
<td>40</td>
<td>31</td>
</tr>
</tbody>
</table>

The optimized steam turbine cycle data is obtained from Baghernejad and Yaghoubi, 2011; Nezamellah et al., 2010. The high pressure turbine inlet pressure and temperature are 9000 kPa and 500°C, respectively. For the gas turbine unit, results of Tsatsaronis and Moran, 1997 are used. Exergoeconomic optimization results showed that the pressure ratio is 5.77; regenerator exit temperature is 637.2°C; turbine inlet temperature is 1190°C.

The multi-objective optimization of Systems I, II and III is conducted by altering the outputs of each subsystems in order to find the optimum amount of outputs (such as hydrogen, power, cooling etc.) for maximum efficiency and minimum cost rates. In this regard, objective functions are selected to be exergy efficiency (to be maximized) and total cost rate (to be minimized). Decision variables for the integrated systems are presented in Table 6.11.

Table 6.11: Decision variables for the integrated systems.

<table>
<thead>
<tr>
<th>Decision Variable</th>
<th>System I</th>
<th>System II</th>
<th>System III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily hydrogen production</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Power output</td>
<td>+</td>
<td>NA</td>
<td>+</td>
</tr>
<tr>
<td>Cooling</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Water heating</td>
<td>NA</td>
<td>+</td>
<td>NA</td>
</tr>
</tbody>
</table>
The primary constraints for both systems are heat transfer fluid temperatures. The lowest exit temperature of molten salt for Systems I and III is set to be 250°C, which is 30°C higher than the melting point of the molten salt. The lowest temperature of water (as heat transfer fluid) for System II is set to be 350°C, which is design temperature of cooling water of SCWR.

6.9 Exergetic Life Cycle Assessment of the Integrated Systems

ExLCA impact analysis focuses on the determination of the exergies of flows, and the exergy destructions and exergy efficiencies of the overall process and its subprocesses. Exergetic LCA is applied to the Cu-Cl based integrated systems. Exergy analysis in Section 6.6 is used to perform ExLCA. Results are presented in Section 7.9.
CHAPTER 7: RESULTS AND DISCUSSION

In this chapter, detailed results of the exergy, exergoeconomic and exergoenvironmental analyses and the corresponding optimizations are provided for the proposed four-step Cu-Cl cycle. Thermodynamic and thermoeconomic results for the Cu-Cl based integrated systems are also provided.

7.1 Simulation Results of the Four-Step Cu-Cl Cycle

In this section, simulation results of the hydrolysis reactor and the four-step Cu-Cl cycle are presented.

7.1.1 Results for Hydrolysis Reactor

As explained in Section 6.1.1, the RGibbs reactor block is used for the simulation of the hydrolysis reactor. Simulation results show that heat input of the hydrolysis reactor is 100.2 MJ per kmol hydrogen produced at a reactor temperature of 390°C. As mentioned earlier, the steam to copper molar ratio is simulated to be 16 for 100% yield of Cu₂OCl₂ at 1 atm reactor pressure. Figures 7.1 shows the variations of percentage yield of Cu₂OCl₂ and percentage consumption of input CuCl₂ with steam to copper molar ratio. The simulation results presented in Figure 7.1 are for 1 atm reactor pressure and 390°C reaction temperature. Figure 7.1 shows that a full conversion of CuCl₂ to Cu₂OCl₂ occurs when the steam to copper molar ratio is 16. Figure 7.2 is based on a literature study and presented for comparison. The variation of Cu₂OCl₂ percentage yield with the steam to copper molar ratio under different reactor pressure (0.4, 0.7 and 1 atm) is presented in Figure 7.3.

Simulations show that decreasing the reactor pressure to 0.7 atm reduces the excess steam requirement for the full conversion of Cu₂OCl₂. The steam to copper molar ratio reduces to 10 for a reactor pressure of 0.4 atm. Therefore, hydrolysis reactor pressure is selected to be 0.4 atm.

The effect of the reactor temperature to the Cu₂OCl₂ yield is also investigated at 0.4 atm reactor pressure (Figure 7.4). The results show that the ideal temperature is 390°C with a steam to copper molar ratio of 10 to get 100% yield of Cu₂OCl₂. Complete
conversion of CuCl$_2$ to Cu$_2$OCl$_2$ can be achieved at lower temperatures (e.g. 375°C) when the flow rate of the excess steam is increased (e.g. when the steam to copper ratio is 12). A lower steam to copper ratio, however, requires a higher reactor temperature for 100% yield of Cu$_2$OCl$_2$.

Figure 7.1: Variations of the Cu$_2$OCl$_2$ yield and Cu Cl$_2$ consumption with steam to copper molar ratio.

Figure 7.2: Variations of the Cu$_2$OCl$_2$ yield with steam to copper molar ratio (Orhan, 2011).

**Reducing Steam to Copper Molar Ratio: Advantages and disadvantages**

In the hydrolysis reactor, the steam to copper ratio can be reduced by decreasing reactor pressure which forces a design change (addition of a compressor to the Cu-Cl cycle) as
explained in section 6.1. Decreasing the steam to copper ratio is crucial when it comes to integration of the individual reactors with respect to: (i) economics, (ii) thermal management and (iii) molar concentration of HCl.

Figure 7.3: Variations of the Cu₂OCl₂ yield with steam to copper molar ratio for various pressures (0.4, 0.7 and 1 atm).

Figure 7.4: Variations of the Cu₂OCl₂ yield with temperature for various steam to copper molar ratios (8, 10 and 12).

**Economics:** Input steam for the hydrolysis reactor affects the equipment sizing within the Cu-Cl cycle, such as the hydrolysis reactor, some of the heat exchangers and the spray dryer. The capital cost of the Cu-Cl cycle is, therefore, directly associated with the steam to copper molar ratio. For example, the number of hydrolysis reactors is
determined based on steam residence time as explained in Section 6.3.2. When the steam to copper molar ratio is 17 at 1 atm, the number of vertical reactor vessels for hydrolysis is 16 (Ferrandon et al., 2008). The number of vertical vessels is reduced to 13 for a reactor pressure of 0.4 atm. Purchase equipment cost correlations showed that each reactor has a bare module cost of $1.28M. In this regard, the capital cost can be decreased with the reduction in steam to copper ratio.

**Thermal management:** The heat exchanger network in Section 6.1.3 shows that the thermal energy for increasing the temperature of the H$_2$O from the electrolyzer temperature to hydrolysis reaction temperature (70°C to 390°C) (including dryer heat requirement) is mainly provided by the steam and HCl mixture exiting the hydrolysis reactor. However, there is heat loss (as a function of heat exchanger effectiveness) to the environment during this heat transfer. A higher steam to copper ratio leads to more heat loss to the surroundings. Figure 7.5 shows the heat loss to the environment (MW) as a function of steam to copper molar ratio and heat exchanger effectiveness.

**Molar concentration of HCl:** The molarity of HCl is very important for the conversion of CuCl to CuCl$_2$ in the electrolysis reaction (hydrogen production step). Increasing the molarity of HCl will increase the hydrogen production. The molarity of HCl is affected by the steam exiting the hydrolysis reactor, since the steam and HCl mixture is one output of the hydrolysis. When the steam to copper ratio is 17, the molarity of the HCl is approximately 3 M, and it is over diluted. Since, experiments are still in progress for the molarity of HCl as 6 – 11 M (Naterer et al., 2013). The molarity of HCl is approximately 5 M for the steam to copper ratio of 10, which should also be improved. Thus, reducing the steam to copper ratio increases the hydrogen production in the electrolysis step.

### 7.1.2 Results for the Four-Step Cu-Cl Cycle

The simulation results of the Aspen Plus model presented in Figure 6.13 are shown in Table 7.1 and 7.2. Table 7.1 shows the heat and work input for the components of the Cu-Cl cycle per kmol hydrogen produced. The spray dryer is the most energy intensive process due to the high steam flow rate. The electrolyzer and compressor power consumptions are the highest.
Figure 7.5: Variations of heat loss with heat exchanger effectiveness and steam to copper molar ratio.

Table 7.1: Heat and work inputs for the components of the Cu-Cl cycle per kmol hydrogen produced

<table>
<thead>
<tr>
<th>Component</th>
<th>Heat Input (MJ)</th>
<th>Work Input (MJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>100</td>
<td>N/A</td>
</tr>
<tr>
<td>Copper oxychloride decomposition</td>
<td>147</td>
<td>N/A</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>N/A</td>
<td>123</td>
</tr>
<tr>
<td>Spray dryer</td>
<td>673\textsuperscript{1}</td>
<td>11.3\textsuperscript{2}</td>
</tr>
<tr>
<td>Compressor</td>
<td>N/A</td>
<td>106</td>
</tr>
<tr>
<td>Pump - 1</td>
<td>N/A</td>
<td>1.12</td>
</tr>
<tr>
<td>Pump - 2</td>
<td>N/A</td>
<td>0.223</td>
</tr>
</tbody>
</table>

\textsuperscript{1}Heat input includes evaporation of the steam at stream number 30.
\textsuperscript{2}Work input of dryer is normalized from Orhan, 2011. Normalization criterion is the steam flow rate.

The mass and mole flow rates, enthalpy, entropy and exergy values are presented in Table 7.2. The results are based on the assumption that the Cu-Cl thermochemical water splitting plant produces 125 tons of hydrogen daily.
Table 7.2: Properties of the four-step Cu-Cl cycle streams.

<table>
<thead>
<tr>
<th>State No</th>
<th>P (kPa)</th>
<th>T (°C)</th>
<th>m (kg/s)</th>
<th>n (kmol/s)</th>
<th>h (kJ/kg)</th>
<th>s (kJ/kg·K)</th>
<th>ex (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>390</td>
<td>245</td>
<td>4.31</td>
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<td>2.884</td>
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<tr>
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<td>8.936</td>
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</tr>
<tr>
<td>3</td>
<td>40</td>
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<td>452</td>
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<td>6.57</td>
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</tr>
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<td>4</td>
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<td>298</td>
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<td>-10787</td>
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</tr>
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<td>10.51</td>
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<td>0.718</td>
<td>4591</td>
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</tr>
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<td>1.526</td>
</tr>
<tr>
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<td>0.9987</td>
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<td>100</td>
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<td>7.361</td>
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<td>-3945</td>
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</tr>
<tr>
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<td>100</td>
<td>283</td>
<td>245</td>
<td>4.31</td>
<td>-3873</td>
<td>2.637</td>
<td>162.5</td>
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</tbody>
</table>
7.1.3 Heat Exchanger Network Results

The heat exchanger network for the four-step Cu-Cl cycle built using Aspen Energy Analyzer is presented in Figure 6.10. The pinch temperature of the network is 100°C for the cold side, and 110°C for the hot side. The heat exchanger network showing the pinch line is presented in Figure 7.6.

The specifications of the heat exchanger network that is designed for the four-step Cu-Cl cycle are presented in Table 7.3. Cold and hot stream inlet and exit temperatures are given. The thermal heat transfer fluid (HTF) used in the analysis is molten salt if the thermal source is solar energy, or steam if the thermal source is nuclear waste energy. Thermal energy sources, however, are not limited to the aforementioned ones. A combination of thermal energy sources also can be used to supply heat to the Cu-Cl cycle. In this case, hot utility, here, is used to heat copper oxychloride from hydrolysis reactor temperature (390°C) to copper oxychloride decomposition reactor temperature (530°C) (streams 8 and 9 in Figure 6.11). Also, 2(CuCl₂·2H₂O) is heated up to 390°C from 283.3°C by means of a hot utility. The heat input of Step 2 (copper oxychloride decomposition) is also provided by the hot utility. This heat flow is not shown in the heat exchanger network figures.

Figure 7.6: Heat exchanger network showing pinch line.
Table 7.3: The specifications of the heat exchangers in the four-step Cu-Cl cycle.

<table>
<thead>
<tr>
<th>Heat Exchanger</th>
<th>Hot Stream</th>
<th>( T_{in} ) (°C)</th>
<th>( T_{out} ) (°C)</th>
<th>Cold Stream</th>
<th>( T_{in} ) (°C)</th>
<th>( T_{out} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEX-1</td>
<td>( \text{O}_2 )</td>
<td>320.0</td>
<td>139.3</td>
<td>( 16\text{H}_2\text{O} )</td>
<td>99.63</td>
<td>104.7</td>
</tr>
<tr>
<td>HEX-2</td>
<td>( \text{CuCl} )</td>
<td>348.0</td>
<td>124.7</td>
<td>( 16\text{H}_2\text{O} )</td>
<td>104.7</td>
<td>150.5</td>
</tr>
<tr>
<td>HEX-3</td>
<td>( \text{HCl (aq)} )</td>
<td>350.1</td>
<td>209.0</td>
<td>( 16\text{H}_2\text{O} )</td>
<td>150.5</td>
<td>300.0</td>
</tr>
<tr>
<td>HEX-4</td>
<td>( \text{O}_2 )</td>
<td>530.0</td>
<td>320.0</td>
<td>( 16\text{H}_2\text{O} )</td>
<td>300.0</td>
<td>305.8</td>
</tr>
<tr>
<td>HEX-5</td>
<td>( \text{CuCl} )</td>
<td>530.0</td>
<td>348.0</td>
<td>( 16\text{H}_2\text{O} )</td>
<td>305.8</td>
<td>390.0</td>
</tr>
<tr>
<td>HEX-6</td>
<td>( \text{HCl (aq)} )</td>
<td>209.0</td>
<td>109.8</td>
<td>( 2(\text{CuCl}_2.2\text{H}_2\text{O}) )</td>
<td>99.63</td>
<td>202.3</td>
</tr>
<tr>
<td>HEX-7</td>
<td>( \text{HCl (aq)} )</td>
<td>390.0</td>
<td>350.1</td>
<td>( 2(\text{CuCl}_2.2\text{H}_2\text{O}) )</td>
<td>202.3</td>
<td>283.3</td>
</tr>
<tr>
<td>HEX-8</td>
<td>( \text{HCl (aq)} )</td>
<td>109.8</td>
<td>109.8</td>
<td>( 2(\text{CuCl}_2.10\text{H}_2\text{O}) )</td>
<td>70.40</td>
<td>80.00</td>
</tr>
<tr>
<td>HEX-9</td>
<td>( \text{CuCl} )</td>
<td>124.7</td>
<td>97.48</td>
<td>Feed ( \text{H}_2\text{O} )</td>
<td>25.00</td>
<td>67.60</td>
</tr>
<tr>
<td>HEX-HU1</td>
<td>Thermal HTF</td>
<td>650.0</td>
<td>625.3</td>
<td>( \text{Cu}_2\text{OCl}_2 )</td>
<td>390.0</td>
<td>530.0</td>
</tr>
<tr>
<td>HEX-HU2</td>
<td>Thermal HTF</td>
<td>400.0</td>
<td>350.0</td>
<td>( 2(\text{CuCl}_2.2\text{H}_2\text{O}) )</td>
<td>283.3</td>
<td>390.0</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>( \text{HCl (aq)} )</td>
<td>524.0</td>
<td>390.0</td>
<td>( \text{Hydrolysis} )</td>
<td>389.0</td>
<td>391.0</td>
</tr>
<tr>
<td>HEX-Dryer</td>
<td>( \text{HCl (aq)} )</td>
<td>109.8</td>
<td>109.0</td>
<td>( 2(\text{CuCl}_2.10\text{H}_2\text{O}) )</td>
<td>87.6</td>
<td>99.60</td>
</tr>
<tr>
<td>HEX-CU1</td>
<td>( \text{HCl (aq)} )</td>
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<td>69.7</td>
<td>Cooling Water</td>
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<td>21.52</td>
</tr>
<tr>
<td>HEX-CU2</td>
<td>( \text{CuCl} )</td>
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<td>70.00</td>
<td>Cooling Water</td>
<td>21.65</td>
<td>21.90</td>
</tr>
<tr>
<td>HEX-CU3</td>
<td>( \text{O}_2 )</td>
<td>139.3</td>
<td>35.00</td>
<td>Cooling Water</td>
<td>21.52</td>
<td>21.65</td>
</tr>
<tr>
<td>HEX-CU4</td>
<td>( \text{H}_2 )</td>
<td>70.00</td>
<td>35.00</td>
<td>Cooling Water</td>
<td>21.90</td>
<td>22.00</td>
</tr>
</tbody>
</table>

7.2 Energy and Exergy Analyses of the Four-Step Cu-Cl Cycle

An exergy model of the four-step Cu-Cl cycle based on simulation results is developed in the Engineering Equation Solver (EES). Balance equations provided in Section 6.2 are applied to determine exergy destructions of each component.

Figure 7.7 shows the exergy destruction (per kmol hydrogen produced) associated with each component of the four-step Cu-Cl cycle. The highest exergy destruction occurs at the electrolyzer. Decreasing the work input of the electrolyzer helps to reduce the exergy destruction rate at this step. Cell voltage, formulated in Equation 6.3, has to be reduced to decrease the electrical work input. Thermochemical reactors also have higher exergy destructions, 77.4 and 65.9 MJ for hydrolysis and copper oxychloride decomposition reactors, respectively. Figure 7.7 also indicates that heat exchanger 5 has the highest irreversibility among other heat exchangers.
Figure 7.7: Exergy destruction (per kmol H₂) of each component in the four-step Cu-Cl cycle.

The energy efficiency for the Cu-Cl cycle based on lower heating value becomes

\[ \eta_{en} = \frac{m_{25} \times LHV_{H_2}}{\dot{W}_{total} + Q_{total}} \]  \hspace{1cm} (7.1)

where the total power input is defined as

\[ \dot{W}_{total} = \dot{W}_{elec} + \dot{W}_{comp} + \dot{W}_{dry} + \dot{W}_{P1} + \dot{W}_{P2} \]  \hspace{1cm} (7.2)

Here, the power components cover electrolysis, compressor, spray dryer and pumps’ power. The total heat transfer rate then becomes

\[ \dot{Q}_{total} = \dot{Q}_{S2} + \dot{Q}_{\text{HEX-HU1}} + \dot{Q}_{\text{HEX-HU2}} \]  \hspace{1cm} (7.3)

The heat inputs to the cycle are heat requirements of Step 2 (copper oxychloride decomposition), HEX-HU1 and HEX-HU2. As explained earlier, heat required by Step 1 (Hydrolysis) is provided by the heat recovery within the cycle. \( LHV_{H_2} \) is 120 MJ/kg.

The exergy efficiency for the Cu-Cl cycle based on lower heating value is as follows:
\[ \eta_{\text{ex}} = \frac{m_{25} \times e_{x_{\text{ch},H_2}}}{W_{\text{total}} + E_{x_{\text{total}}}} \]  

(7.4)

where \( E_{x_{\text{total}}} \) is the exergy content of the heat input, \( e_{x_{\text{ch},H_2}} \) is chemical exergy of the hydrogen and its value is 118 MJ/kg.

The energy efficiency of the four-step Cu-Cl cycle is 55.4\% and exergy efficiency is calculated to be 66.0\%. In previous studies, heat to work conversion efficiency of 50\% is assumed when defining the energy efficiency of the cycle. The efficiency of the four-step is calculated to be 35.7\% when heat to work conversion efficiency is taken into account.

A comparison of the energy efficiency for the four-step Cu-Cl cycle calculated in this research with the efficiency values available in the literature is as follows:

- 54\% has been demonstrated from Aspen Plus simulations for the Cu–Cl cycle by Argonne National Lab (Lewis et al., 2005). It is, however, stated by Naterer et al. (2009) that 43\% efficiency would be more realistic.
- Orhan (2011) calculated the efficiency of the four-step Cu-Cl cycle as 43.8\%. Although the calculation performed is for the four-step Cu-Cl cycle, the configuration of the cycle is different. Further details are given in Orhan (2011).

### 7.3 Exergoeconomic Analysis

The exergy analysis is provided in the previous section to gain a further understanding regarding irreversibilities within components of the Cu-Cl cycle. This analysis, however, does not provide any information about economic constraints, cost of irreversibilities and component related costs. An exergoeconomic analysis, therefore, is carried out so that the cost formation can be determined for the Cu-Cl cycle. Table 7.4 shows the specific cost, cost flow rate and exergy flow rate of each stream in the four-step Cu-Cl cycle. Specific costs of streams are calculated by solving cost balance equations presented in Section 6.3.1.

The assumptions for the exergoeconomic analysis are given as follows: (i) The maintenance factor is 1.06 (Bejan et al., 1996), and (ii) The material factor is taken as 1.06, since a porcelain coating over carbon steel is used due to the acidic environment within the cycle (Ferrandon et al., 2008).
Table 7.4: Exergy rate, cost rate and specific cost of flows.

<table>
<thead>
<tr>
<th>State No</th>
<th>$\dot{E}_x$ (MW)</th>
<th>$\dot{C}$ ($/s$)</th>
<th>c ($$/kJ)$</th>
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<td>0.001891</td>
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<tr>
<td>2</td>
<td>123.6</td>
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<td>3</td>
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</tr>
<tr>
<td>4</td>
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<td>444.5</td>
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<tr>
<td>5</td>
<td>221.9</td>
<td>446.5</td>
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<td>178.9</td>
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<td>139.7</td>
<td>281</td>
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<tr>
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<td>0</td>
<td>0</td>
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<td>0.001925</td>
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<tr>
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<td>0.002072</td>
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<td>0.002144</td>
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<td>280</td>
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<tr>
<td>31-2</td>
<td>39.76</td>
<td>85.43</td>
<td>0.002148</td>
</tr>
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</table>
In addition, the following assumptions are made:

- The interest rate is 5% (Parametric studies are conducted for different interest rates).
- The equipment lifetime is selected to be 15 years (Parametric studies are also conducted).
- The plant capacity factor is taken as 0.85.
- The unit cost of electricity is taken as 0.09 $/kWh (Toronto, Hydro, 2012) (Parametric studies are conducted).
- The unit cost of thermal energy is taken as 0.02 $/kWh based on 2005 statistics (Ferrandon et al., 2008). The value is then normalized for 2012 (Parametric studies are conducted).

The cost rate of hydrogen (state 25) is calculated to be 4.878 $/s for 1.45 kg/s hydrogen mass flow rate. Hence, the unit cost of hydrogen is calculated to be 3.36 $/kg hydrogen produced. The cost estimate of the Argonne National Lab (ANL) is 3.30 $/kg hydrogen (Lewis et al., 2009a; Lewis et al., 2009b). The updated cost of ANL using CEPCI is found to be 3.6 $/kg hydrogen. Moreover, Orhan (2011) calculated the unit cost of the hydrogen production as 2.8 $/kg hydrogen. The updated value of the hydrogen cost is 2.73 $/kg. The 2012 value is lower than the 2011 hydrogen production value due to a decreasing cost index in 2012 (Chemical Engineering Journal, 2013).

Figure 7.8 shows the cost rate of exergy destruction for the various components of the four-step Cu-Cl cycle. The hydrolysis reactor is the component with the highest cost rate of exergy destruction.

The percentage of the equipment related costs for each component is presented in Figure 7.9. The hydrolysis reactor and compressor are the two most expensive components of the four-step Cu-Cl cycle.

Cost distribution among investment and exergy destruction rates for components with the greatest cost rates are presented in Figure 7.10. Figure 7.10 shows that costs associated with exergy destructions are dominant relative to component related costs.
Figure 7.8: Cost rate of exergy destruction for the four-step Cu-Cl cycle components.

Figure 7.9: Equipment related cost rate for the four-step Cu-Cl cycle components.

A sensitivity analysis is also conducted in order to determine the effects of the interest rate used in the analysis. Thus, variations of total cost flow rate with lifetime of the plant are investigated for various interest rates (Figure 7.11). Figure 7.12 shows the variations of total cost rate per kg hydrogen produced with plant daily capacity for three plant lifetimes (10, 15 and 20 years). The figure shows that the cost flow rate per kg hydrogen produced decreases with increasing plant lifetime. The cost flow rate per kg hydrogen produced is the lowest for a daily capacity of 100 tons.
Figure 7.10: Cost distributions among investment and exergy destruction rates.

Figure 7.11: Variations of total cost flow with lifetime of the Cu-Cl cycle for different interest rates.
Figure 7.12: Variations of cost flow per kg hydrogen produced with daily production capacity of the Cu-Cl cycle.

The exergoeconomic factors and relative cost differences of some major components of the four-step Cu-Cl cycle are presented in Table 7.5. Exergoeconomic factors indicate that the cost associated with exergy destruction is dominant over the component related cost for all major components, excluding the compressor and pumps. For components with a very low exergoeconomic factor, it would be worthwhile to consider improving the component efficiency by increasing the capital investment.

Variations of the exergoeconomic factor for the four-step Cu-Cl cycle with lifetime of the cycle for various interest rates is given in Figure 7.13. The exergoeconomic factor decreases with increasing lifetime of the cycle, as the unit cost for purchased equipment decreases.

The effect of unit electricity price on total cost flow rate and the exergoeconomic factor for the four-step Cu-Cl cycle is also investigated. Figure 7.14 shows that total cost flow dramatically increases with increasing electricity price, since cost related with the exergy destruction is dominant for the Cu-Cl cycle. Exergoeconomic factor, however, decreases with increasing electricity price. Similarly, Figure 7.15 presents the effects of
thermal energy price on total cost flow rate and exergoeconomic factor for the four-step Cu-Cl cycle.

Table 7.5: Exergoeconomic factors and relative cost differences of some major components of the four-step Cu-Cl cycle.

<table>
<thead>
<tr>
<th>Component</th>
<th>f (%)</th>
<th>RCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>0.06</td>
<td>0.4839</td>
</tr>
<tr>
<td>Copper oxychloride decomposition</td>
<td>0.37</td>
<td>105.5</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>1.59</td>
<td>236.5</td>
</tr>
<tr>
<td>Spray dryer, Hex 6 &amp; 8</td>
<td>0.45</td>
<td>0.0139</td>
</tr>
<tr>
<td>Compressor</td>
<td>52.87</td>
<td>0.0878</td>
</tr>
<tr>
<td>HEX 1</td>
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<tr>
<td>HEX 2</td>
<td>0.17</td>
<td>0.5935</td>
</tr>
<tr>
<td>HEX 3</td>
<td>0.31</td>
<td>0.2195</td>
</tr>
<tr>
<td>HEX 4</td>
<td>0.48</td>
<td>0.2107</td>
</tr>
<tr>
<td>HEX 5</td>
<td>0.03</td>
<td>-3.6</td>
</tr>
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<td>HEX 7</td>
<td>0.14</td>
<td>0.289</td>
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<td>HEX 9</td>
<td>0.27</td>
<td>2.255</td>
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<tr>
<td>Pump - 1</td>
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<td>1.622</td>
</tr>
<tr>
<td>Pump - 2</td>
<td>57.05</td>
<td>1.529</td>
</tr>
</tbody>
</table>

Figure 7.13: Variations of exergoeconomic factor of the four-step Cu-Cl cycle with lifetime for various interest rates.
Figure 7.14: Variations of exergoeconomic factor and cost flow rate of the four-step Cu-Cl cycle with electricity price.

Figure 7.15: Variations of exergoeconomic factor and cost flow rate of the four-step Cu-Cl cycle with thermal energy price.
7.4 Exergoenvironmental Analysis

The exergy analysis is provided in the previous section to gain a further understanding of the irreversibilities within components of the Cu-Cl cycle. This analysis, however, does not provide any information about environmental impact constraints, environmental impact of irreversibilities and component related environmental impacts. Exergoenvironmental analysis, therefore, is carried out for the four step Cu-Cl cycle to determine the locations of the associated environmental impact formations. Specific environmental impacts of streams are calculated by solving environmental impact balance equations presented in Section 6.4.1 simultaneously. Table 7.6 shows the specific environmental impact, environmental impact flow rate and exergy flow rate of each stream in the four-step Cu-Cl cycle.

The assumptions for the exergoeconomic are also valid for the exergoenvironmental analysis. Additional assumptions regarding the environmental impacts of energy sources are given as follows:

- The unit environmental impact of electricity is taken as 22 mPt/kWh (Eco-indicator 99 manual) (Parametric studies are conducted).

- The unit environmental impact of thermal energy is taken as 6mPt/kWh (SimaPro 7) (Parametric studies are conducted).

Figure 7.16 shows the environmental impact rate of exergy destruction for the four-step Cu-Cl cycle components. The hydrolysis reactor has the highest environmental impact rate percentage of exergy destruction (67%), which is followed by heat exchangers 5 and 3.

Figure 7.17 presents the component related environmental impact rate for the four-step Cu-Cl cycle components. The hydrolysis reactor and the electrolyzer are the components with the highest environmental impacts. Table 7.6 shows exergy flow rates, environmental impact flow rates and the unit environmental impact of flows.

Environmental impact distribution among investment and exergy destruction rates for components with the greatest rates are presented in Figure 7.18. Figure 7.18 shows that environmental impacts associated with exergy destructions are dominant compared to component related costs.
Table 7.6: Exergy flow rates, environmental impact flow rates and the unit environmental impact of flows.

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Some parametric studies are also conducted to evaluate the effect of lifetime, power and thermal sources. Figure 7.19 shows lifetime effect on total environmental impact rate and the exergoenvironmental factor. The higher the lifetime of the cycle, the
lower the environmental impact rate. The exergoenvironmental factor also decreases with lifetime, indicating that the ratio of environmental impact of exergy destruction, to component related environmental impact, increases.

Figure 7.16: Environmental impact rate of exergy destruction for the four-step Cu-Cl cycle components.

Figure 7.17: Component related environmental impact rate for the four-step Cu-Cl cycle components.
Figure 7.18: Environmental impact distributions among component related and exergy destruction rates for the four-step Cu-Cl cycle components.

Figure 7.19: Variations of environmental impact rate and exergoenvironmental factor with lifetime of the Cu-Cl plant.

Figure 7.20 shows the total environmental impact rate for the four-step Cu-Cl cycle using electricity generation mixed for various countries. Eco-indicator points per kWh are obtained using SimaPro 7. France has the most environmentally benign power
and hydrogen production among others, whereas impact rate for the power mix in Italy is the highest. Figure 7.21 shows the variation of exergoenvironmental factor and total environmental impact flow rate with environmental impact rate of the input thermal energy.

Figure 7.20: Total environmental impact rate for the four-step Cu-Cl cycle using electricity generation mixed for various countries.

Figure 7.21: Variations of exergoenvironmental factor and total environmental impact flow rate with environmental impact of input thermal energy.
7.5 Multi-objective Optimization

Multi-objective optimization with aforementioned objective functions (Equations 6.71-6.73), constraints (Table 6.5) and five decision variables, are performed with the help of genetic algorithms. In the analysis, five optimization scenarios with the objective functions of exergy efficiency (single-objective), total cost rate (single-objective), environmental impact rate (single-objective), along with exergoeconomic (multi-objective) and exergoenvironmental (multi-objective) optimizations, are performed. Figure 7.22 illustrates the performance of training of the artificial neural network (ANNO), which is built to correlate decision variables to objective functions, via regression results. Figure 7.22 shows that the regression results are satisfactory and the ANN can be used for the optimization.

Figure 7.22: Regression results for the ANN of the four-step Cu-Cl cycle.
The corresponding optimization scenarios can be seen in Figures 7.23-7.27. The number of generations for single objective optimization is selected to be 100, which is the default option of the optimization tool box. For multi-objective optimization, on the other hand, stopping criteria is selected to be 200 multiplied by decision variables. However, the figures are presented for the generations where the convergence criteria have met.

Figure 7.23: Single objective optimization of the four-step Cu-Cl cycle over generations with respect to exergy efficiency.

Figure 7.24: Single objective optimization of the four-step Cu-Cl cycle over generations with respect to total cost rate.
Figure 7.25: Single objective optimization of the four-step Cu-Cl cycle over generations with respect to total environmental impact rate.

Figure 7.26: Multi-objective optimization of the four-step Cu-Cl cycle with respect to exergy efficiency and total cost rate.

The optimization results show that the highest efficiency achieved is 68.3% (Figure 7.23), the lowest cost and environmental impact rates are 111 (Figure 7.24) and 22.7 (Figure 7.25), respectively.
As previously mentioned, all points on the Pareto frontier are potentially an optimum solution for the analysis and therefore a weighting factor is needed to be assigned for each objective and/or decision is needed to be made (often based on experience or importance of each objective) in order to select a single final solution among them. In this selection process, a traditional method called LINMAP decision-making (Yu, 1985) is used to select a desirable final solution as shown in Figures 7.26 and 7.27. This method creates a hypothetical ideal point in which all objectives have their corresponding optimum values independent of each other and would stay below the Pareto frontier. Even though this point would be impossible in reality, it would serve a useful purpose by assisting the decision makers to select the point on the Pareto frontier that has the closest distance to this ideal point as the desirable final solution (Sayyadi and Babaelahi, 2011).

![Figure 7.27: Multi-objective optimization of the four-step Cu-Cl cycle with respect to exergy efficiency and total environmental impact rate.](image)

Table 7.7 shows the values for the decision variables in the base case design along with the four different optimization criteria. Figure 7.28 shows the normalized value of the objectives with respect to each optimization criteria. It can be seen that each single objective optimization approach pays attention only to its own criterion without taking
others into consideration. Exergetic single-objective optimization scenario maximizes exergy efficiency; however no attention is paid to economic and environmental objectives. Similarly, exergoeconomic single-objective optimization scenario has the lowest unit costs for each component at the expense of exergy efficiency, and finally, exergoenvironmental single-objective optimization has the lowest Eco-indicator points. In multi-objective optimization, however, these objectives are considered simultaneously, which provides optimized solutions with values in between the extremes, yielded by the single-objective approaches, as a result of the trade-offs between the solutions of the two conflicting objectives.

Table 7.7: Decision variables for the base case design and four different optimization criteria.

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Figure 7.28: Normalized values of different objectives with respect to various optimization functions.
In summary, the four-step Cu-Cl cycle is optimized using a multi-objective evolutionary algorithm using exergoeconomic and exergoenvironmental objectives. The multi-objective optimization approach provides a solution set within extremes of the single-objective results by evaluating two objectives simultaneously trade-off between them to obtain desirable solution sets.

7.6 Energy and Exergy Analyses of the Integrated Systems

The results of the comprehensive thermodynamic analysis of the Cu-Cl based integrated multi-generation system are presented in this section. EES software is used to study the performance of the integrated systems and its components. The parametric studies are carried out by varying certain important system parameters. The assumptions considered throughout the analysis are listed as follows:

- Constant ambient temperature and pressure.
- Steady state operation.
- Adiabatic compressors, turbines and heat exchangers.
- Isentropic efficiency for turbines and compressors of 0.9.
- Heat exchanger effectiveness of 0.85 for all heat exchangers.
- Hydrogen storage and fuel cell unit is not included to thermodynamic calculations. Since, only steady state operations are considered.
- Efficiency values of heliostat solar tower and SCWR are not taken into account. Hence, inputs for both systems are considered to be the energy content of the heat transfer fluid.
- Heat capacity of the molten salt for System I and System III is calculated as (Bauer et al., 2013):

\[ C_p(J/g \cdot K) = 1.5404 + 3.0924 \times 10^{-5}T(\degree C) \]  

(7.5)

7.6.1 System I

Mass flow rates, enthalpy, entropy and exergy values of the integrated system I are presented in Table 7.8. Enthalpy, entropy and exergy of streams 1-12 are not shown due to calculations based on specific heat.
Table 7.8: State properties of the integrated System I.

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<th>s (kJ/kg·K)</th>
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Figure 7.29 shows the energy and exergy efficiencies of System I and its sub-units. The energy efficiency of the overall system is 71.0% whereas the exergy efficiency is 38.0%. However, if the heat released by the condenser of the steam turbine cycle is not utilized as hot water, the energy efficiency value would become 45.0% and the corresponding exergy efficiency is 36.1%. The COP of the absorption cooling system is 77.0% and the exergetic COP is 30.0%. The exergy efficiency of the Rankine cycle (STC) is greater than its energy efficiency, since exergy of output power is the power itself, even though exergy of input heat is lower than energy of the heat input.

![Energy and exergy efficiency of System I and its sub-units.](image)

Figure 7.29: Energy and exergy efficiency of System I and its sub-units.

Figure 7.30 shows the percentage contributions of System I and System II outputs to (a) total energy and (b) total exergy flows. The energy percentages of all outputs are close to each other. The exergy content of hydrogen dominates the System I exergy share,
and is 84%. Energy of cooling is defined as the amount of heat extracted from the cooling heat transfer fluid (water for both systems).

Figure 7.30: Percentage contributions of System I outputs to (a) total energy and (b) total exergy flow.

Figure 7.31 shows the impact of the heat exchanger effectiveness on energy and exergy efficiencies. Variations of efficiencies with “no hot water” cases are also presented. Both energy and exergy efficiencies increase with increasing effectiveness due to the reduction in the amount of energy loss to the environment.

Figure 7.31: Variations of energy and exergy efficiencies with heat exchanger effectiveness for System I.
7.6.2 System II

Mass flow rates, enthalpy, entropy and exergy values of the integrated system II are presented in Table 7.9. The energy and exergy efficiencies of the System II and its sub-units are shown in Figure 7.32. The overall energy efficiency of System II is 79% and the exergy efficiency is 35%. The absorption cooling system and the Cu-Cl cycle used in System II have similar efficiency values as the ones in System I.

Table 7.9: State properties of the integrated System II.

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Figure 7.33 presents the percentage contributions of System II outputs to flows of (a) total energy and (b) total exergy. The exergy of the output is 90% of total exergy.
output for System II. Similarly, energy of cooling is defined as the amount of heat extracted from the cooling heat transfer fluid (water for both systems).

![Energy and exergy efficiency of System II and its sub-units](image)

**Figure 7.32**: Energy and exergy efficiency of System II and its sub-units.

![Percentage contributions of System II outputs](image)

**Figure 7.33**: Percentage contributions of System II outputs to (a) total energy and (b) total exergy flow.

The effect of heat exchanger effectiveness on energy and exergy efficiencies of System II is presented in Figure 7.34, showing that utilizing the rejected heat out of the system as a system product as hot water significantly increases the energy efficiencies of the systems. Exergy efficiency results, however, are very close for the both “utilized hot water” and “no hot water” cases in both Systems I and II.
7.6.3 System III

Mass flow rates, enthalpy, entropy and exergy values of the integrated System III are presented in Table 7.10. Figure 7.35 presents the energy and exergy efficiencies of the System III and its sub-units. The overall energy efficiency of System III is calculated to be 75.9% and the exergy efficiency is 34.1%. The absorption cooling system, steam turbine and the Cu-Cl cycle used in System III have similar efficiency values as the ones in Systems I and II.

The percentage contributions of System III outputs to flows of (a) total energy and (b) total exergy are shown Figures 7.36. The power output of System III is shown as 0%, since the system is designed in a way that the power outputs of the steam turbine cycle and gas turbine unit is equal to power input of the Cu-Cl cycle. The exergy of the output hydrogen is 94% of total exergy output for System III. Similarly, the effect of heat exchanger effectiveness on energy and exergy efficiencies of System III is presented in Figure 7.37.

Figure 7.34: Variations of energy and exergy efficiencies with heat exchanger effectiveness for System II.
Table 7.10: State properties of the integrated System III.

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</tr>
<tr>
<td>56</td>
<td>637</td>
<td>555</td>
<td>562.1</td>
<td>0.8402</td>
<td>642.1</td>
<td>1.124</td>
</tr>
<tr>
<td>57</td>
<td>1315</td>
<td>527</td>
<td>572.2</td>
<td>1.564</td>
<td>548.6</td>
<td>1.288</td>
</tr>
<tr>
<td>58</td>
<td>890</td>
<td>101</td>
<td>572.2</td>
<td>1.652</td>
<td>12.34</td>
<td>1.228</td>
</tr>
<tr>
<td>59</td>
<td>180</td>
<td>101</td>
<td>572.2</td>
<td>0.5832</td>
<td>-802.1</td>
<td>1.061</td>
</tr>
<tr>
<td>60</td>
<td>55</td>
<td>101</td>
<td>572.2</td>
<td>0.2441</td>
<td>-933.5</td>
<td>1.043</td>
</tr>
<tr>
<td>61</td>
<td>25</td>
<td>1200</td>
<td>10.1</td>
<td>-6.339</td>
<td>-4659</td>
<td>2.301</td>
</tr>
</tbody>
</table>

Figure 7.35: Energy and exergy efficiency of System III and its sub-units.
Figure 7.36: Percentage contributions of System III outputs to (a) total energy and (b) total exergy flow.

Figure 7.37: Variations of energy and exergy efficiencies with heat exchanger effectiveness for System III.

7.7 Exergoeconomic Analysis of Cu-Cl Based Integrated Systems

An exergoeconomic analysis is carried out where the cost formation can be determined for the integrated systems. The results of the exergoeconomic analysis are provided in the following subsections. The unit cost of thermal energy for Systems I and III is taken as 0.02 $/kWh at year 2005 (Ferrandon et al., 2008). Unit cost of the heat transfer fluid for
the nuclear reactor is taken as 0.0024 $/MJ (Ansari et al., 2010). The unit cost values are then normalized for 2012. Parametric studies are conducted.

7.7.1 System I

Cost balance equations in Section 6.7.1 are solved for the System I. Table 7.11 shows the component related cost rate and cost rate of exergy destruction for subsystems of System I. The exergoeconomic factor of each subsystem is also presented in Table 7.11. Figure 7.38 (a) and (b) shows the percentages of component related cost and cost rate of exergy destruction for the subsystems of System I.

Table 7.11: Component related cost rate and cost rate of exergy destruction for subsystems of System I.

<table>
<thead>
<tr>
<th>Subsystem</th>
<th>Component Related Cost ((\dot{Z})) ($/s)</th>
<th>Cost Rate of Exergy Destructions ((\dot{C}_d)) ($/s)</th>
<th>Exergoeconomic Factor (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-step Cu-Cl cycle</td>
<td>0.718</td>
<td>1.36</td>
<td>0.346</td>
</tr>
<tr>
<td>STC</td>
<td>12.5</td>
<td>2.05</td>
<td>0.859</td>
</tr>
<tr>
<td>ACS</td>
<td>0.0158</td>
<td>0.214</td>
<td>0.0687</td>
</tr>
<tr>
<td>Total</td>
<td>13.2</td>
<td>3.62</td>
<td>0.785</td>
</tr>
</tbody>
</table>

A sensitivity analysis is also conducted in order to determine the effects of the interest rate used in the analysis. Thus, variations of the total cost flow rate and the exergoeconomic factor with lifetime of the plant are investigated with respect to various interest rates (Figures 7.39 and 7.40).

Figure 7.41 presents the effect of thermal energy price on total cost flow rate and exergoeconomic factor for the four-step Cu-Cl cycle. Total cost rate increases with increasing thermal energy price. Exergoeconomic factor, however, decreases since the component related cost does not change, but cost of exergy destruction increases.

7.7.2 System II

Exergoeconomic analysis of System II is conducted via cost balance equations given in Section 6.7.2. Table 7.12 presents the component related cost and cost rate of exergy destruction for subsystems of the integrated System II. Percentages of component related cost and cost rate of exergy destruction for the subsystems of System II are illustration in Figure 7.42 (a) and (b).
Figure 7.38: Percentages of component related cost (a), and cost rate of exergy destruction (b) for the subsystems of System I.

Figure 7.39: Variations of total cost rate with lifetime for System I for different interest rates.
Figure 7.40: Variations of exergoeconomic factor with lifetime for System I for different interest rates.

Figure 7.41: Variations of exergoeconomic factor and cost flow rate of the four-step Cu-Cl cycle with thermal energy price for System I.
Table 7.12: Component related cost rate and cost rate of exergy destruction for subsystems of System II.

<table>
<thead>
<tr>
<th>Subsystem</th>
<th>Component Related Cost ((\dot{Z})) ($/s)</th>
<th>Cost Rate of Exergy Destructions ((\dot{C}_d)) ($/s)</th>
<th>Exergoeconomic Factor (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-step Cu-Cl cycle</td>
<td>0.718</td>
<td>0.517</td>
<td>0.581</td>
</tr>
<tr>
<td>ACS</td>
<td>0.0240</td>
<td>0.160</td>
<td>0.130</td>
</tr>
<tr>
<td>Water Heating (WH)</td>
<td>0.00336</td>
<td>0.535</td>
<td>0.00624</td>
</tr>
<tr>
<td>Total</td>
<td>0.745</td>
<td>1.21</td>
<td>0.381</td>
</tr>
</tbody>
</table>

Figure 7.42: Percentages of component related cost (a), and cost rate of exergy destruction (b) for the subsystems of System II.

Figures 7.43 and 7.44 show the variation of total cost flow rate and exergoeconomic factor with lifetime of the plant are investigated with respect to various interest rates: 5% (base model), 2.5%, 7.5% and 10%. The figures indicate that impact of interest rate significantly increases with the system lifetime. The effect of thermal energy price on total cost rate and exergoeconomic factor of System II is presented in Figure 7.45. Total cost rate increases with increasing thermal energy price. Exergoeconomic factor, however, decreases with the cost of the thermal energy.
Figure 7.43: Variations of total cost rate with lifetime for System II for different interest rates.

Figure 7.44: Variations of exergoeconomic factor with lifetime for System II for different interest rates.
7.7.3 System III

Cost balance equations in Section 6.7.3 are solved for the System III. Table 7.13 shows the component related cost rate and cost rate of exergy destruction for subsystems of System III. Figure 7.46 (a) and (b) shows percentages of component related cost and cost rate of exergy destruction for the subsystems of System III. Similarly, Figures 7.47 and 7.48 show the variations of total cost flow rate and exergoeconomic factor with lifetime of the plant are investigated with respect to various interest rates.

Table 7.13: Component related cost rate and cost rate of exergy destruction for subsystems of System III.

<table>
<thead>
<tr>
<th>Subsystem</th>
<th>Component Related Cost Rate ($/s)</th>
<th>Cost Rate of Exergy Destruction ($/s)</th>
<th>Exergoeconomic Factor (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-step Cu-Cl cycle</td>
<td>0.718</td>
<td>1.28</td>
<td>0.359</td>
</tr>
<tr>
<td>GTU</td>
<td>0.0666</td>
<td>1.63</td>
<td>0.0393</td>
</tr>
<tr>
<td>STC</td>
<td>4.786</td>
<td>5.17</td>
<td>0.481</td>
</tr>
<tr>
<td>ACS</td>
<td>0.0133</td>
<td>0.159</td>
<td>0.077</td>
</tr>
<tr>
<td>Total</td>
<td>5.58</td>
<td>8.24</td>
<td>0.581</td>
</tr>
</tbody>
</table>
Figure 7.46: Percentages of component related cost (a), and cost rate of exergy destruction (b) for the subsystems of System III.

Figure 7.47: Variations of total cost rate with lifetime for System III for different interest rates.
The effect of thermal energy price on total cost rate and exergoeconomic factor of System III is presented in Figure 7.49. Exergoeconomic factor decreases with increasing energy price, since the impact of component related cost decreases.
7.8 Optimization of Cu-Cl Based Integrated Systems

Multi-objective optimization with exergy efficiency and total cost rate as objective functions, constraints as mentioned in Section 6.8 and three decision variables, are performed with the help of genetic algorithms for the Cu-Cl based integrated systems. In the analysis, three optimization scenarios with the objective functions of exergy efficiency (single-objective), total cost rate (single-objective), along with exergoeconomic (multi-objective) optimizations are performed. Similarly, the number of generations for single objective optimization is selected to be 100, which is the default option of the optimization tool box. For multi-objective optimization, on the other hand, stopping criteria is selected to be 200 multiplied by decision variables. However, the figures are presented in this section for the generations where the convergence criteria have met.

7.8.1 System I

The optimization scenarios can be seen in Figures 7.50-7.52. Optimization results show that the highest efficiency achieved is 47.4% (Figure 7.50), the lowest cost is 3.36 $/s (Figure 7.51). LINMAP optimized point indicates that the optimum exergy efficiency is 45.8% and total cost rate is 50.2 $/s (Figure 7.52).

![Figure 7.50: Single objective optimization of System I over generations with respect to exergy efficiency.](image-url)
Figure 7.51: Single objective optimization of System I over generations with respect to total cost rate.

Figure 7.52: Multi-objective optimization of System I with respect to exergy efficiency and total cost rate.

Table 7.14 shows the values for the decision variables in the base case design along with the different optimization criteria. Exergy efficiency and total cost rates for the baseline and optimized cases are provided in Figure 7.53.
Table 7.14: Decision variables for System I.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily hydrogen production (kg/day)</td>
<td>2.50×10⁵</td>
<td>9.62×10⁴</td>
<td>5.00×10⁴</td>
<td>5.82×10⁴</td>
</tr>
<tr>
<td>Cooling (kW)</td>
<td>2.00×10⁵</td>
<td>1.28×10⁵</td>
<td>1.0×10⁵</td>
<td>1.59×10⁵</td>
</tr>
<tr>
<td>Power output (kW)</td>
<td>3.50×10⁵</td>
<td>9.79×10⁵</td>
<td>1.0×10⁵</td>
<td>7.71×10⁵</td>
</tr>
</tbody>
</table>

Figure 7.53: Optimization results of System I with respect to exergy efficiency and total cost rate.

7.8.2 System II

The optimization scenarios for System II can be seen in Figures 7.54-7.56. Optimization results show that the highest efficiency achieved is 50.3% (Figure 7.54), the lowest cost is 0.611 $/s (Figure 7.55). LINMAP optimized point indicates that the optimum exergy efficiency is 45.3% and total cost rate is 1.18 $/s.

Table 7.15 shows the values for the decision variables in the base case design along with the different optimization criteria. Exergy efficiency and total cost rates for the baseline and optimized cases for System II are provided in Figure 7.57.
Figure 7.54: Single objective optimization of System II over generations with respect to exergy efficiency.

Figure 7.55: Single objective optimization of System II over generations with respect to total cost rate.

Table 7.15: Decision variables for System II.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily hydrogen production (kg/day)</td>
<td>2.50×10^5</td>
<td>2.97×10^5</td>
<td>5.00×10^4</td>
<td>1.77×10^5</td>
</tr>
<tr>
<td>Cooling (kW)</td>
<td>4.00×10^3</td>
<td>1.55×10^3</td>
<td>1.00×10^5</td>
<td>1.00×10^5</td>
</tr>
<tr>
<td>Water heating (kW)</td>
<td>3.50×10^3</td>
<td>1.12×10^3</td>
<td>1.00×10^5</td>
<td>1.00×10^5</td>
</tr>
</tbody>
</table>
7.8.3 System III

Figures 7.58-7.60 shows the optimization scenarios for System III. Optimization results show that the highest efficiency achieved is 49.12% (Figure 7.58), the lowest cost is 2.89 $/s (Figure 7.59). LINMAP optimized point indicates that the optimum exergy efficiency is 46.67% and total cost rate is 6.72 $/s (Figure 7.60).
Table 7.16 presents the values for the decision variables in the base case design along with the different optimization criteria. Exergy efficiency and total cost rates for the baseline and optimized cases for System III are provided in Figure 7.61.

Figure 7.58: Single objective optimization of System III over generations with respect to exergy efficiency.

Figure 7.59: Single objective optimization of System III over generations with respect to total cost rate.
Figure 7.60: Multi-objective optimization of System III with respect to exergy efficiency and total cost rate.

Table 7.16: Decision variables of System III.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily hydrogen production (kg/day)</td>
<td>2.50x10^5</td>
<td>2.15x10^5</td>
<td>5.00x10^4</td>
<td>1.61x10^5</td>
</tr>
<tr>
<td>Cooling (kW)</td>
<td>1.50x10^5</td>
<td>2.31x10^5</td>
<td>1.00x10^3</td>
<td>1.99x10^5</td>
</tr>
<tr>
<td>Power output (kW)</td>
<td>3.50x10^5</td>
<td>1.00x10^5</td>
<td>1.00x10^5</td>
<td>1.00x10^5</td>
</tr>
</tbody>
</table>

Figure 7.61: Optimization results of System III with respect to exergy efficiency and total cost rate.
7.9 Exergetic Life Cycle Assessment of the Cu-Cl Based Integrated Systems

ExLCA results of the integrated systems are presented in Figure 7.62-7.64. ExLCA allows us to better understand the irreversibilities within the systems over their life cycles. ExLCA of the integrated System I shows that the greatest irreversibility occurs at the heliostat solar plant. The absorption cooling system, however, has the lowest exergy efficiency.

Figure 7.62: Life cycle exergy diagram of the integrated System I.

Figure 7.63 presents ExLCA of the integrated System II. The greatest irreversibilities are caused by the nuclear side, the uranium processing and the operation of nuclear plant. The four-step Cu-Cl cycle has the highest exergy efficiency compared to other subsystems.

Life cycle exergy diagram of the Cu-Cl based integrated System III is presented in Figure 7.64. The main source of irreversibility of this integrated system is the solar plant. The gas turbine unit and the hydrogen plant using the Cu-Cl thermochemical cycle have the highest exergy efficiencies.
Figure 7.63: Life cycle exergy diagram of the integrated System II.

7.10 Comparison of the Integrated Systems

In this section the optimized Cu-Cl based integrated systems are compared with respect to energy and exergy efficiency and cost. Figure 7.65 shows the energy and exergy efficiency values of the exergoeconomically optimized integrated systems. System III as the highest energy efficiency (81.15%), System II has the lowest (67.42%). All three systems’ exergy efficiency values are close to each other; System III also has the highest exergy efficiency (46.65%).
Figure 7.64: Life cycle exergy diagram of the integrated System III.

Figure 7.65: Energy and exergy efficiency of the integrated systems.
Figure 7.6, on the other hand, presents the system efficiencies if the rejected heat from the systems cannot be utilized as drying air and hot water. System I has the highest exergy efficiency for this case (48.2%), whereas System III has the highest energy efficiency (50.7%).

![Energy and exergy efficiency of the integrated systems without water heating and drying air.](image)

Irreversibilities within each integrated systems and percentage contribution of subsystems to each integrated system can be observed in Figure 7.67. Steam turbine cycle is the primary cause for the irreversibilities within System I. The four-step Cu-Cl cycle is the dominant subsystem with respect to irreversibilities for System II. The four-step Cu-Cl cycle along with steam turbine cycle and gas turbine units are primary contributors to exergy destructions in System III.

The impact of component related cost and cost rate of exergy destruction to the total cost rate for the integrated systems is presented in Figure 7.68. The component related cost is the main contributor to the total cost rate for System I, whereas cost rate of exergy destruction is dominant for the integrated System III. For System II, however, equally distribution of the cost rates is observed.
Figure 7.67: Percentage contributions of each subsystem to exergy destructions for the integrated Systems I, II and III.

Figure 7.68: Impact of component related cost and cost rate of exergy destruction to the total cost rate for the integrated systems.
CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions
The production, transformation and use of energy have caused many environmental issues such as, acid rain, global warming and stratospheric ozone depletion. These environmental concerns, along with the economic and political implications of possible fossil-fuel shortages, have led to the search for alternative and cleaner energy technologies. One of the more prominent technologies is hydrogen. It appears to be capable of playing a significant role in improving environmental performance and sustainability, in part due to it not emitting greenhouse gases during oxidation. The objective of this thesis is to contribute to the development of the hydrogen production using the Cu-Cl cycle by developing integrated multi-generation systems.

In this thesis, three novel Cu-Cl based integrated systems are designed and introduced:

- System I: Solar tower with molten salt energy storage integrated with a steam turbine and LiBr-H$_2$O absorption cooling system.
- System II: Generation IV SCWR integrated with the Cu-Cl cycle and LiBr-H$_2$O absorption cooling system.
- System III: Solar tower with molten salt energy storage integrated with the Cu-Cl cycle, LiBr-H$_2$O absorption cooling system, gas turbine system and steam turbine cycle. The Cu-Cl cycle uses solar energy for its thermal energy requirement, while the steam turbine cycle is driven by the gas turbine system via energy content of exhaust gases.

Prior to integration of the Cu-Cl cycle with multi-generation systems, the four-step Cu-Cl cycle that is currently under experimental investigation at UOIT, is improved and optimized. A novel configuration of the four-step Cu-Cl cycle, reducing the excess steam requirements, is modeled in order to better understand and improve the system performance and efficiency. Steam requirement is decreased by decreasing the hydrolysis reactor pressure and the new design is successfully simulated in Aspen Plus simulation software. A heat exchanger network using Aspen Energy Analyzer is built for thermal
management within the cycle. Thermodynamic, economic and environmental analyses are then conducted for the simulated four-step Cu-Cl cycle using various engineering tools: exergy, cost analyses, life cycle assessment and exergoenvironmental and exergoeconomic analyses. Five optimization scenarios with the objective functions of exergy efficiency (single-objective), total cost rate (single-objective), environmental impact rate (single-objective), along with exergoeconomic (multi-objective) and exergoenvironmental (multi-objective) optimizations are performed.

Subsequently, the optimized four-step Cu-Cl cycle is integrated with three multi-generation systems. Thermodynamic and economic analyses of three integrated systems are performed. A multi-objective optimization study is carried out where the results from exergy and exergoeconomic analyses are used according to the developed objective functions and system constraints in order to optimize the system output parameters using Pareto Optimal optimization techniques. Optimized multi-generation systems are compared in terms of energy and exergy efficiency and total cost rate. Exergetic life cycle assessment is also performed to identify and locate the life cycle irreversibilities of each system.

Development, analysis and life cycle assessment of Cu-Cl based integrated systems reported in this thesis have allowed several concluding remarks to be drawn:

- Simulation results show that steam to copper molar ratio can be reduced to 10 from an initial value of 16 at 390°C and 0.4 atm.
- Heat exchanger network built in a way that heat requirements of drying and hydrolysis step is supplied using recovered heat.
- Hot utility is used for the thermal energy requirement of the copper oxychloride decomposition step, and to heat copper oxychloride from 390°C to 530°C and 2(CuCl$_2$.2H$_2$O) from 283.3°C to 390°C.
- Energy and exergy efficiency of the four-step Cu-Cl cycle is calculated to be 55.4% and 66.0%, respectively.
- Electrolysis is the step with highest exergy destruction followed by hydrolysis and copper oxychloride decomposition.
- The hydrolysis reactor is identified as the component with the highest total cost and environmental impact rate.
Exergoeconomic and exergoenvironmental analysis results showed that the rate of exergy destruction dominates the component related rates.

Under the baseline conditions, total cost rate and environmental impact rate are determined to be 165 $/s and 37.4 Pt/s.

Based on the single objective optimizations, it is determined that the exergy efficiency could be increased by up to 3.3% using exergy-based optimization, the cost can be reduced by up to 33% using cost-based optimization and the environmental impact rate can be reduced by up to 39% using environmental impact-based optimization, all at the expense of the non-optimized objectives.

Based on the exergoeconomic optimization, it is concluded that 0.8% higher exergy efficiency and 4.5% lower cost can be achieved, compared to baseline parameters.

Based on the exergoenvironmental optimization, 0.46% higher exergy efficiency and 30% lower environmental impact rate can be achieved.

Optimization results for the multi-generation systems show that the highest efficiency achieved is 47.4%, 50.3% and 49.2% for System I, II and III, respectively.

LINMAP optimized point indicates that the optimum exergy efficiency is 45.8%, 45.3% and 46.7% for System I, II and III, respectively.

Steam turbine cycle is the primary cause for the irreversibilities within System I. The four-step Cu-Cl cycle is the dominant subsystem with respect to irreversibilities for System II. The four-step Cu-Cl cycle along with steam turbine cycle and gas turbine units are primary contributors to exergy destructions in System III.

Component related cost is the main contributor to the total cost rate for System I, whereas cost rate of exergy destruction is the dominant one for the integrated System III. For System II, however, equal distribution of the cost rates is observed.

ExLCA results indicate that utilization of the energy sources are the main contributors to lifetime irreversibilities.
8.2 Recommendations

The results obtained from this thesis research also suggest several areas for future studies. The recommendations below should assist in understanding the thermodynamic losses through the cycle to overall improve efficiency, reduce product costs, and mitigate uncertainties. These improvements will yield better simulations that will facilitate future commercialization. The recommendations are summarized as follows:

- Further experimental studies on operating the hydrolysis reactor at partial pressure to reduce steam requirement are required in order to validate the results.
- Alternative ways to reduce steam to copper ratio in the hydrolysis reactor should be investigated to eliminate the compressor and corresponding power input.
- Experimental studies on integration of the individual steps should be carried out. The optimum steam to HCl ratio for both the hydrolysis reactor and the electrolysis requires further investigation.
- Experimental and theoretical studies on heat transfer coefficients of materials within the Cu-Cl cycle should be conducted to better size heat exchangers within the cycle and to improve both economic and environmental analyses.
- Further experimental studies on residence times of the materials in the reactors should also be studied in order to better estimate equipment sizing for economic and environmental analyses.
- Studies on activity coefficients of the chemicals in the electrolysis step are also required to better estimate cell voltage of the electrolyzer.
- Alternative novel Cu-Cl based integrated multi-generation systems should be designed and compared with the ones presented in this thesis. Integration of both nuclear and solar plants into a single integrated system should also be studied and compared.
- Hydrogen storage and conversion to electricity via fuel cell units linked with the Cu-Cl cycle should be studied with respect to thermodynamics, cost and environmental impact.
References


Nyoni B., 2011. “Simulation of the sulphur iodine thermochemical cycle”, Master Dissertation, Faculty of Engineering and Applied Science, the North-West University, South Africa, November.


APPENDIX A: ASPEN PLUS PROCESS SIMULATION SOFTWARE

Details on unit operation model types are presented in this appendix. Please note that following materials are adapted from Aspen Plus user guides (Aspen Technology, Inc., Cambridge, MA.).

In Aspen Plus simulation each block represent a unit operation model such as reactors, heat exchangers, pressure changers, mixers/splitters, separators, or even user defined models among others. These unit operating models perform specific functions based on feed input, thermodynamic models and operating conditions. The reactants, products or energy transfer within the unit operation models and interactions with the external environment take place through the material and energy streams. Major types of unit operation models are as follows:

A.1 Mixers and Splitters

This section describes the models that can be used to mix or split flowsheet streams. The Mixer unit operation model combines streams. FSplit and SSplit combine feed streams and then split the resulting stream, based on specifications.

Mixer combines material streams (or heat streams or work streams) into one outlet stream. If material streams are mixed, an optional water decant stream to decant free water from the outlet can be used. An outlet pressure or pressure drop for material streams can also be specified. The mixer model determines the combined outlet stream temperature and phase condition by performing an adiabatic phase equilibrium flash calculation on the composite feed streams. Mixer can be used to model mixing tees, or other types of stream mixing operations.

FSplit combines material streams (or heat streams or work streams) and divides the resulting stream into two or more outlet streams. All outlets have the same composition and properties. FSplit can be used to model flow splitters and purges or vents. Specifications for all but one outlet stream has to be provided. FSplit calculates the flowrate of the unspecified stream.

SSplit combines material streams and divides the resulting stream into two or more outlet streams. SSplit allows specification of streams with various substreams. The
splits of each substream, for all but one outlet stream have to be specified. SSplit calculates the flowrate of each substream in the unspecified outlet stream. SSplit can be used to perfectly separate a stream containing both liquid and solid phases into two streams each containing only one pure phase. SSplit can also be used to model other solid stream splitters, bleed valves, purges or vents.

A.2 Separators

The Separator Blocks, Sep and Sep2, combine feed streams and then split the resulting stream, based on your specifications. When the details of the separation are unknown or unimportant, Sep and Sep2 can be used instead of rigorous separation models (such as distillation or absorption models) to save computational time. The flash models, Flash2 and Flash3, determine the thermal and phase conditions of a mixture with one or more inlet streams. Heating or cooling curve tables for these models can be generated. The flash models represent single stage separators such as knock-out drums. They perform a phase equilibrium flash calculation based on your specifications. Adiabatic, isothermal and isobaric flashes, and dew or bubble points, are among the calculations these models perform.

Flash2 performs rigorous 2 (vapor-liquid) or 3 (vapor-liquid-liquid) phase equilibrium calculations. Flash2 produces one apor outlet stream, one liquid outlet stream, and an optional water decant stream. Flash2 can be used to model flashes, vaporators, knock-out drums, and anyother single-stage separators, with sufficient vapor disengagement space. Optionally, percentage of the liquid phase can be specified to be entrained in the vapor stream.

Flash3 performs rigorous 3 phase vapor-liquid-liquid equilibrium calculations, to produce one vapor outlet stream and two liquid outlet streams. Flash3 can be used to model any single-stage separator with sufficient vapor- liquid disengagement space as well as two liquid phase settling space. Entrainment of each liquid phase in the vapor stream can be specified. The vapor outlet stream can have a flow rate of zero for a decanter with no vapor- liquid disengagement.

Decanter models knock-out drums, decanters, and other single-stage separators with sufficient residence time for separation of two liquid phases but without a vapor
phase. Decanter determines the thermal and phase conditions of a mixture with one or more inlet streams, at the specified temperature or heat duty.

Sep combines inlet streams and separates the resulting stream into two or more streams, according to splits you specify for each component. The splits for each component in each substream can be specified. The Sep model can be used to represent component separation operations such as a distillation column when fractionation achieved or desired by the column is known but the details of the column energy balance are unknown or unimportant.

Sep2 combines inlet streams and separates the resulting stream into two outlet streams. Sep2 is similar to Sep, but offers a wider variety of specifications, such as component purity or recovery. These specifications make it even easier to represent component separation operations such as a distillation column when fractionation achieved or desired by the column is known but the details of the separation are unknown or unimportant.

A.3 Heat Exchangers

All heat exchangers determine the thermal and phase conditions of a mixture with one or more inlet streams. The heat exchanger models simulate the performance of heaters or two or multi stream heat exchangers. Heating or cooling curve tables can be generated for all models described in this section.

Heater performs these types of single phase or multiphase calculations:

- Bubble or dew point calculations
- Add or remove any amount of user specified heat duty
- Match degrees of superheating or subcooling
- Determine heating or cooling duty required to achieve a certain vapor fraction

Heater produces one outlet stream, with an optional water decant stream. The heat duty specification may be provided by a heat stream from another block. Heater can be used to model heaters or coolers (one side of a heat exchanger), valves when you know the pressure drop, pumps and compressors whenever you do not need work-related results. Heater can also be used to set or change the thermodynamic condition of a stream.
HeatX can perform shortcut or detailed rating calculations for most types of two-stream heat exchangers. The main difference between the two calculation methods is the procedure for the calculation of the overall heat transfer coefficient. The shortcut method always uses a user specified (or default) value for the overall heat transfer coefficient. The detailed method uses rigorous heat transfer correlations for film coefficients and combines the resistances due to shell and tube side films with the wall resistance to calculate the overall heat transfer coefficient. The geometry is needed to be known to use the detailed method.

MHeatX represents heat transfer between multiple hot and cold streams, as in an LNG exchanger. It can also model two-stream heat exchangers. An MHeatX block is divided into multiple heaters connected by heat streams. This configuration usually leads to faster flowsheet convergence. MHeatX does not use or calculate heat transfer coefficients, but it can calculate the overall UA for the exchanger and perform a detailed zone analysis.

HxFlux is used to perform heat transfer calculations between a heat sink and a heat source, using convective heat transfer. The driving force for the convective heat transfer is calculated as a function of log-mean temperature difference or LMTD. Variables among the inlet and outlet stream temperatures, duty, heat transfer coefficient, and heat transfer area can be specified. HxFlux calculates the unknown variable and determines the log mean temperature differences, using either the rigorous or the approximate method.

Hetran is the interface to the Aspen Hetran program for designing and simulating shell and tube heat exchangers with a wide variety of configurations. Aerotran is the interface to the Aspen Aerotran program for designing and simulating air-cooled heat exchangers with a wide variety of configurations.

A.4 Columns
The models for shortcut distillation are DSTWU, Distl, and SCFrac. DSTWU and Distl are for single columns. They can perform free-water calculations in the condenser and allow to use water decant streams to decant free water from the condenser. SCFrac performs shortcut distillation calculations for petroleum refining units, such as crude units and vacuum towers.
Aspen Plus provides five rigorous multistage separation models: RadFrac, MultiFrac, PetroFrac, BatchFrac and RateFrac. Extract is a rigorous model for simulating liquid-liquid extractors. It is appropriate only for rating calculations.

DSTWU performs a Winn-Underwood-Gilliland shortcut design calculation for a single-feed, two-product distillation column, with a partial or total condenser. For the specified recovery of the light and heavy key components, DSTWU estimates the minimum for either reflux ratio or number of theoretical stages. DSTWU estimates reflux ratio given the number of theoretical stages, number of theoretical stages given the reflux ratio, optimum feed stage location, and condenser and reboiler duties. DSTWU can produce tables and plots of reflux ratio versus number of stages.

Distl is a shortcut multicomponent distillation rating model. This model uses the Edmister approach to separate an inlet stream into two products. Number of theoretical stages, reflux ratio and overhead product rate must be specified. Distl estimates the condenser and reboiler duties. A partial or a total condenser also can be specified.

SCFrac models petroleum refining towers, such as crude units and vacuum towers. SCFrac performs shortcut distillation calculations for columns with a single feed, one optional stripping steam stream, and any number of products. SCFrac models an n-product refining tower with n−1 sections. Based on given product specifications and fractionation indices, SCFrac estimates product composition and flows, number of stages per section and heating or cooling duty for each section. SCFrac does not handle solids.

RadFrac is a rigorous model for simulating all types of multistage vapor-liquid fractionation operations. In addition to ordinary distillation, it can simulate absorption, reboiled absorption, stripping, reboiled stripping, and extractive and azeotropic distillation. RadFrac is suitable for three-phase systems, narrow-boiling and wide-boiling systems and systems exhibiting strong liquid phase nonideality. RadFrac can detect and handle a free-water phase or other second liquid phase anywhere in the column. Free water can be decanted from the condenser. RadFrac can handle solids on every stage. RadFrac can model columns where chemical reactions are occurring. Reactions can have fixed conversions, or they can be equilibrium, rate-controlled or electrolytic. RadFrac can model columns where two liquid phases exist and different chemical reactions occur in the two liquid phases. RadFrac can also model salt precipitation. RadFrac can operate in
rating mode or design mode. In rating mode RadFrac calculates temperature, flow rate and mole fraction profiles. These profiles are based on specified column parameters, such as reflux ratio, product rates, and heat duties. All rating mode flow specifications can be in mole, mass, or standard liquid volume units. Component or stage efficiencies can be specified. RadFrac accepts both Murphree and vaporization efficiencies. Murphree efficiencies can be manipulated to match plant performance. In design mode, temperatures, flow rates, purities, recoveries, or stream properties can be specified anywhere in the column. Examples of stream properties are volume flow and viscosity. All flow, flow ratio, composition, and recovery specifications in mole, mass, or standard liquid volume units can be specified. RadFrac has extensive capabilities for sizing and rating trays and packings. User can choose from several common tray types, and random and structured packings.

MultiFrac is a rigorous model for simulating general systems of interlinked multistage fractionation units. MultiFrac models a complex configuration consisting of any number of columns each with any number of stages, any number of connections between columns or within columns, and arbitrary flow splitting and mixing of connecting streams. MultiFrac can handle operations with side strippers, pumparounds, bypasses, external heat exchangers, single-stage flashes and feed furnaces. Typical MultiFrac applications include heat-integrated columns, such as Petlyuk towers, air separation column systems, absorber/stripper combinations and ethylene plant primary fractionators. MultiFrac can also be used for petroleum refining fractionation units, such as atmospheric crude units and vacuum units. But for these applications PetroFrac is more convenient to use. MultiFrac should only be used when the configuration is beyond the capabilities of PetroFrac. MultiFrac can detect a free-water phase in the condenser or anywhere in the column. It can decant the free-water phase on any stage. Although MultiFrac assumes equilibrium stage calculations, either Murphree or vaporization efficiencies can be specified. MultiFrac may be used for sizing and rating trays and packings. MultiFrac can model both random and structured packings.

PetroFrac is a rigorous model designed for simulating complex vapor-liquid fractionation operations in the petroleum refining industry. Typical operations include preflash tower, atmospheric crude unit, vacuum unit, FCC main fractionators, delayed
coker main fractionators and vacuum lube fractionators. PetroFrac can also be used to model the primary fractionator in the quench section of an ethylene plant. PetroFrac can model the feed furnace together with the fractionation towers and strippers in an integrated fashion. With this feature, it can easily analyze the effect of furnace operating parameters on tower performance. PetroFrac can detect a free-water phase in the condenser or anywhere in the column. It can decant the free-water phase on any stage. Although PetroFrac assumes equilibrium stage calculations, either Murphree or vaporization efficiencies can be specified. PetroFrac can be used to size and rate columns consisting of trays and/or packings. PetroFrac can model both random and structured packings.

RateFrac is a rate-based model for non-equilibrium separation. It simulates actual tray and packed columns, rather than idealized representations. RateFrac explicitly accounts for the interphase mass and heat transfer processes. It simulates single and interlinked columns involving vapor-liquid fractionation operations such as absorption, distillation, and stripping. RateFrac should be used for systems with both a vapor and a liquid phase (RateFrac can detect a free-water phase only in the condenser), nonreactive systems, reactive systems and electrolyte systems. RateFrac does not use empirical factors, such as efficiencies and the Height Equivalent of a Theoretical Plate (HETP). RateFrac treats separation as a mass and heat transfer rate process, instead of an equilibrium process. The degree of separation achieved between the contacting phases depends on the extent of mass and heat transfer between phases. The transfer rates between phases are strongly affected by the extent to which the phases are not in equilibrium. RateFrac assumes that thermodynamic equilibrium prevails only at the vapor-liquid interface separating the contacting phases.

BatchFrac is the unit operation model for batch distillation. It is a rigorous model for simulating multistage batch distillation columns. BatchFrac uses a robust and efficient algorithm to solve the unsteady-state heat and material balance equations that describe the behavior of batch distillation processes. Rigorous heat balances, material balances, and phase equilibrium relationships are applied at each stage. BatchFrac can handle a wide variety of batch distillation problems, including narrow-boiling, wide-boiling, highly non-ideal, three-phase and reactive. BatchFrac can detect the presence of a free-water phase in the condenser, or of any second liquid phase anywhere in the column. BatchFrac has complete flexibility in handling interstage decanters. BatchFrac should be used to simulate batch distillation
columns with equilibrium-controlled reactions or rate-controlled reactions. These reactions can occur on any stage, including the reboiler and condenser. BatchFrac assumes equilibrium stages are used (However, you can specify vaporization efficiencies.), there is constant liquid holdup and no vapor holdup and column hydraulics are not modeled.

Extract is a rigorous model for simulating liquid-liquid extractors. It is appropriate only for rating calculations. Extract can have multiple feeds, heater/coolers, and sidestreams. To calculate distribution coefficients, either an activity coefficient model or an equation of state capable of representing two liquid phases should be used.

A.5 Reactors

Chemical reactions occur under diverse conditions in many different types of equipment. Aspen Plus provides seven models for chemical reactor simulations: RStoic, RYield, REquil, RGibbs, RCSTR, RPlug and RBatch.

RStoic, RYield, RGibbs, and RCSTR can have any number of material feed streams, which are mixed internally. Heats of reaction are not required for any reactor model. Aspen Plus calculates heats of reaction using heats of formation. For RCSTR, RPlug, and RBatch, reaction kinetics information must be given using:

- The built-in power law model.
- A user-written Fortran subroutine (For more information, see Aspen Plus User Models).

RStoic models a reactor when (i) reaction kinetics are unknown or unimportant, (ii) stoichiometry is known and (iii) the extent of reaction or conversion can be specified. RStoic can handle reactions that occur independently in a series of reactors. It can also perform product selectivity and heat of reaction calculations.

RYield models a reactor by specifying reaction yields of each component. This model is useful when (i) reaction stoichiometry and kinetics are unknown and (ii) yield distribution data or correlations are available.

REquil models reactors when some or all reactions reach equilibrium. REquil can calculate single-phase chemical equilibrium, or simultaneous phase and chemical
equilibria. REquil calculates equilibrium by solving stoichiometric chemical and phase equilibrium equations.

RGibbs models single-phase chemical equilibrium, or simultaneous phase and chemical equilibria. The reactor temperature and pressure, or pressure and enthalpy must be specified. RGibbs minimizes Gibbs free energy, subject to atom balance constraints. This model does not require reaction stoichiometry. RGibbs can determine phase equilibrium without chemical reaction, particularly for multiple liquid phases. Any number of liquid phases are allowed. Solids in RGibbs can be modeled either as single condensed species and/or as solid solution phases.

RCSTR rigorously models a continuous-stirred tank reactor. The model can be used when (i) reaction kinetics are known, and (ii) the contents of the reactor have the same properties as the outlet stream. RCSTR can model equilibrium reactions simultaneously with rate-based reactions.

RPlug rigorously models plug flow reactors. A cooling stream around the reactor is optional. RPlug can be used to model reactors with cocurrent and countercurrent coolant streams. RPlug handles rate-based kinetic reactions only.

RBatch rigorously models batch or semi-batch reactors. Holding tanks are used to interface the batch reactor with the steady-state streams of an Aspen Plus simulation. For semi-batch reactors, a continuous vent and any number of continuous or delayed feeds can be specified. RBatch handles rate-based kinetic reactions only.

**A.6 Pressure Changers**

Pump and compressor models change pressures when energy-related information, such as power requirement, is needed or known. Free water can be decanted from the Pump or Compr products, or from the MCompr intercoolers. Pipeline calculates the pressure drop and heat transfer in a pipe segment or a pipeline. Pipeline can model any number of segments to describe the pipe geometry. Pipe calculates the pressure drop and heat transfer for a single pipe segment with fittings. Valve rigorously models the pressure drop in control valves.
Pump simulates a pump or hydraulic turbine. This model calculates either the power requirement or the power produced, given an outlet pressure specification. Pump can calculate the outlet pressure, given a power specification.

The Compr block can be used to simulate polytropic centrifugal compressor, polytropic positive displacement compressor, isentropic compressor and isentropic turbine. MCompr is used for multi-stage compressors. Power requirement is calculated or input. A Heater model can be used for pressure change calculations only. Compr is designed to handle both single and multiple phase calculations.

The MCompr block can be used to simulate multi-stage polytropic centrifugal compressor, multi-stage polytropic positive displacement compressor, multi-stage isentropic compressor and multi-stage isentropic turbine. MCompr can have an intercooler between each stage, and an aftercooler after the last stage. One-, two-, or three-phase flash calculations can be performed in the intercoolers. Each cooler can have a liquid knockout stream, except the cooler after the last stage. Intercooler specifications apply to all subsequent coolers. Rating can be done by specifying a compressor performance curve. This can be done by specifying dimensional curves (head versus flow and power versus flow) and dimensionless curves (head coefficient versus flow coefficient). Compr cannot handle performance curves for a turbine.

Any number of inlet work streams can be specified for pumps and compressors. One outlet work stream can be specified for the net work load from pumps or compressors. The net work load is the sum of the inlet work streams minus the actual (calculated) work.

The Valve block can be used to simulate control valves and pressure drop. The pressure drop across a valve is related to the valve flow coefficient. Flow is assumed to be adiabatic. Valve can perform single or multiple phase calculations. The effect of head loss from pipe fittings can be included. There are three types of calculations adiabatic flash for specified outlet pressure (pressure changer), valve flow coefficient for specified outlet pressure (design) and outlet pressure for specified valve (rating). Valve can check for choked flow. Cavitation index can be calculated.

The Pipe block calculates the pressure drop and heat transfer in a single pipe segment. The Pipeline block can be used for a multiple-segment pipe. Pipe can perform...
single or multiple phase calculations. If the inlet pressure is known, Pipe calculates the outlet pressure. If the outlet pressure is known, Pipe calculates the inlet pressure and updates the state variables of the inlet stream. Entrance effects are not modeled.

**A.7 Manipulators**

Stream manipulators modify or change stream variables for convenience. They do not represent real unit operations. Mult multiplies streams by a specified factor. The heat and material balances are not maintained. The outlet stream has the same composition and properties as the inlet. Dupl copies the inlet stream to any number of outlet streams. This model does not satisfy material and energy balances. Dupl is useful for simultaneously processing a given stream in different types of units. ClChng changes the class of streams between blocks and flowsheet sections. It copies substreams from the inlet stream to the corresponding substreams of the outlet stream. Selector is a switch between different inlet streams. Any number of streams may enter the block, and one designated stream from among these is copied to the outlet stream. The Selector block can be used with material, heat, or work streams.

**A.7 Solids**

Crystallizer models a mixed suspension, mixed product removal (MSMPR) crystallizer. It performs mass and energy balance calculations. Crusher simulates the breaking of solid particles. Screen simulates the separation of various sizes of solid particles in a mixture. Each of the two outlet streams contain particles of a more uniform size. Screen calculates the separation efficiency of the screen from the sizes of screen openings. FabFl simulates baghouse fabric filter units. Cyclone simulates cyclone separators. Cyclone separators remove solid particles from a gas stream using the centrifugal force of a gas vortex. VScrub simulates venturi scrubbers. Venturi scrubbers remove solid particles from a gas stream by direct contact with an atomized liquid stream. ESP simulates dry electrostatic precipitators. Dry electrostatic precipitators separate solids from a gaseous stream. HyCyc simulates hydrocyclones. Hydrocyclones separate solids from the inlet liquid stream by the centrifugal force of a liquid vortex. CFuge simulates centrifuge filters. Centrifuge filters separate liquids and solids by the centrifugal force of a rotating basket. Filter simulates continuous rotary vacuum filters. Filter assumes the separation efficiency
of the solids equals 1, so the outlet filtrate stream contains no residual solids. SWash models the separation of solid particles from an entrained liquid of a solids stream. SWash does not consider a vapor phase. CCD simulates a counter-current decanter or a multistage washer.

A.8 User Models

The Aspen Plus provides several methods for users to create their own unit operation models:
- Fortran
- Excel
- COM Models based on the CAPE-OPEN standard
- Exported Aspen Modeler flowsheets (from products such as Aspen Custom Modeler™ and Aspen Dynamics™)

These models can simulate any unit operation model. For each type of model, users write their own program or spreadsheet to calculate the values of outlet streams, based on the specified inlet streams and parameters.
APPENDIX B: CLASSIFICATION OF CAPITAL COST ESTIMATES

There are five generally accepted classifications of capital cost estimates that are most likely to be encountered in the process industries:

1. Derailed estimate
2. Definitive estimate
3. Preliminary estimate
4. Study estimate
5. Order-of-magnitude estimate

The information required to perform each of these estimates is provided in Table B.1.

Table B.1 Summary of Capital Cost Estimating Classifications

<table>
<thead>
<tr>
<th>Classification</th>
<th>Data:</th>
<th>Diagrams:</th>
<th>Note:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order-of-Magnitude (also known as Ratio or Feasibility) Estimate</td>
<td>This type of estimate typically relies on cost information for a complete process taken from previously built plants. This cost information is the adjusted using appropriate scaling factors, for capacity, and for inflation, to provide the estimated capital cost.</td>
<td>Normally requires only a block flow diagram.</td>
<td></td>
</tr>
<tr>
<td>Study (also known as Major Equipment or Factored) Estimate</td>
<td>This type of estimate utilizes a list of the major equipment found in the process. This includes all pumps, compressors and turbines, columns and vessels, fired heaters, and exchangers. Each piece of equipments roughly sized and approximate cost determined. The total cost of equipments then factored to give the estimated cost.</td>
<td>Based on PFD as described Chapter 1. Costs from generalized charts.</td>
<td>Most individual student designs are in this category.</td>
</tr>
<tr>
<td>Preliminary Design (also known as Scope) Estimate</td>
<td>This type of estimate requires more accurate sizing of equipment than used in the study estimate. In addition, approximate layout of equipment is made along with estimates of piping, instrumentation, electrical requirements. Utilities are estimated.</td>
<td>Based on PFD as described in Chapter 1. Includes vessel sketches for major equipment, preliminary plot plan, and elevation diagram.</td>
<td>Most large student group designs are in the category.</td>
</tr>
<tr>
<td>Definitive (also known as Project Control) Estimate</td>
<td>This type of estimate requires preliminary specifications for all the equipment, utilities, instrumentation, electrical, and off-sites.</td>
<td>Final PFD, vessel sketches, plot plan, and elevation diagrams, utilities balances, and a preliminary P&amp;ID.</td>
<td></td>
</tr>
<tr>
<td>Detailed (also known as Firm or Contractor’s) Estimate</td>
<td>This type of estimate requires complete engineering of the process and all related off-sites and utilities. Vendor quotes for all expensive items will have been obtained. At the end of a detailed estimate, the plant is ready to go to the construction stage.</td>
<td>Final PFD and P&amp;ID, vessel sketches utility balances, plot plan and elevation diagrams, and piping isometrics. All diagrams are required to complete the construction of the plant if it is built.</td>
<td></td>
</tr>
</tbody>
</table>
The accuracy range and the approximate cost for performing each class of estimate are given in Table B.2.

Table B.2 Classifications of Cost Estimates

<table>
<thead>
<tr>
<th>Class of Estimate</th>
<th>Level of Project Definition (as % of Complete Definition)</th>
<th>Typical Purpose of Estimate</th>
<th>Methodology (Estimating Method)</th>
<th>Expected Accuracy Range ( +/- Range Relative to Best Index of 1)</th>
<th>Preparation Effort (Relative to Lowest Cost Index of 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 5</td>
<td>0% to 2%</td>
<td>Screening or Feasibility</td>
<td>Stochastic or Judgment</td>
<td>4 to 20</td>
<td>1</td>
</tr>
<tr>
<td>Class 4</td>
<td>1% to 15%</td>
<td>Concept Study or Feasibility</td>
<td>Primarily Stochastic</td>
<td>3 to 12</td>
<td>2 to 4</td>
</tr>
<tr>
<td>Class 3</td>
<td>10% to 40%</td>
<td>Budget, Authorization, or Control</td>
<td>Mixed but Primarily Stochastic</td>
<td>2 to 6</td>
<td>3 to 10</td>
</tr>
<tr>
<td>Class 2</td>
<td>30% to 70%</td>
<td>Control or Bid/ Tender</td>
<td>Primarily Deterministic</td>
<td>1 to 3</td>
<td>5 to 20</td>
</tr>
<tr>
<td>Class 1</td>
<td>50% to 100%</td>
<td>Check Estimate or Bid/ Tender</td>
<td>Deterministic</td>
<td>1</td>
<td>10 to 100</td>
</tr>
</tbody>
</table>

In Table B.2, the accuracy range associated with each class of estimate and the costs associated with carrying out the estimate are ranked relative to the most accurate class of estimate (Class 1). In order to use the information in Table B.2, it is necessary to know the accuracy of a Class 1 estimate. For the cost estimation of chemical plant, a Class 1 estimate (detailed estimate) is typically +6% to -4% accurate. This means that by doing such an estimate, the true cost of building the plant would likely be in the range of 6% higher than and 4% lower than estimated price. Likewise, the effort to prepare a Class 5 estimate for a chemical process is typically in the range of 0.015% to 0.30% of the total installed cost of the plant.

The capital cost estimates are essentially paper-and-pencil studies. The cost of making an estimate indicates the personnel hours required in order to complete the estimate. From Table B.2, the trend between the accuracy of an estimate and the cost of the estimate is clear. If greater accuracy is required in the capital cost estimate, then more time and money must be expended in conducting the estimate. This is the direct result of the greater detail required for the more accurate estimating techniques. This research
focuses on the preliminary and study estimation classification. This approach provides estimates accurate in the range of +40% to -25%.