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Process analysis and simulation of solar thermochemical hydrogen generation

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PROCESS ANALYSIS AND SIMULATION OF SOLAR THERMOCHEMICAL
HYDROGEN GENERATION

by

Mohammad Arif Khan

Bachelor of Science
Bangladesh University of Engineering and Technology, Dhaka, Bangladesh
2000

A thesis submitted in partial fulfillment
of the requirements for the

**Master of Science Degree in Mechanical Engineering
Department of Mechanical Engineering
Howard R. Hughes College of Engineering**

**Graduate College
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ABSTRACT

Process Analysis and Simulation of Solar Thermo-chemical Hydrogen Generation

by

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Hydrogen is an attractive fuel for the future because it is renewable as an energy resource and it is also flexible as an energy carrier. Process analysis and simulation flowsheets for solar thermochemical cycles have been developed in the framework of ASPEN PLUS™ (chemical analysis simulator) in order to study hydrogen generation. Chemical mass balance, conversion rate, operating temperature and pressure are comparatively assessed for a wide range of hydrogen production processes, including processes which are hydrocarbon based (methane reforming), non hydrocarbon based (copper-chlorine cycle) and water splitting thermochemical cycles. Then process analysis and simulation models have been built up with the help of detailed reaction models, chemical components data, reactor dimensions, specification, and operating parameters.

In this study three different kind of solar thermochemical cycles (methane reforming process, sulfur-iodine cycle and copper-chlorine cycle) have been analyzed to produce hydrogen gas. Methane reforming processes (steam methane reforming, partial oxidation and autothermal reforming) have been analyzed and simulation flowsheets have been developed. In this analysis, the temperature of all the reforming reactors are varied in the

range of 500-1000 °C due to the transient nature of the solar energy. The results show that the POX reforming system is better than the other two systems for the production of the same amount of hydrogen from CH₄.

Process analysis and simulation flowsheets for all the three sections of the sulfur-iodine (S-I) cycle have been developed. This chemical cycle and flowsheets have been developed by General Atomics (GA). A potential solar concentrated heat source will produce the high temperature for H₂SO₄ and HI decomposition. While the results and efficiency analysis presented in this study are preliminary, the ASPEN PLUS models promise to be useful to evaluate and improve the overall S-I cycle.

The copper-chlorine (Cu-Cl) cycle has also been studied and analyzed in this study as a promising cycle which can produce hydrogen at a lower temperature than the S-I cycle. Argonne National Laboratory (ANL) has recently initiated exploratory research to develop a Cu-Cl cycle that operates at 550°C. A process analysis and simulation model has been developed for this cycle. A preliminary assessment of cycle efficiency is completed. Details of the simulation flowsheet and efficiency are discussed.

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CHAPTER 1

INTRODUCTION

Hydrogen, first on the periodic table of the elements, is the least complex and most abundant element in the universe. Using hydrogen as fuel can fundamentally change our relationship with the natural environment. As a nearly ideal energy carrier, hydrogen will play a critical role in a new, decentralized energy infrastructure that can provide power to vehicles, homes, and industries. Hydrogen boasts many important advantages over other fuels: it is non-toxic, renewable, clean to use, and packs much more energy per pound. Hydrogen is also the fuel of choice for energy-efficient fuel cells. Hydrogen, which exists as a gas under normal atmospheric conditions, is odorless, colorless, and tasteless. It can be transported safely.

To appreciate the various benefits of hydrogen as an energy carrier, it is important to understand the shortcomings of fuels we depend upon today. Conventional petroleum-based fuels like gasoline or diesel, as well as natural gas and coal, all contain carbon. When these fuels are burned, their carbon recombines with oxygen from the air to form carbon dioxide (CO_2), the primary greenhouse gas that causes global warming. To stabilize atmospheric CO_2 concentrations at levels that avoid irreversible climate changes, it will be necessary to reduce carbon emissions from fuel combustion several fold within this century [1-2].

The main processes for hydrogen production include steam-methane reforming (SMR), catalytic decomposition of natural gas, partial oxidation of heavy oil, coal gasification, water electrolysis, thermochemical water splitting, photochemical, electrochemical and biological process. The first four processes are based on fossil fuels. SMR, coal gasification and water electrolysis are the most important industrial processes for hydrogen production today. As far as the long term is concerned, electrolysis and thermochemical water splitting cycles seem to be the two possible routes which do not involve hydrocarbons. These processes need large amounts of energy (heat or electricity), which can be delivered by solar energy. As hydrogen generation through direct thermolysis process encountered with high temperature (around 2500°C), thermochemical water splitting is one of the best process to generate hydrogen gas at relatively low temperature (less than 1000°C).

Various thermochemical cycles have been successfully tested and evaluated including their chemistry. Of the identified thermochemical processes, the sulfur family of processes, including sulfur-iodine (S-I) and hybrid-sulfur, appear to have the highest efficiencies and hence to be the most promising. The sulfur-iodine cycle proposed by the General Atomics (GA) Company is one such cycle developed for large-scale hydrogen production. The calcium-bromine cycle, also known as the UT-3 cycle, invented by the University of Tokyo, gained considerable attention in addition to the GA proposed S-I cycle.

The main objective of this study is to simulate the solar thermochemical hydrogen generation cycles using the chemical analysis simulator ASPEN PLUS 12.1. Here the S-I

cycle has been taken as a base cycle as its overall efficiency is higher than any other thermochemical cycle studied, and it is fully flowsheeted.

Thermodynamic evaluation of various kinds of reforming process has also been studied here. Process analysis of steam methane reforming (SMR), partial oxidation (POX) and auto-thermal (ATR) processes have been compared with each other in terms of hydrogen generation. At the end, the low-temperature (550°C) copper-chlorine cycle has been studied and analyzed for hydrogen generation. Argonne National Laboratory (ANL) is currently working on this cycle which can be a good alternative to the GA proposed S-I cycle due to its low operating temperature.

Various studies on thermochemical processes have been reported in the literature (Huang and Raisi [3]; Ozturk, Hammache and Bilgen [4]; Roth and Knoche [5]; Norman, Mysels, Sharp and Williamson [6]; Bilgen and Bilgen [7]). But only GA has described and analyzed the S-I thermochemical process with flowsheet and simulation results [8]. The UT-3 cycle has also been studied and analyzed by Sakurai, Miyake, Tsutsumi and Yoshida [9]; Aihara, Umida, Tsutsumi and Yoshida [10]; Tadokoro, Yamaguchi, Sakai, Kameyama, Yoshida, Aochi, Nobue, Aihara, Amir, Kondo and Sato [11]. The chemistry of these cycles has been studied extensively. The efficiency of hydrogen generation, for a stand alone plant, is predicted to be 36%-40%, depending upon the efficiency of the membrane separation processes. Higher overall efficiencies, 45%-49%, are predicted for a plant that co-generates both hydrogen and electricity. It is not evident from the published reports if these numbers are based on steady-state operation or if they take into account the additional inefficiencies associated with the transient operation. The Cu-Cl cycle has been studied and analyzed experimentally at Argonne National Laboratory

(ANL) [12-13]. Though all the chemistry equations of this cycle have been approved and validated, it is not fully flowsheeted yet. The overall efficiency of this cycle is 41% based on thermodynamics.

Process analysis and simulation of the S-I cycle has been done using ASPEN PLUS 12.1 in this study. The process analysis flowsheet of Section-1 (Chapter-3, Section 3.2.1.) has been developed by following the GA's Final Report [3]. The simulation flowsheet of Section-2 (Chapter-3, Section 3.2.2.) has been developed by following the flowsheet reported by Ozturk, Hammache and Bilgen [4]. Roth and Knoche [5] have described how to modify the simulation of Section-3 (Chapter-3, Section 3.2.3.) to get convergence at the end. Thermodynamic evaluation of methane reforming systems has been completed by following the experimental work of Seo, Shirley and Kolaczowski [14]. ANL is developing low temperature cycles designed for producing hydrogen at 500-550°C. For this temperature region the copper-chlorine (Cu-Cl) cycle is the most promising cycle. A simulation flowsheet has been developed by following the report and paper published from ANL [12-13].

1.1 Basics of the Solar Thermochemical Water Splitting Cycle

Solar energy on the Earth being an intermittent source, its utilization for thermochemical applications requires specific design and conception, and a suitable coupling for a proper operation of chemical processes. In the earlier studies, this aspect has been considered and the flowsheets have been developed to suit the intermittent characteristics of the heat source. In general, the following operation may be devised.

- 1) The thermochemical process is run intermittently, in which case the high temperature solar energy is used directly in the process.
- 2) The thermochemical process can be devised to run in a cyclic manner, consisting of day and night operations. During day operation, the high temperature solar heat is used to produce some intermediate chemicals, which are stored. These stored chemicals are used during night operation.
- 3) The thermochemical process is run continuously. The high temperature solar energy is used directly during sunshine hours and also stored in a thermal storage system. The thermal energy is supplied to the process during night operation from the thermal storage system.

From the chemical engineering point of view, the first system is not preferred, since intermittent operation of a chemical process will result in start-up and shutdown problems. The second option is used in several solar-thermochemical process coupling studies (Bilgen and Bilgen [7]; Kameyama and Funk [18]). The third option is the ideal case for the operation of a chemical process. It represents a straightforward option if the high temperature solar energy can be stored at the desired temperature level.

Thermochemical production of hydrogen involves the separation of water into hydrogen and oxygen through chemical reactions at high temperatures. Ideally, water can be separated directly (thermolysis); however this process requires temperatures in excess of 2500°C.

Because these temperatures are impractical, the thermochemical water-splitting cycles achieve the same result (i.e., separation of water into hydrogen and oxygen) at

lower temperatures. A thermochemical water-splitting cycle is a series of chemical reactions that sum to the decomposition of water. To be useful, each reaction must be spontaneous and clean. Chemicals are chosen to create a closed loop where water can be fed to the process, oxygen and hydrogen gas are collected, and all other reactants are regenerated and recycled.

Recent studies conducted through the Nuclear Energy Research Initiative (NERI) have identified more than 100 thermochemical water-splitting cycles. A few of the most promising cycles have been selected for further research and development, based on the simplicity of the cycle, the efficiency of the process, and the ability to separate a pure hydrogen product. Among them the sulfur-iodine cycle (S-I) and hybrid-sulfur cycle appear to have the highest efficiencies and hence to be the most promising. The S-I cycle uses iodine (I₂) and sulfur dioxide (SO₂) as chemical components to split water. First, water reacts with I₂ and SO₂ to form hydrogen iodide (HI) and sulfuric acid (H₂SO₄).

Then the HI and H₂SO₄ are separated from each other. The I₂ and SO₂ are then recovered from the HI and H₂SO₄ and recycled, and hydrogen and oxygen gases are collected.

The reaction that requires the highest heat input is the thermal decomposition of H₂SO₄; typically in the range of 850°C. High temperatures are necessary to produce large quantities of hydrogen in a cost-effective manner, because the efficiency of the process decreases rapidly with decreasing the temperature. Another leading candidate is the

hybrid-sulfur process. This process uses the same high-temperature step as the S-I process but replaces the lower -temperature chemical reactions with an electrolytic cell.

The power requirements for this electrochemical step are much less than direct electrolysis of water. The process adds the complication of an electrolysis step but reduces the complexity of the chemical plant. Other thermochemical cycles that use other chemical systems may also be feasible for large-scale cost-effective hydrogen production. For example, the calcium-bromine (Ca-Br) cycle (extensively studied in Japan) is a promising thermochemical process. The advantage of the Ca-Br cycle is that it requires lower temperature ($\sim 750^\circ\text{C}$) than that of the sulfur-Iodine cycle. However, unlike the S-I and sulfur-hybrid cycles, which contain only gases and liquids, the Ca-Br cycle contains solids. The cycle cannot be operated in steady-state mode without moving the solids [8].

1.2 Solar Energy to Generate Hydrogen Gas

Solar thermal power is one of the main candidates to provide a major share of renewable clean energy needed in the future. Solar radiation is the largest renewable energy resources on earth. Approximately 1% of the world's desert area utilized by solar thermal power plants would be sufficient to generate the world's entire electricity demand [1-2]. Solar thermochemical hydrogen generation is mainly based on the use of concentrated solar radiation as the energy source of high-temperature process heat for driving an endothermic chemical transformation. All concentrating solar thermal power technologies rely on four basic elements: concentrator, receiver, transport-storage, and power conversion. The concentrator captures and concentrates solar radiation, which is

then delivered to the receiver. The receiver absorbs the concentrated sunlight, transferring its heat energy to a working fluid. The transport-storage system passes the fluid from the receiver to the power conversion system; in some solar-thermal plants a portion of the thermal energy is stored for later use [15]. There are three solar thermal power systems currently being developed all over the world: parabolic troughs, power towers, and dish/engine systems.

Parabolic Trough:

The parabolic trough or solar farm (Fig. 1.1) consists of long parallel rows of identical concentrator modules, typically using trough-shaped glass mirrors. Tracking the sun from East to West by rotation on one axis, the trough collector concentrates the direct solar radiation onto an absorber pipe located along its focal line. A heat transfer medium, typically oil, at temperatures up to 400°C, is circulated through the pipes. The hot oil converts water to steam driving the steam turbine generator of a conventional power block [16].

Figure 1.1 Solar parabolic trough or solar farm

Solar Central Receiver or Power Tower:

The solar central receiver or power tower (Fig. 1.2) is surrounded by a large array of two-axis tracking mirrors, termed heliostats, reflecting direct solar radiation onto a fixed receiver located on the top of the tower. Within the receiver, a fluid – water, air, liquid metal and molten salt have been tested – transfers the absorbed solar heat to the power block where it is used to heat a steam generator. Advanced high temperature power tower concepts are now under investigation, which heat pressurized air up over 1000°C in order to feed it into the gas turbines of modern combined cycles [16].

Figure 1.2 Solar central receiver or power tower

Solar Dish/Engine Systems:

Dish/Engine systems use an array of parabolic dish-shaped mirrors (stretched membrane or flat glass facets) to focus solar energy onto a receiver located at the focal point of the dish (Fig. 1.3). Fluid in the receiver is heated to 1000°C and used to generate electricity in a small engine attached to the receiver. Engines currently under

consideration include Stirling and Brayton cycle engines. Several prototype dish/engine systems, ranging in size from 7 to 25 kW_e have been deployed in various locations in the U.S. and abroad. High optical efficiency and low startup losses make dish/engine systems the most efficient (29.4% record solar to electricity conversion) of all solar technologies. In addition, the modular design of dish/engine systems make them a good match for both remote power needs in the kilowatt range as well as hybrid end-of-the-line grid-connected utility applications in the megawatt range [16].

Figure 1.3 Solar concentrated dish generator

The capability of these collection systems to concentrate solar energy is described in terms of their mean flux concentration ratio. The solar flux concentration ratio typically obtained is at the level of 100, 1000, and 10,000 suns for trough, tower, and dish systems, respectively [17]. Higher concentration ratios imply lower heat losses from smaller areas and, consequently, higher attainable temperatures at the receiver. To some extent, the flux

concentration can be further augmented with the help of non-imaging secondary concentrators, e.g., compound parabolic concentrators (CPC), when positioned in tandem with the primary parabolic concentrating systems. Towers and troughs are best suited for large, grid-connected power projects in the 30-200 MW_e size, whereas, dish/engine systems are modular and can be used in single dish applications or grouped in dish farms to create larger multi-megawatt projects. Parabolic trough plants are the most mature solar power technology available today and the technology most likely to be used for near-term deployments. Power towers, with low cost and efficient thermal storage, promise to offer dispatchable, high capacity factor in the near future. The modular nature of dishes will allow them to be used in smaller, high-value applications. Towers and dishes offer the opportunity to achieve higher solar-to-electric efficiencies and lower cost than parabolic trough plants, but uncertainty remains as to whether these technologies can achieve the necessary capital cost reductions and availability improvements. Parabolic troughs are currently a proven technology primarily waiting for an opportunity to be developed. Power towers require the workability and maintainability of the molten-salt technology to be demonstrated and the development of low cost heliostats. Dish/engine systems require the development of at least one commercial engine and the development of a low cost concentrator [16].

CHAPTER 2

PROCESS ANALYSIS AND SIMULATION USING ASPEN PLUS®

Process simulation allows us to predict the behavior of a process by using basic engineering relationships, such as mass and energy balances, and phase and chemical equilibrium. Given reliable thermodynamic data, realistic operating conditions, and rigorous equipment models, actual plant behavior can be simulated. Process simulation enables us to run many cases, conduct “what if” analysis, and perform sensitivity studies and optimization runs. With simulation, better plant design can be obtained with increased profitability in existing plants. Process simulation is useful throughout the entire lifecycle of a process, from research and development through process design to production.

Process flowsheets are the language of chemical processes. They describe an existing process or a hypothetical process in sufficient detail to convey the essential features. Analysis or simulation is the tool engineers use to interpret process flowsheets, to locate malfunctions, and to predict the performance of processes. The heart of analysis is the mathematical model, a collection of equations that relates the process variables, such as stream temperature, pressure, flow rate, and composition, to surface area, valve settings, geometrical configuration, and so on. The steady-state simulations solve for the unknown variables, given the values of certain known quantities. There are several levels of

analysis. In order of increasing complexity, they involve: material balances, material and energy balances, equipment sizing, and profitability analysis. Additional equations are added at each level. New variables are introduced, and the equation-solving algorithms become more complicated. Fortunately, most chemical processes involve conventional process equipment: heat exchangers, pumps, distillation columns, absorbers, and so on. For these process units, the equations do not differ among chemical processes. The physical and thermodynamics properties and chemical kinetics constants differ, but not the equations [19].

To use a flowsheet simulator effectively, it is very essential to distinguish between process flowsheets and simulation flowsheets associated with process simulators. A process flowsheet is a collection of blocks or units to represent process units and streams to represent the flow of materials to and from the units. The process flowsheets emphasize the flow of material and energy in a chemical process. A simulation flowsheet, on the other hand, is a collection of simulation units to represent computer programs (subroutines or models) that simulate the process units and streams to represent the flow of information among the simulation units. A simulation flowsheet emphasize information flows. Four of the major process simulations are ASPEN PLUS[®] and HYSYS by Aspen Technology; CHEMCAD[®] by ChemStations, Inc.; and PRO/II[®] by Simulation Sciences, Inc. Among the four chemical analysis simulator mentioned above, ASPEN PLUS and HYSYS are widely used.

HYSYS is an interactive, object-oriented program, which differs from many of the alternative simulators (e.g., ASPEN PLUS, PRO/II, and CHEMCAD) in two main respects. First, it has the facility for interactively interpreting commands, as they are

entered one at a time, whereas most of the other flowsheet simulators require that a 'Run' button be pressed after new entries are completed. Second, although HYSYS, like many other simulators, uses subroutines or procedures to model the process units, it has the unique feature that information propagates in both forward and reverse directions. These two features make the program fast responding and relatively easy to use. In addition, like many other simulators, HYSYS allows the overall flowsheet to be decomposed into sections, to be simulated separately using alternative options. HYSYS is built upon proven technologies, with more than 25 years experience supplying process simulation tools to the oil & gas and refining industries. It provides an intuitive and interactive process modeling solution that enables engineers to create steady state models for plant design, performance monitoring, troubleshooting, operational improvement, and business planning and asset management.

CHEMCAD, working under Windows®, is able to handle a variety of processes for the chemical, petrochemical, pharmaceutical and environmental technologies. It is very easy to create a flowsheet, to choose the required the chemical components for a particular process, and to find the correct thermodynamic properties with this simulator. The PRO/II process simulation program performs rigorous mass and energy balances for a wide range of chemical processes. From oil and gas separation to reactive distillation, PRO/II offers the most comprehensive and easy-to-use simulation solution available. The product's PROVISION graphical user interface (GUI), provides a fully interactive, Windows®-based environment that is ideal for building and modifying both simple and complex PRO/II models. This is not much known in academics, but it is widely used in industries.

ASPEN PLUS (Advanced System for Process Engineering) from Aspen Technology solves the critical engineering and operating problems that arise throughout the lifecycle of a chemical process, such as designing a new process, troubleshooting a process unit or optimizing operations of a full process. The process simulation capabilities of ASPEN PLUS enable engineers to predict the behavior of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetics. With reliable thermodynamic data, realistic operating conditions and the rigorous ASPEN PLUS equipment models, they can simulate actual plant behavior. This process simulator was developed at the Massachusetts Institute of Technology (MIT), USA, and is equipped with up-to-date databanks for thermochemical properties based on the Design Institute for Physical Properties (DIPPR), a data compilation project under American Institute of Chemical Engineers (AIChE), as well as a combustion databank based on the Joint Army-Navy-Air Force (JANAF) Tables, including 59 combustion species and radicals at temperature up to 6000 K [20]. ASPEN PLUS is the chemical process simulator with the best tools for handling non-ideal chemical systems. It incorporates the capability of modeling electrolytes via several different modeling techniques including an electrolytic version of the non-random two liquid (NRTL) techniques. An electrolytic NRTL (ELECNRTL) model can handle everything from concentrated electrolytes through dilute electrolytes to non-polar species, such as iodine, so it should be able to handle the chemistry of the S-I and Cu-Cl cycles. In fact, ASPEN PLUS included an ELECNRTL model for sulfuric acid, good at 200°C, right out at the box. It also has an ELECNRTL model for hydrochloric acid, good at 100°C. In addition, ASPEN PLUS includes the capability of regressing model parameters simultaneously to

several different types of experimental data in order to generate a thermodynamic model for a specific chemical system [8]. That's why ASPEN PLUS has been chosen as the process simulator for this study.

A process can be translated into an ASPEN PLUS process simulation model by performing the following steps:

1. Define the process flowsheet
 - Define the unit operations in the process.
 - Define the process streams that flow to and from the unit operations.
 - Select models from the ASPEN PLUS Model Library to describe each unit operation and place them on the process flowsheet.
 - Place labeled streams on the process flowsheet and connect them to the unit operation models.
2. Specify the chemical components in the process. ASPEN PLUS databanks contain specifications of all the components.
3. Specify thermodynamic models to represent the physical properties of the components and mixtures in the process. These models are built into ASPEN PLUS.
4. Specify the component flow rates and the thermodynamic conditions (for example, temperature and pressure) of feed streams.
5. Specify the operating conditions for the unit operation models.

Specifications such as flowsheet configuration, operating conditions, and feed compositions can be interactively changed to run new cases and analyze process alternatives. In addition to process simulation, a wide range of other tasks such as

estimating and regressing physical properties, generating custom graphical and tabular output results, fitting plant data to simulation models, optimizing process and interfacing results to spreadsheets can be performed by ASPEN PLUS.

In this study three different cases of solar thermochemical hydrogen generation have been performed using ASPEN PLUS. Process analysis and simulation of methane reforming systems has been simulated from the experimental work by Y.-S. Seo, A. Shirley and S.T. Kolaczowski [14]. Process analysis simulation flowsheets of the S-I cycle have been developed by following GA final report (for Section-1), Ozturk and Hammache (for Section-2), and Roth and Knoche (for Section-3) [4, 5, 8]. A flowsheet of the copper-chlorine cycle has been simulated on the basis of current research demonstrated by ANL [12-13].

CHAPTER 3

SOLAR THERMOCHEMICAL HYDROGEN PRODUCTION

For quite some time hydrogen has been hailed as a potential, pollution free energy source. As a consequence there have been considerable advances in the research and development devoted to hydrogen production. Among the generation methods investigated, water electrolysis is the only industrially established clean hydrogen production technology available at present. High temperature water electrolysis involves the separation of water into hydrogen and oxygen through direct thermolysis at high temperatures (in excess of 2500°C) [8].

At this high temperature only 10% of the water is decomposed. In addition, a means of preventing the hydrogen and oxygen from recombining upon cooling must be provided or no net production would result [8]. In order to avoid hydrogen generation at high temperature, low temperature methane reforming and thermochemical processes are preferred over water electrolysis to produce hydrogen gas. Worldwide production of hydrogen is about 100 million kilograms per day, most of which is produced from methane reforming. Research continues into methane reforming, with concentration on better catalysts and heat sources other than natural gas to provide the process heat to drive the reaction. As the methane reforming process is highly endothermic there is an opportunity to supply this heat from concentrated solar radiation. Thermochemical water

splitting processes also need process heat to be supplied from outside source. Concentrated solar radiation can also be used in this case.

In this study, three methane reforming process have been simulated by ASPEN PLUS and compared in terms of hydrogen generation. The S-I cycle and the Cu-Cl cycle have also been simulated in the later part of this study.

3.1 Comparative Analysis of Three Methane Reforming Processes

In general, technologies for the production of hydrogen from methane are based on the following three reforming processes [21-22]:

- Steam methane reforming (SMR)
- Partial oxidation (POX)
- Autothermal reforming (ATR)

A common route for hydrogen production is steam reforming of natural gas (NG) or other hydrocarbon materials. The steam methane reforming process has been the most important chemical process in the production of hydrogen. Using solar energy, the demand for fossil fuels and therefore CO₂-emissions can be reduced up to 40% compared with conventional steam reforming processes for producing hydrogen [23]. The SMR process was used as an early prototype because it leads to the best gas quality. But it has a disadvantage of slow start-up, which makes it more suitable for a stationary system rather than for a mobile system. The process of catalytic partial oxidation (POX) to convert methane into hydrogen has been investigated intensively in the past decade. The autothermal process (ATR), which integrates POX with SMR is also getting much more interest [14].

A reforming system is generally comprised of the following components:

- A pretreatment process
- A reforming reactor
- A shift reactor and
- A gas-purification process.

The pretreatment process requires removing the sulfur compounds present in the natural gas. The main reaction (methane reforming) occurs in the reforming reactor. Synthesis gases produced from reforming reactions contain an appreciable amount of carbon monoxide. Therefore, it is further processed in a water-gas shift reactor where the carbon monoxide is converted into carbon dioxide, producing hydrogen by reaction with steam. The gas-purification process has been used to further clean the product gas from carbon monoxide.

3. 1. 1. Steam Methane Reforming (SMR) Process

The steam reforming reactions for methane are:

Overall reaction:

The reforming reaction (1) is thermodynamically favored by high temperature and low pressure. The second reaction, the water-gas shift reaction, does not depend on pressure and is favored by low temperature. Since the overall reaction is highly endothermic, an external heat source (e.g. concentrated solar dish) is required to supply the process heat. For complete conversion of methane high temperature in the catalyst

system is essential. As this process is very endothermic, heat transfer from the outside of the reactor controls the temperature of SMR reactor. In this simulation, the temperature of the SMR reactor is varied in the range 500-1000°C. As the reactor temperature increases, the methane conversion also increases. In order to prevent the formation of solid carbon, the reactor temperature should be more than 850°C [14]. In this analysis the pressure is fixed at 1 bar.

The process analysis flowsheet of SMR process and the simulation result is illustrated in Fig. 3.1 and Table 3.1 respectively. In Fig. 3.1, it can be seen that a total of six reaction blocks and eleven material streams have been used to summarize the flowsheet. A steam generator is used at the beginning to generate steam required for both the reforming reactor and the shift reactor. The input conditions of CH₄ and water are 20°C and 1 bar for the SMR process. The mole fraction of hydrogen production in this process is 0.562. The result from the experimental work [14] for the same process is 0.5744. The results differ by 2.02 %. This is because the temperature of the shift reactor has been increased considerably in this process analysis. In the experimental study temperature of the SMR reactor was fixed at 800°C while in this simulation analysis the reactor temperature is taken as 900°C for 99% conversion of CH₄.

Figure 3.1 Process flowsheet for SMR system

Table 3.1 Result Summary of SMR system

SMR Reformer system												
Stream ID		CH4	H2O-1	STEAM-1	SMR-IN	SMR-OUT	COOL-IN	COOL-OUT	H2O-2	STEAM-2	SHIFT-IN	PRODUCT
Temperature	C	20.0	20.0	103.3	400.0	900.0	51.1	65.6	20.0	102.8	65.6	676.7
Pressure	bar	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Vapor Frac		1.000	0.000	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	1.000
Mole Flow	kmol/hr	1.100	1.728	1.728	2.828	5.024	36.000	36.315	1.819	1.819	4.709	6.415
Mass Flow	kg/hr	17.650	31.124	31.124	48.774	48.774	648.550	654.225	32.765	32.765	43.098	75.863
Volume Flow	ccm/hr	26.770	0.031	53.292	158.184	485.976	0.657	0.667	0.033	56.013	148.749	506.730
Enthalpy	MMBtu/hr	-0.078	-0.469	-0.392	-0.434	-0.133	-9.686	-9.733	-0.493	-0.413	-0.187	-0.503
Mole Flow	kmol/hr											
CH4		1.100			1.100	0.002					0.002	0.059
O2												
N2												
H2						3.411					3.411	3.604
H2O			1.728	1.728	1.728	0.513	36.000	36.315	1.819	1.819	0.198	1.710
CO						0.982					0.982	0.562
CO2						0.116					0.116	0.480
Mole Frac												
CH4		1.000			0.389	409 PPM					437 PPM	0.009
O2												
N2												
H2						0.679					0.724	0.562
H2O			1.000	1.000	0.611	0.102	1.000	1.000	1.000	1.000	0.042	0.267
CO						0.195					0.208	0.088
CO2						0.023					0.025	0.075

3.1.2. Partial Oxidation (POX) Process

The general reactions for the analysis of the POX process can be written as:

Partial oxidation is an exothermic reaction, releasing energy as it proceeds [21]. This generates two moles of H_2 and 36 kJ of energy for each mole of CH_4 reacted at standard conditions.

The water-gas shift reaction is used for removing the carbon monoxide. This is a highly desirable reaction in fuel cells as it converts a poison for the electrode to H_2 to fuel. Thus, conditioning of the flow stream is achieved while increasing efficiency. Compared with the reforming stage, CO clean-up sub-systems using the water-gas shift reaction usually operate at considerably lower temperatures, where lower CO concentrations (and higher efficiency) are favored thermodynamically.

The preheat temperature of reactants (CH_4 and air) can exert an important effect on the POX reactor. Reactants entering the POX reactor should be heated to a certain temperature to sustain the catalytic reaction of the reforming catalysts. The preheat temperature of reactants is one of the key operating parameters in the POX reactor [14]. Thermodynamic analysis of the POX reactor shows that to increase the preheat temperature at a fixed air ratio makes both the reactor temperature and conversion higher.

The process analysis flowsheet of the POX process and the simulation result are illustrated in Fig. 3.2 and Table 3.2 respectively. In the POX process only one steam generator has been used to carry on the water-gas shift reaction. The input condition of air and CH_4 is set to 20°C and 1 bar for this process.

Figure 3.2 Process flowsheet for POX system

Table 3.2 Result summary for POX system

POX Reformer System											
Stream ID		AIR	CH4	POX-IN	POX-OUT	COOL-IN	COOL-OUT	H2O	STEAM	SHIFT-IN	PRODUCT
Temperature	C	20.0	20.0	312.2	900.0	20.0	68.0	20.0	102.8	68.0	676.7
Pressure	bar	1.00	1.00	1.00	1.00	1.00	0.99	1.00	1.00	0.99	1.00
Vapor Frac		1.000	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	1.000
Mole Flow	kmol/hr	3.600	1.486	5.086	7.261	36.000	35.683	2.614	2.614	7.578	10.163
Mass Flow	kg/hr	103.973	23.847	127.820	127.820	648.550	642.831	47.085	47.085	133.539	180.624
Volume Flow	cum/hr	87.723	36.169	247.671	707.841	0.650	0.657	0.047	80.493	243.268	802.908
Enthalpy	MMBtu/hr	-0.001	-0.105	-0.058	0.008	-9.766	-9.557	-0.709	-0.593	-0.241	-0.675
Mole Flow	kmol/hr										
CH4			1.486	1.486	0.007					0.007	0.022
O2		0.784		0.784							
N2		2.816		2.816	2.816					2.816	2.816
H2					2.895					2.895	3.603
H2O					0.064	36.000	35.683	2.614	2.614	0.381	2.258
CO					1.454					1.454	0.688
CO2					0.025					0.025	0.777
Mole Frac											
CH4			1.000	0.292	990 PPM					948 PPM	0.002
O2		0.218		0.154							
N2		0.782		0.554	0.388					0.372	0.277
H2					0.399					0.382	0.355
H2O					0.009	1.000	1.000	1.000	1.000	0.050	0.222
CO					0.200					0.192	0.068
CO2					0.003					0.003	0.076

In the POX process analysis five reaction blocks and ten material streams have been used to summarize the flowsheet. The mole fraction of hydrogen production in this process is 0.355. The result from the experimental work [14] for the same process is 0.380. The variation of the result is 6.57 % due to the temperature differences of the experimental (802°C) and simulation analysis (900°C). Input condition of the reactor has been varied in this simulation analysis until 1 mol/sec of hydrogen produced at 900°C. But in the experimental work of Seo and Shirley [14], hydrogen has been produced 1 mol/sec of at 802°C.

3. 1. 3. Autothermal Reforming (ATR) Process

The ATR process integrates SMR with POX. The general reactions for the analysis of the ATR process are given below:

In the simulation to find favorable operating conditions of the ATR reactor, the reactor pressure and the preheat temperature are set to 1 bar and 400°C.

The process analysis flowsheet of the ATR process and the simulation result are illustrated in Fig. 3.3 and Table 3.3 respectively. As it is known that the ATR process integrates SMR with POX, and air and water are mixed with CH₄ before it enters into the heater. Steam generators are used for both the reforming reactor and the shift reactor. The input conditions of air, CH₄, and water are 20°C and 1 bar for this process. From the process flowsheet illustrated in the Fig. 3.3 it can be seen that six reaction blocks and twelve material streams have been used. The mole fraction of hydrogen production in this

Figure 3.3 Process flowsheet for ATR system

Table 3.3 Result summary of ATR system

ATR Reformer System													
Stream ID		CH4	AIR	H2O-1	STEAM-1	ATR-IN	ATR-OUT	COOL-IN	COOL-OUT	H2O-2	STEAM-2	SHIFT-IN	PRODUC
Temperature	°C	20.0	20.0	20.0	103.3	398.9	900.0	20.0	67.0	20.0	103.3	67.0	650.0
Pressure	bar	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.01
Vapor Frac		1.000	1.000	0.000	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	1.000
Mole Flow	kmol/hr	1.468	3.473	0.255	0.255	5.196	7.399	36.000	35.826	2.553	2.553	7.572	10.036
Mass Flow	kg/hr	23.546	100.198	4.600	4.600	128.344	128.344	648.550	645.424	45.995	45.995	131.471	177.466
Volume Flow	m ³ /hr	35.713	84.635	0.005	7.876	290.467	720.340	0.650	0.659	0.046	78.755	240.575	765.336
Enthalpy	MMBtu/hr	-0.104	-0.001	-0.069	-0.058	-0.098	-0.023	-9.766	-9.598	-0.693	-0.579	-0.243	-0.680
Mole Flow	kmol/hr												
CH4		1.468				1.468	0.003					0.003	0.047
O2			0.728			0.728	trace					trace	
N2			2.746			2.746	2.746					2.746	2.746
H2							3.006					3.006	3.600
H2O				0.255	0.255	0.255	0.180	36.000	35.826	2.553	2.553	0.353	2.223
CO							1.399					1.399	0.627
CO2							0.066					0.066	0.794
Mole Frac													
CH4		1.000				0.282	358 PPM					349 PPM	0.005
O2			0.209			0.140	trace					trace	
N2			0.791			0.528	0.371					0.363	0.274
H2							0.406					0.397	0.359
H2O				1.000	1.000	0.049	0.024	1.000	1.000	1.000	1.000	0.047	0.221
CO							0.189					0.185	0.062
CO2							0.009					0.009	0.079

process is 0.359. The result from experimental work [14] for the same process is 0.3842. The variation of the result is 7.0%, due to the temperature difference between experimental (788°C) and simulation process (900°C). In the experimental work [14], 1 mol/sec of hydrogen has been produced at 788°C but for generating same amount of hydrogen it takes 900°C for this simulation.

3. 1. 4. Analysis of Thermal Energy

Basically all three processes are comprised of a steam generator, a heater, a reforming reactor, a heat exchanger and a shift reactor. The input conditions of air, methane and water are set to 20°C and 1 bar. Steam generators are required for both the reforming reactor and the shift reactor. The steam generators used in these processes are run at 103°C. The water flow rate for the shift reactor is determined based on the complete conversion of CO to hydrogen. The heater is employed to heat the reactants to a temperature sufficient to sustain the catalytic reaction in the reforming reactor. The outlet temperature of the heater is set to 400°C for the SMR, 312°C for the POX and 400°C for the ATR process. The synthesis gas produced by each reforming reactor contains a large amount of CO together with hydrogen. To convert this CO to hydrogen, a water-gas shift reactor is used in the process simulation.

In this process analysis the shift reactor and the reforming reactor are modeled with a Gibbs Reactor from ASPEN PLUS model library. For a multireaction system such as the SMR, POX or ATR which involves numerous dissociation, recombination and elementary reactions, the Gibbs reactor is preferred because it is based on the minimization of the total Gibbs free energy of the product mixture [20]. The result summary given in Tables 3.1, 3.2, and 3.3 is actually taken from the ASPEN PLUS data

browser. The tables summarize the mole and mass fraction of each chemical component involved in the process. They also show are the temperature, pressure, mole flow, volume flow, and enthalpy for all the material flows for each system.

The variation of the equilibrium compositions with reactor temperatures for all the three processes is described below.

Figure 3.4 Effect of temperature on equilibrium compositions in SMR reactor

The reactor temperature is found to affect the equilibrium compositions and, therefore, the conversion of CH_4 (Fig. 3.4) in the SMR reactor. As the reactor temperature is raised from 500°C to 1000°C , the conversion of CH_4 and the production of H_2 increase considerably. If the operating temperature of the reactor is limited to less than 800°C in order to maintain thermal durability of the reactor and also of the catalyst, then

it is difficult to obtain a satisfactory conversion that is greater than 0.99. The reactor temperature also significantly affects the formation of CO. From the above figure it is evident that formation CO is increased with the increase of temperature. Durability of the catalyst is likely to be damaged at higher temperature.

Figure 3.5 Effect of temperature on equilibrium compositions in POX reactor

In order to maintain the conversion rate of CH₄ higher in the POX reactor, the temperature of the reactor should be more than 800°C. The mole fractions of H₂ and CO are increased as the temperature of the POX reactor is increased (Fig. 3.5). It is clear from the above figure that total combustion to form CO₂ is favored at lower temperature. Equilibrium conversions greater than 99% are achievable only at temperatures close to 850°C.

In the case of the ATR reactor complete conversion of CH_4 can be achieved at temperature slightly over 800°C . Again CO formation increased at higher temperature. So it is desirable to keep the reforming temperature near 800°C for complete conversion of CH_4 . Also it can be seen from the above figure that after 800°C , generation of H_2 decreased.

Figure 3.6 Effect of temperature on equilibrium compositions in ATR reactor

3. 1. 5. Efficiency Analysis of Three Reforming Processes

The process diagram for evaluating the thermal efficiency is depicted in Fig. 3.7. The fuel, water, and air enter the reformer and react to form hydrogen and carbon dioxide.

Figure 3.7 Schematic of the energy control volume to define the thermal efficiency

The definition of thermal efficiency for the process shown in Figure 3.7. is

$$\eta = \frac{N_{H_2} LHV_{H_2}}{LHV_F + Q_{in}} \quad (8)$$

where N_{H_2} = Number of moles of H_2 produced per mole of fuel,

Q_{in} = External heat added to the process.

LHV_{H_2} = Lower heating value of hydrogen

LHV_F = Lower heating value of fuel

Heating value of the fuel, $HV_f = -\Delta H_R = (h_P^f - h_R^f)$

3.1.5.1. The SMR process: $CH_4(g) + 2H_2O(g) = 4H_2(g) + CO_2(g)$

Steam methane reforming is an endothermic reaction, absorbing energy as it proceeds. This generates four moles of H_2 and absorbs 165 kJ/mol of energy for each mole of CH_4 reacted.

Enthalpy formation at 1173°K [24]:

$$\text{For H}_2: h_{1100\text{K}}^f - h_{298\text{K}}^f = 23.723 \text{ kJ/mol}$$

$$\text{For CO}_2: h_{1100\text{K}}^f - h_{298\text{K}}^f = 38.894 \text{ kJ/mol}$$

$$\text{For H}_2\text{O}: h_{1100\text{K}}^f - h_{298\text{K}}^f = 30.167 \text{ kJ/mol}$$

$$\text{LHV of CH}_4 = 74.873 \text{ kJ/mol}$$

$$\text{HHV of CH}_4 = 89.200 \text{ kJ/mol}$$

Theoretical efficiency of the SMR process:

$$\text{Heating value of fuel, HV}_F = -\Delta H_R = -(\Delta h_P^f - \Delta h_R^f) = 1.416 \text{ kJ/mol}$$

$$\text{External heat input} = 165.00 \text{ kJ/mol}$$

Putting the values of enthalpy of formation in equation (8), the theoretical efficiency is found to be:

$$\eta = 57\% \text{ (theoretical)}$$

$$\text{External heat input from ASPEN PLUS simulation data browser} = 183.416 \text{ kJ/mol}$$

$$\eta = 52\% \text{ (from ASPEN PLUS)}$$

Partial oxidation is an exothermic reaction, releasing energy as it proceeds. This generates three moles of H_2 and 77 kJ of energy for each mole of CH_4 reacted.

Theoretical efficiency of the POX process:

$$\text{Heating value of fuel, HV}_F = -\Delta H_R = -(\Delta h_P^f - \Delta h_R^f) = 8.086 \text{ kJ/mol}$$

$$\text{External heat input} = 77.00 \text{ kJ/mol}$$

Putting the values of enthalpy of formation in the efficiency in equation (8), the theoretical efficiency found to be:

$$\eta = 71.58\% \text{ (theoretical)}$$

External heat input from ASPEN PLUS simulation data browser = 105.77 kJ/mol

$$\eta = 62.5\% \text{ (ASPEN PLUS)}$$

3.1.5.3. The ATR process: $2\text{CH}_4 (\text{g}) + 3\text{H}_2\text{O} (\text{g}) + 1/2\text{O}_2 (\text{g}) = 2\text{CO}_2 (\text{g}) + 7\text{H}_2 (\text{g})$

The ATR process integrates the SMR and POX process. This process is the combination of combustion and reforming reactions.

Theoretical efficiency of ATR process:

$$\text{Heating value of fuel, } \text{HV}_F = -\Delta H_R = -(\Delta h_P^f - \Delta h_R^f) = 38.160 \text{ kJ/mol}$$

External heat input = 258.00 kJ/mol

So, theoretical efficiency for ATR process is

$$\eta = 56\% \text{ (theoretical)}$$

External heat input from ASPEN PLUS simulation data browser = 265.00 kJ/mol

$$\eta = 54.77\% \text{ (ASPEN PLUS)}$$

3.1.5.4. Comparison of the three reforming processes

From the above efficiency analysis of the three reforming processes, it is evident that POX process is the most efficient process. The SMR and ATR processes are less efficient than the POX process as these two processes involve steam generation and part of the fuel is used to generate the steam.

Table 3.4 shows the comparative analysis of the three reforming systems described in this study. For calculation, heat transfer efficiency is taken as 0.80 for all the three systems. Each unit in a reforming system may have different heat-transfer efficiency but the simulation assumes the same heat-transfer efficiency for all units to simplify the calculation. The term 'CH₄ equivalent' refers to a CH₄ flow rate, the combustion of which will release energy equivalent to the 'total net energy'. A combustion heat of 890 kJ/mol

of CH_4 is used to calculate the CH_4 equivalent from the total net energy. In the table 'total CH_4 ' is the sum of 'input' CH_4 and ' CH_4 equivalent'.

Table 3.4 Comparative analysis of three reforming systems

	SMR	POX	ATR
CH_4 input (mol/sec)	0.3056	0.4129	0.4077
H_2 production (mol/sec)	1.0	1.0	1.0
Heat transfer efficiency	0.80	0.80	0.80
Total net energy (kW)	109.13	3.01	13.6
CH_4 equivalent (mol/sec)	0.123	0.003	0.0153
Total CH_4 (input + CH_4 equivalent, mol/sec)	0.4286	0.4159	0.4230

In this analysis, the output flow rate of hydrogen is set to 1.0 mol/sec in order to compare the three systems with one another. The total CH_4 flow rate, including the CH_4 equivalent, required to generate 1 mol/sec of hydrogen is 0.4286 mol/sec for the SMR, 0.4159 mol/sec for the POX and 0.4230 mol/sec for the ATR. The SMR reforming system has the highest CH_4 consumption rate and the POX system has the lowest CH_4 consumption rate to produce the same amount of hydrogen. The previous work of Y.-S. Seo, A. Shirley and S.T. Kolaczowski [14] has also shown experimentally that the POX system has the lowest CH_4 consumption rate of 0.364 mol/sec for the production of 1.0 mol/sec of hydrogen. The results show that, in terms of energy cost, the POX reforming system is better than the SMR and ATR reforming systems.

The simulation results of this study are very close to the results of the experimental work [14] of the same process analysis. In both the cases SMR produces higher mole fraction of hydrogen and POX produces lower mole fraction of hydrogen. In terms of energy cost, the POX reforming system is superior to the other system for the production of the same amount of hydrogen from methane. So it can be concluded that the POX reforming system is superior to the other systems in terms of the energy cost to produce the same amount of hydrogen from methane. The difference in CH_4 consumption between the SMR and POX systems becomes larger if the heat transfer efficiency decreases.

3. 1. 6. Results of the Simulation of Three Reforming Processes

The ASPEN PLUS process simulator is found to be a powerful package to simulate the process analysis for the production of hydrogen gas from methane. The results of the simulation are summarized as follows.

1. For H_2 generation CH_4 can be reformed by the SMR, POX or ATR process. The POX process is considered to be the best solution over the remaining two processes.
2. The POX reforming system is superior to the other systems in terms of energy consumption to produce the same amount of hydrogen. It has been operated with fewer reaction blocks and material streams.
3. The SMR process has the highest CH_4 consumption and as well as the highest hydrogen production rate.
4. Thermodynamic equilibrium can be reached in all cases.
5. The POX process has better efficiency (62.5%) than the other two processes.

6. A process simulation model has been constructed and it should be optimized to improve better performance.
7. Equilibrium compositions have been varied with a temperature range from 500°-1000°C to get the optimum temperature at which almost all the CH₄ converts into H₂ gas.

The outcome of these process analyses demonstrate that hydrogen gas can be produced from methane reforming without producing harmful carbon monoxide. For certain applications, like in fuel cell technology, carbon monoxide has to be removed from hydrogen in order to prevent poisoning of the electro-catalyst [21]. In this analysis, the temperature of all the three reforming systems is varied in the range 500-1000 °C due to the transient nature of the solar energy and also to check the conversion of methane over the temperature range. Moreover as the SMR process is very endothermic, heat transfer from outside of the reactor controls the temperature of SMR reactor. A solar concentrated dish receiver is capable of supplying this high temperature to the reactor wall to decompose methane.

3. 2. Process Analysis and Simulation of Sulfur-iodine (S-I) Cycle

A thermochemical water-splitting cycle accomplishes the same overall result of direct thermolysis (2500°C) more effectively while using much lower temperatures. The sulfur-iodine (S-I) cycle is a prime example of a thermochemical water-splitting cycle which can produce hydrogen at a lower temperature (850°C) than direct thermolysis. It consists of the following three reactions that sum to the dissociation of water [8].

Based on the chemical engineering considerations, it is possible to separate the cycle into three sections [3]:

- Section 1: Acid production (H_2SO_4 and HI) and separation
- Section 2: H_2SO_4 concentration and decomposition.
- Section 3: Concentration and decomposition of HI and purification of H_2 .

The S-I cycle divided into three sections shown in Fig. 3.8:

Figure 3.8 Sections in the S-I cycle [8]

The chemistry of the S-I cycle was first demonstrated by General Atomics (GA) in 1974. A process flowsheet was generated by GA in 1984. Analysis of this cycle in the past thirty years has been focused mostly on the utilization of nuclear power as the high temperature heat source for performing the decomposition of sulfuric acid. Thermodynamic as well as kinetic considerations indicate that both the extent and rate of sulfuric acid decomposition can be improved at very high temperature (in excess of 800°C) available only from solar concentrators. The schematic diagram of S-I cycle is shown in Fig. 3.9.

Figure 3.9 Schematic diagram of the S-I cycle [8]

Section-1 is the H_2SO_4 -HI production and the O_2 separation step. Recycled I_2 from Section-3 reacts with water and SO_2 in a countercurrent reactor with a mixture of gaseous SO_2 - O_2 . It results in formation of a solution of two acids, H_2SO_4 and HI. This solution contains two phases; the lower density phase, which contains all the H_2SO_4 acid at a concentration of about 50% by weight with traces of I_2 and SO_2 , and the higher density phase, which contains all the HI with considerable amounts of I_2 in an H_2O solution. Both phases are separated and the concentration of H_2SO_4 is increased to 57% by weight by reacting the H_2SO_4 phase with molten iodine and SO_2 . The 57% by weight sulfuric acid is then transferred to Section-2 for concentration and decomposition. The lower phase containing HI, H_2O , I_2 and SO_2 goes through a degassing step, which removes practically all the SO_2 and is then transferred to Section 3 for purification and separation of HI. As

the mixture $\text{SO}_2\text{-O}_2$, coming directly from the SO_3 decomposition reaction of Section-2, passes through the reactor, the SO_2 is removed by reaction with I_2 and H_2O and the gas leaving the top of the main solution reactor practically pure oxygen with small amounts of iodine. The iodine is removed in a scrub column and pure oxygen leaves the system as a product [4].

Section-2 is the H_2SO_4 concentration and decomposition step. The 57% by weight sulfuric acid is concentrated in a series of flash evaporators. It is then decomposed to H_2O and SO_3 , and the SO_3 is decomposed to SO_2 and O_2 at 850°C using concentrated solar radiation. At this temperature, this reaction is basically slow, but thermodynamically favored. The gaseous mixture of SO_2 and O_2 is then separated from the H_2O and unreacted H_2SO_4 before it is sent back to Section-1. Section-2 is the most complicated and technologically demanding part and has been subject to many modifications and innovations [4].

Section-3 is the HI separation step. The HI is separated from $\text{HI-I}_2\text{-H}_2\text{O}$ solution coming from Section-1. The HI is purified to a level where it can be sent for decomposition. Purified HI at 5 MPa is decomposed at 120°C in a decomposition reactor. The hydrogen product is separated from most of the I_2 and some HI in a liquid gas separator. The gaseous H_2 product is then scrubbed with H_2O , and pure hydrogen is the resulting product. The I_2 is returned to the main solution reaction in Section 1.

The challenging problems to simulate the Sulfur-Iodine cycle are listed below [8]:

1. The chemical species include strong acids (H_2SO_4 and HI) that dissociate and thus an electrolytic model must be used for accurate and reliable process analysis and simulation.
2. In Section-1, a two-phase solution occurs; with a light phase containing sulfuric acid and a heavy phase containing iodine and hydrogen iodide. This phase separation is the key to successful implementation of the S-I cycle and must be simulated accurately.
3. Section-2 has units that operate at a very high temperature that exceed the critical temperature of water (374°C). At these temperatures, ions tend to exist as pairs and this must be correctly accounted for in the simulation.
4. Section-3 exhibits complex behavior of the $\text{HI-I}_2\text{-H}_2\text{O}$ system that includes multiple liquid phases. While the process conditions apparently do not include regions where multiple liquid phase behavior actually occurs, the simulation must correctly account for this behavior, if only to avoid such regions.
5. Even after the complex behavior is correctly modeled, the complexity of the nonideality causes serious convergence difficulties. These convergence difficulties must be overcome.

The prime objective of this study is to develop building blocks and flowsheet models for the S-I cycle. The reasons for choosing the S-I cycle for simulation are that it is the base cycle for this research implemented by General Atomics (GA) and it is the only thermochemical cycle which is fully flowsheeted. The physical properties model used is the ELECNRTL model which captures the nonideality of the ionic liquid solutions, but

needs to be coupled with chemistry model that describes the dissociation reactions that occur in solution. Because of the complexity and variety of phenomena that occur in various parts of the process, many chemistry models have been developed.

3.2.1. Section-1: H₂SO₄ and HI Acid Generation

Section-1 is the main section which generates the sulfuric acid and hydroiodic acid through the following reaction:

Fig. 3.10 shows the process flowsheet and Figure 3.11 shows the simulation flowsheet of Section-1, respectively. The main reaction occurs in several pieces of equipment. The two reactive columns (C-101 and C-104) in Fig. 3.11 scrub process streams to remove costly iodine.

Figure 3.10 Flowsheet of Section-1 of S-I cycle [8]

It is assumed that the reaction can be described as a vapor-phase equilibrium reaction in a distillation column (Redfrac). The main reaction takes place in the heat exchange reactor (R-101). This is a rather complicated piece of equipment. It has been assumed that the reaction is a kinetically-controlled liquid-phase reaction and the RCSTR model in ASPEN PLUS is used to model the reactor. It is expected that accurate modeling of this reactor will require laboratory or pilot-plant data. The output from the heat exchange reactor consists of three phases, which are separated in separator S-101. The gas phase contains residual SO_2 in O_2 . The SO_2 is removed by chemical reaction in column C-101. Column C-103 is a three-phase device in which the vapor and the light liquid phase (sulfuric-acid phase) move up the column and the heavy iodine phase moves up the column. The other pieces of equipment in Section-1 have been described using standard models in ASPEN PLUS, i.e., FLASH2 (separator), FLASH3 (separator), MIXER

Figure 3.11 Simulation flowsheet of Section-1 (S-I cycle)

(mixing block), PUMP, COMPR (compressor), FSPLIT (separator), RADFRAC (column), and HTX (heat exchanger).

3.2.2. Section-2: H₂SO₄ Concentration and Decomposition

Section-2 in the S-I cycle contains two important steps: sulfuric acid purification and decomposition. The purification step is important because if a high purity of sulfuric acid can be obtained before the stream enters the acid decomposition unit operation, the decomposition step can be carried out with high efficiency. The reaction involved in this section is as follows.

Sulfuric Acid Concentration: A series of chemical engineering unit operations are employed to vaporize and separate water from H₂SO₄ solution for heat recovery and boiling water during the sulfuric acid decomposition process. After vaporization, low pressure water vapor is condensed, and then the liquid water is pumped out of the system. The sulfuric acid solution flows through four connected and heated chambers. Water is boiled off in each chamber so that both the temperature and the acid concentration of the solution increase as the solution flows through the concentrator. The water vapor boiled off in each chamber is mixed above the chambers and leaves as a single stream [3].

Sulfuric Acid Decomposition: Concentrated H₂SO₄ is decomposed into sulfur trioxide and water and then the former is further decomposed into sulfur dioxide and oxygen. Before the sulfuric acid can be decomposed, it must be heated to the vaporization temperature and vaporized. Some of the heat required to preheat the stream prior to vaporization is recovered from the liquid product of the isobaric concentrator but the

remainder of the heat required for heating, vaporizing and decomposing the sulfuric acid can be provided from concentrated solar radiation [3].

Acid Concentration Subsection: The sulfuric acid with 57% by weight concentration flowing out from Section I is circulated through EV1, S1, HX1, S2, PI, HX2, S3 and P2 (Fig. 3.12) into the SO_3 absorption tower T. Stream 1 is at 0.18 MPa; it is expanded at EV1 to 0.008 MPa; hence, the evaporation of some water and its separation is achieved in S1. The biggest portion of the evaporation of water and its separation is achieved by heating through HX1, HX2 and S2, S3. The pressure of stream 7 is increased by pump P1 to 0.02 MPa, which is the operating pressure of HX2 and HX5. The outlet gases stream 10 from S3 is cooled down from 425.7 to 370 K in HX5. The outlet stream from HX5 is then divided into two streams, 21 and 22, in such a way as to recuperate enough energy to use in heat exchangers HX6 and HXI. Stream 21 is condensed through condenser C2, pumped through P6 and sent to Section I; its energy is wasted. To increase the quality of the steam in stream 22, it is compressed to 0.08 MPa through compressor CO. Its energy is then recovered in heat exchangers HX6 and HXI. It is condensed in the latter, pumped through P4 and sent to Section-1. The pressure of stream 11 is increased to 1.2 MPa by pump P2, which is the operating pressure of the tower T and other subsections. Stream 12 flows in a counter current mode with incoming stream 19 from the acid evaporation subsection. Stream 19 is cooled in direct contact with the cold sulfuric acid, during which all gaseous H_2SO_4 condenses and the SO_3 is absorbed. Liquid H_2SO_4 coming from the bottom of tower T is pumped through P3 to the acid evaporation section [4].

Figure 3.12 Flowsheet of Section-2 of S-I cycle [4]

Acid Evaporation Subsection: Stream 15 contains all liquid products which are transferred to the acid evaporation subsection. It is heated from 638.2 to 707.8 K, hence partial evaporation of the sulfuric acid and partial production of SO_3 are performed in HX3. The mixture of gas and liquid is then circulated through HX4 where all sulfuric acid is evaporated, and the SO_3 production is achieved at 800 K. The outgoing gaseous stream 17 from HX4 is sent to the SO_3 decomposition subsection.

SO_3 Decomposition Subsection: The gaseous products in stream 17 are sent to the decomposition reactor D where the SO_3 is catalytically decomposed at 1120 K. This high temperature can be supplied by the solar concentrated energy. The outlet gases in stream

18 from the decomposition reactor D is sent to heat exchanger HX3, where it is cooled to 693.6 K before entering the absorption tower T.

Figure 3.13 Simulation flowsheet of Section-2 of S-I cycle

The SO_3 is completely absorbed in tower T, and the product SO_2 , together with other gases, comes out in stream 13. The outlet gases in stream 13, containing 1 mol SO_2 , are finally cooled to the condensing temperature of the water in heat exchangers HX2, HX 1, and separated in S4 and S5. Stream 32 contains 0.5 mol O_2 , 0.9288 mol SO_2 and 0.1 mol H_2O at 366.2 K and 1.2 MPa. Stream 32 is heated to 465.5 K in HX6 then expanded to 0.2 MPa through expander EXP. Outgoing stream 34 from expander EXP is heated to 376.8 K in HX5 before going into Section-1.

A process simulation model has been developed and is shown in Fig. 3.13. Instead of helium reactor which was used to decompose SO_2 by Ozturk, Hammache and Bilgen [4], a continuous process reactor has been used in this simulation. Though simulation results are useful for process analysis more work needs to be done for accurate process design.

Temperature Stability of H_2SO_4 Decomposition:

When the decomposition temperatures remain above 750°C , the process remains stable with H_2SO_4 conversions close to 100% with about 98% SO_2 yield. Results of the Fig. 3.14 indicate that when the reaction temperatures are lower than 800°C , the extent of H_2SO_4 conversion and SO_2/O_2 yields drop dramatically. The process stability over a wide range of temperature shows great promise for the possible utilization of solar energy as a heat source for the sulfuric acid decomposition step. The graph shown in Fig. 3.14 describes the process stability over H_2SO_4 decomposition and SO_2 yield.

Figure 3.14 Temperature stability of H_2SO_4 decomposition

3.2.3. Section-3: HI Separation and Decomposition Step

In Section-3 HI is separated and decomposed from the HI-I₂-H₂O solution coming from Section-1. Process analysis of this section is rather complicated because of complex behavior of the HI-I₂-H₂O solution which includes multiple liquid phase and possible solid precipitation. The iodine-water binary mixture is highly non-ideal. Iodine may precipitate as a solid at 113.6°C.

The stream coming from Section-1 is pumped to 22 bars and preheated to the boiling temperature of 262°C and then enters a distillation column. The product from the bottom consists of mostly iodine and small parts of water and HI. To close the water balance, a side stream must be taken out of the column. This stream consists of water, HI and a small amount of iodine. The ratio of HI/H₂O mole fractions of the side stream is lower than the ratio of feed stream. The overhead product of the column is scrubbed in a packed column with water to remove the residual hydrogen iodide from the hydrogen. The high pressure and relatively low temperature of the scrubber result in a relatively low water content in the hydrogen product. Fresh deionizer water, the overall water input to the process, is used to scrub the product hydrogen [5, 8].

Simulation Flowsheet Analysis of Section-3:

The process flowsheet of Section-3 indicates simulations of the reactive distillation column. In GA's final report it has been stated that due to convergence difficulties and time limitations, a complete simulation of Section-3 was not completed. The reactive distillation flowsheet developed in this study is based on information presented by Roth and Knoche [5]. By adding a heater or heat exchanger on the stream line (top and bottom

line coming out from reactive distillation column) and making a recycle loop in the simulation flowsheet, the flowsheet can be converged.

Two ASPEN PLUS simulation flowsheets of hydrogen production by reactive distillation of HI-I₂-H₂O mixtures have been developed in this study. The first simulation file (liquid draw), described by Fig. 3.15, simulates the reactive distillation as a 7-tray column with HI dissociation to form H₂ and I₂ on all trays. The column feed is at its bubble point at 265°C and enters the column on tray 5. A liquid side draw is taken from tray 3. The distillate rate is set to 5 kmol/hr and the boil up rate is set to 2.0 [5].

The convergence strategy developed is as follows. The column first converged without the H₂ production. Now the equilibrium constant for HI dissociation to H₂ was set to a relatively low value and the reactions were assumed to occur on trays 2-7. Finally, the equilibrium constant for HI dissociation to H₂ was gradually raised to the correct value.

Figure 3.15 Simulation flowsheet of Section-3 of S-I cycle (liquid draw)

Figure 3.16 Simulation flowsheet of Section-3 of S-I cycle (vapor draw)

Once convergence is achieved, estimations are generated for the column. The column is now converged reliably at given feed and operating conditions. The simulation predicts that as the side draw is increased, the H_2 production decreases and the water content of the bottom decreases. The second simulation flowsheet of the same column configuration as the first case has been developed, but with a vapor side draw, shown in Fig. 3.16.

The simulation results indicate that the liquid side draw is better because the hydrogen production is higher and also very little hydrogen escapes in the liquid side draw.

3. 2. 4. Efficiency Analysis of S-I Cycle

Energy requirements for all the three sections of the S-I cycle are summed and net heat and power demands are also calculated. All the energy values are based on the generation of one mole of hydrogen by the process. Efficiency is defined as the ratio of hydrogen heating value to the sum of the heat and electrical inputs required. The total net energy requirement for the process is divided into the heating value for hydrogen to obtain an estimate for the thermal efficiency of the process. The following table depicts the overall energy balances for each section.

Table 3.5 Energy balance for the three sections of S-I Cycle

kJ/mole H ₂	Section 1	Section 2	Section 3	Process Section Total
Gross Power Load	1.33	4.91	63.82	70.06
Power Recovery	44.51	0.26	0	44.77
Net External Power Load	-43.18	4.64	63.82	25.28
Net External Heat Demand	0	144.20	596.24	740.44
Net External Energy Demand	-43.18	148.84	660.06	765.72

The efficiency of the sulfur-iodine cycle can be calculated by using the following

equation:

$$\varepsilon = \frac{\Delta H}{Q + \frac{E}{\eta}}$$

where, ε = Thermal efficiency

ΔH = Hydrogen heating value

Q = External heat demand for cycle

E = External power demand for cycle

η = Efficiency of external electrical power generation

The higher heating value of hydrogen is 282.2 kJ/mol. The net external heat demand is 740.44 kJ/mol H_2 . The net external power requirement is 25.28 kJ/mole H_2 . If electrical energy supplied from outside the process (at assumed 50% efficiency for power generation), an estimate for the thermal efficiency of the process is

$$\varepsilon = \frac{282.2}{740.44 + \frac{25.28}{0.50}} = 0.36 = 36\%$$

The efficiency of S-I cycle estimated here does not match the efficiency given in GA's final report. Assuming 50% efficiency for power generation, the overall efficiency of the proposed S-I cycle of GA was 41% and assuming 100% efficient electrical power generation for the process it came close to 49%. The efficiency of S-I cycle mainly depends on the decomposition of H_2SO_4 (Section-2) to SO_3 . The decomposition of SO_3 needs higher temperature (in excess of 830°C). Increasing the process temperature to 900°C will let the process operate at higher efficiency.

3.2.5. Results of the Simulations of S-I Cycle

Results of the simulation of Section-1 are summarized as follows:

1. A thermodynamic simulation model has been developed using ASPEN PLUS for Section-1.
2. Equilibrium and kinetic of the building blocks have been developed to capture the main reactive processes in this section.
3. Though the simulation model converged, several experimental, modeling and computational challenges remain.
4. Predicted chemical composition for the simulation may not be accurate for actual process design.
5. Section-1 requires no thermal energy; it is an exporter of heat to the environment. This heat energy can be utilized in the subsequent sections.
6. Though the results of simulation of Section-1 are preliminary, it will be very helpful for modifying and improving future process analysis and design for S-I cycle.

Results of the simulation of Section-2 are summarized as follows:

1. A process analysis flowsheet of Section-2 of the S-I cycle has been developed.
2. Though the simulation results are converged, operating conditions and estimations for some of the building blocks should be modified for better efficiency.
3. Almost 100% of the H_2SO_4 feed in the section 2 decomposes into SO_2 at the end of the process analysis. SO_2 is then separated from O_2 and sent to Section-1 to produce acid.

4. The efficiency of the S-I cycle is mostly dependent on this section. The decomposition temperature of SO_3 plays an important role for improving the cycle efficiency. Efficiency will be increased with an increase in SO_3 decomposition temperature.
5. The process stability over a wide temperature range shows great promise for the possible utilization of concentrated solar energy as a heat source for the H_2SO_4 decomposition step.

Results of the simulation of Section-3 are summarized as follows:

1. Two simulation flowsheets for Section-3 by reactive distillation of $\text{HI-I}_2\text{-H}_2\text{O}$ mixtures have been developed. The first simulation flowsheet has a liquid draw from the column and second has a vapor draw.
2. From the data browser it can be seen that all the variables (total mole flow, mass enthalpy, H_2O mole flow, I_2 mole flow, HI mole flow, etc.) have been converged within the given tolerance limit.
3. The simulation results suggest that the liquid side draw is better because the hydrogen production is higher and also very little hydrogen escapes in the liquid side draw.
4. Though the process analysis simulation of Section-3 has been converged, operating condition and physical property estimation should be modified to get better results.
5. As the reaction involved in Section-3 is endothermic reaction, the process heat for this section should be supplied from a solar heat source.

3.3. Process Analysis and Simulation of Copper-Chlorine Cycle

Copper-chlorine (Cu-Cl) cycle is a good alternative for hydrogen gas generation at low temperature in which chemicals are combined with water and heated to cause chemical reactions that produce hydrogen (and oxygen) at 550°C – a temperature compatible with current power plant technologies. The chemicals are not consumed, and are recycled. Argonne National Laboratory's Chemical Engineering Division is currently working on this cycle. The cycle is referred as Argonne Low Temperature Cycle-1 (ALTC-1). This cycle is considered promising over other cycles for the following reasons [13]:

1. The maximum cycle temperature ($<550^{\circ}\text{C}$) allows the use of multiple and proven heat sources
2. The intermediate chemicals are relatively safe, inexpensive and abundant
3. Minimal solids handling is needed
4. All reactions have been proven in the laboratory and no significant side reactions have been observed.

One potential disadvantage with ALTC-1 cycle is that one of the reactions is electrochemical, which imposes a significant energy cost. However, the experimental data suggest that the electrolytic step can be performed at voltages significantly lower than in direct water electrolysis.

The Cu-Cl thermochemical cycle was first proposed by Carty et al. and was designated H-6 in a Gas Research Institute (GRI) report [12]. In that study, H-6 consisted of four reactions, three thermal and one electrochemical. ANL's preliminary study indicated that two additional reactions should be added to the original H-6 cycle. So the

proposed ALTC-1 cycle consists of six reactions. Reaction-1 is the hydrogen generation reaction and Reaction-6 is oxygen generation reaction [12]. The other reactions close the cycle. The reactions involved in ALTC-1 cycle are given in the following table:

Table 3.6 Reactions involved in Cu-Cl cycle

Reaction No.	Reaction	Temp. °C	ΔG kcal/mol	ΔH kcal/mol
1.	$2\text{Cu(s)} + 2\text{HCl(g)} = 2\text{CuCl(l)} + \text{H}_2\text{(g)}$	450	3.85	-13.50
2.	$4\text{CuCl(s)} + 4\text{Cl}^-\text{(aq)} = 4\text{CuCl}_2^-\text{(aq)}$ Electrochemical step	30	8.27	0.06
3.	$4\text{CuCl}_2^-\text{(aq)} = 2\text{CuCl}_2\text{(aq)} + 2\text{Cu(s)} + 4\text{Cl}^-\text{(aq)}$ Electrochemical step	30	14.50	2.93
4.	$2\text{CuCl}_2\text{(aq)} = 2\text{CuCl}_2\text{(s)}$	100	6.0	19.90
5.	$2\text{CuCl}_2\text{(s)} + \text{H}_2\text{O(g)} = \text{CuO(s)} + \text{CuCl}_2\text{(s)} + 2\text{HCl(g)}$	400	9.50	28.00
6.	$\text{CuO(s)} + \text{CuCl}_2\text{(s)} = 2\text{CuCl(l)} + 1/2\text{O}_2\text{(g)}$	550	-1.93	31.00

The first step in cycle development is to determine its thermodynamic feasibility. The free energies and the enthalpies for the reactions shown in the above table were obtained by using HSC Chemistry 5.11 which contains a thermodynamic database. At the temperature indicated in the table, based on cycle stoichiometry to produce 1 mol of hydrogen, the free energy change of each reaction step is ± 10 kcal, except for the

electrochemical step, which has ΔG of 14.50 kcal/mol at 30°C. The current research of this cycle at ANL concludes that all of these reactions are viable on thermodynamic basis using the values of the free energies.

According to Carty [12], who proposed this cycle in a Gas Research Institute (GRI) report in 1981, reactions whose free energy change lies within ± 10 kcal for a given temperature are considered likely candidates for a cyclic process. Small positive free energy changes are acceptable if nonequilibrium reactor configurations can be utilized, such as continuous product removal, reactants in excess, and where there are a smaller number of product gases than reactant gases. Reactions with a positive free energy change of 10 to 25 kcal/mol can generally be accomplished electrochemically.

3.3.1. Study of the Reaction Kinetics of Cu-Cl Cycle

H₂ Production (Reaction-1): $2\text{HCl (g)} + 2\text{Cu(s)} = 2\text{CuCl (l)} + \text{H}_2 \text{ (g)}$

The reaction between HCl and Cu is a heterogeneous exothermic reaction. It has been suggested that the reaction proceeds rapidly at 230°C, the temperature at which 93% of HCl is decomposed and the Gibbs free energy change is -3.95 kcal/mol. However no hydrogen is detected at this temperature. Hydrogen starts to be produced in significant amounts at temperature above 350°C. 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 [13].

For a batch process, a reaction tank in which Cu powder/granules are fed with a continuous bleed of HCl gas could be utilized. However, a continuous process reactor can be used in this step. Process heat from a solar concentrator is used to heat the mixture to the reaction temperature. The copper could be introduced at room temperature and

heated to the desired reaction temperature, or it could be preheated before placing it in the reactor. Obviously, preheating will reduce the overall length of this reactor [25].

Copper Production by Electrolysis:

CuCl is very sparingly soluble in water but soluble in HCl. The electrochemical disproportionation of CuCl is therefore being conducted at room temperature in an HCl aqueous solution.

Recovery of CuCl₂(s) from the Aqueous Solution Containing CuCl₂ and HCl:

The output from the eletrolyzer will be an aqueous solution containing CuCl₂ and HCl. This step involves recovery of the CuCl₂(s) from the solution for the subsequent oxygen production step. This step also involves addition of sufficient thermal energy to remove (by vaporization) the water and HCl in order to recover the solid CuCl₂. Process heat from the solar panel should be used to preheat the solution to 110°C before the mixture is forced through settling chamber [25].

Oxygen Production Step:

The first step of this two-step process involves steam oxidation of CuCl₂ at 400° C. The second step involves additional heating of the reaction byproduct to 550°C where the

$\text{CuO(s)} + \text{CuCl}_2\text{(s)}$ react to form CuCl(l) and $\text{O}_2\text{(g)}$. Process heat from the solar heat source is used to provide the thermal energy needed to carry out these reactions.

The net heat input to the Cu-Cl thermochemical cycle is to be provided by the solar panels. Of the chemical reactions, the oxygen production step has the highest temperature requirement, 550°C . Several factors require raising the design value to achieve the necessary oxygen production temperature. First, the process heat will be delivered through a heat exchanger and there will be an associated temperature drop along the length of the heat exchanger as heat is transferred. If this temperature drop is taken as 40°C , then to achieve an average temperature on the primary side of the heat exchanger of 550°C , the coolant must enter at 570°C . Second, there is a temperature drop of roughly 20°C when passing across sodium heat exchanger tubes. Thus, a solar heat source capable of delivering temperature of about 580°C is needed to satisfy the oxygen production process step [25].

3.3.2. Process and Simulation Flowsheet of Cu-Cl Cycle

The Cu-Cl cycle is considered as a closed cycle since all materials are recycled with the exception of water which is split into hydrogen and oxygen. The process involves six separate reactions: four thermal steps driven by heat and two electrolytic steps driven by electric energy.

Figure 3.17 Schematic diagram of Cu-Cl cycle developed by ANL

The reactor provides the heat while a Rankine cycle driving a generator provides the electrical energy. A schematic diagram (Fig. 3.17) of Cu-Cl cycle is shown above for better understanding.

In the given diagram solar panels are used to produce the heat to complete the last three steps of this cycle. Heated steam coming from the solar panels will enter into the reactor to generate HCl at 400°C. CuCl₂ from the aqueous CuCl₂ dryer reacts with steam to produce HCl. The other products of this reaction, CuO and CuCl, are then sent to another reactor to form O₂ at 500°C. The other product of this reaction, CuCl, recycles back to the electrolysis step. HCl produced by the HCl generation reactor then passes through the HCl-dryer where dry and pure HCl is stored in a tank and some portion of it along with H₂O is stored in another tank. HCl from the dry HCl tank is sent to the hydrogen generation reactor where it reacts with Cu recovered from the electrorefiner at 450°C. Process heat from the solar reactor is used to heat the mixture to the reaction temperature. The copper could be introduced at room temperature and heated to the desired reaction temperature, or it could be preheated before placing it in the reactor. The produced gas is not pure and a small amount of HCl is mixed with H₂. To extract pure H₂ gas, this mixture passes through a separator where pure H₂ gas recovery takes place and the unwanted HCl is sent back to the dry HCl tank.

Flowsheet Analysis of Cu-Cl Cycle:

Two ASPEN PLUS process blocks (one reactor and one separator) have been combined together to model an electrolyzer which is shown in Fig. 3.18. Two general reactors (one for the cathode and one for the anode) can be combined with electrons and ions as reactants, and with a stream flowing between the two reactors to account for the electrical flow. This would be the most rigorous way of simulation. But the simulation of the Cu-Cl cycle used a single reactor that is in electrical balance (both cathode and anode steps) and then followed this reactor with a component separator to generate the cathode

product and anode product streams. Here in the process flowsheet Block ELCTRLYZ does the electrolysis reactions, but Block SEP-1 separates the reaction products into anode and cathode streams, so it can be said that both blocks together act as the electrolyzer.

Figure 3.18 Simulation flowsheet of Cu-Cl cycle

The reactions have been defined in the individual reactor blocks instead of globally. Block ELCTRLYZ does the electrolysis reactions, Block CU-HYDRO does the CuCl_2 hydrolysis which produces HCl, Block O2-REACT does the oxygen production reaction, and Block H2-REACT contains the hydrogen production reaction. The reaction mechanisms specified for these blocks can be found in the reaction tab of these blocks.

Sometimes it took two reaction definitions to get the desired reaction to take place: one reaction for the solid species and another for the dissolved species.

3.3.3. Efficiency Analysis of the Cu-Cl Cycle

Efficiency of the Cu-Cl cycle can be calculated following the efficiency calculation procedure of the sulfur-iodine cycle. All the energy values are based on the generation of one mole of hydrogen by the process. Efficiency is defined as the ratio of hydrogen heating value to the sum of the heat and electrical inputs required. For the electrical energy, an efficiency of 50% is assumed for any electrical generation not supplied by the process. In equation form:

$$\varepsilon = \frac{\Delta H}{Q + \frac{E}{\eta}}$$

ε = Thermal efficiency

ΔH = Hydrogen heating value

Q = External heat demand for cycle

E = External power demand for cycle

η = Efficiency of external electrical power

Here Q is the sum of the endothermic enthalpies (heat inputs) and E is the sum of the work inputs, which are converted to heat inputs by dividing the work inputs by the efficiency for converting heat to electricity, η . This calculation is referred to as the lower heating value (LHV) basis.

Table 3.7 Energy balance of Cu-Cl cycle

External Heat Input Devices	Heat Input kJ	Power Devices	Power Device Energy Load kJ	Heat Recovery Devices	Heat Recovery kJ
Heater-1	14849	ELCTRLYZ	861.51	Heater-2	-72.107
Heater-4	10436	Pump-1	144.36	Heater-3	-13587
Heater-5	346.12	Pump-2	72.36	Heater-6	-1292.30
Heater-7	1220.69	Pump-3	15.37	Heater-8	-8883.74

Total heat input = 26851.81 kJ

Total heat recovery = -23835.15 kJ

Total power recovery = 1093.6 kJ

$$\varepsilon = \frac{241.826}{26851.81 + (-23835.15 - \frac{1093.60}{0.50})} = 29.15\%$$

So, based on thermodynamic analysis, the efficiency of the Cu-Cl cycle for the simulation is 29.15%. More reliable efficiency values can be obtained after the chemistry of the cycle is well defined.

3.3.4. Result summary of the simulation of Cu-Cl cycle

1. The thermodynamic feasibility of the reactions involved in the Cu-Cl cycle has been checked out. It can be concluded that all reactions are thermodynamically viable based on the values of the free energy.
2. A process flowsheet for the Cu-Cl cycle has been developed for hydrogen generation with a solar heat source.
3. Though the simulation results converged, operating conditions for the heat exchanger and reactors should be modified for better efficiency.
4. Based on thermodynamic analysis, the efficiency of the Cu-Cl cycle is 29% which is less than the efficiency calculated by the Chemical Engineering Division of ANL (41%).
5. More reliable efficiency values can be obtained after the chemistry model of the cycle is well defined.
6. Process heat for the O₂ and HCl generation steps will be supplied from a solar concentrated heat source.

CHAPTER 4

CONCLUSION AND SUGGESTIONS

In this project three different solar thermochemical cycles have been analyzed to produce hydrogen gas. In all cases simulation flowsheets have been developed and converged solutions have been obtained. At the end of the simulation of each cycle, efficiency has been calculated. Though the simulation results are converged, the operating conditions and input parameters should be optimized for better efficiency. Here some of the concluding remarks and suggestions have been pointed out for future work.

Methane Reforming Process:

- Each reforming reactor is expected to have its own favorable operating characteristics. As equilibrium is assumed, these may vary in practical situations. Nevertheless, the results provide a valuable indication of the starting point for experimental research.
- The thermal energy required in each of the reforming systems (which is comprised of a reforming reactor, a water-gas shift reactor, a steam generator and a heat exchanger) has been evaluated by performing material and energy balances for each system.
- The temperature strongly affects the conversion and the selectivity of the process towards hydrogen and carbon dioxide formation.

- The results show that the POX reforming system is superior to the other two systems for the production of the same amount of hydrogen from CH_4 .
- The Efficiency of the POX reforming system (62.5%) is also found to be better than the SMR (52%) and ATR (54.77%) systems.
- Process heat for the reactors will supplied from solar heat. Selecting an efficient and cost effective solar receiver or concentrator is a very challenging issue.
- Results of the simulation of the three reforming processes have been compared with the experimental results of Seo, Y.-S., Shirley, A., and Kolaczowski, S. T. [14] and they are found to be close. The POX system has been found to be the better choice over the other two systems for the production of the same amount of hydrogen from CH_4 at the end of experimental and simulation results.
- The solar flux concentration ratio typically obtained is at the level of 100, 1000, 10000 suns (unit of solar concentration ratio) for trough, tower and dish systems respectively. Higher concentration ratios imply lower heat losses from smaller areas and, consequently, higher attainable temperatures at the receiver. In this context, a solar dish concentrator will be a better selection as a potential heat source for this research.
- The methane reforming simulation modeling started here can be extended to evaluate the technical and environmental implications of alternatives in process design and operations.

Sulfur-Iodine Cycle:

- Thermochemical water splitting cycles promise efficient hydrogen production by using the inherently transient heat sources as solar energy.
- Process analysis and simulation flowsheet for all the three sections of the S-I cycle have been developed with chemical analysis simulator ASPEN PLUS.
- The simulation flowsheet of Section-1 has been developed by following General Atomics Final Report 2003. The simulation flowsheet of Section-2 has been developed by following Ozturk, Hammache and Bilgen [4]. The flowsheet of Section-3 has been developed by following Roth and Knoche [5].
- All the simulation models developed have been converged with the given reaction models and operating condition.
- It is expected that accurate modeling of RCSTR (continuous stirred tank reactor) used in Section-1 will require laboratory or pilot-plant data.
- Process heat from an outside source is necessary for Section-2 and Section-3 as these two sections are endothermic. A potential solar concentrated heat source will produce the energy for H_2SO_4 and HI decomposition.
- The efficiency of the overall S-I cycle has been calculated and it is found to be 36%. The efficiency calculated by GA is 41% (assuming 50% efficiency for power generation) and 48% (assuming 100% efficient electrical power generation).

- The efficiency of S-I cycle indicated above is from thermodynamic data from ASPEN PLUS. As a full scale pilot plant is yet to built, the actual efficiency for the S-I cycle may vary from the above the efficiency range.
- While the results presented in this research are preliminary, the ASPEN PLUS models promise to be useful to evaluate and improve the overall S-I cycle.
- As Section-1 is exothermic and Section-2 and Section-3 are endothermic, the thermal duty coming out from Section-1 can be used in Section-2 and Section-3 to decompose acids. This action might reduce some overall cost and increase overall efficiency.
- The efficiency of a thermochemical cycle will increase with temperature as higher temperatures provide more opportunity for heat recuperation and reuse within the process [8]. In the case of the S-I cycle, the equilibrium decomposition of sulfuric acid to sulfur trioxide and the equilibrium decomposition of sulfur trioxide both increase with an increase in temperature.
- Cost analysis and estimation of S-I cycle has not been done in this study. It is very important to analyze and estimate the cost of hydrogen gas from this cycle. It would give a good idea whether the cycle is practically feasible or not.

Copper-Chlorine Cycle:

- A process analysis flowsheet has been developed by following the current experimental and simulation work done by ANL.
- Thermodynamic feasibility of the reactions involved in the Cu-Cl cycle has been determined using HSC Chemistry 5.11.
- It is evident from Table 3.6 that the free energy of each of the reactions is very low which is a characteristic of simple reactions. This indicates that use of catalysts is unnecessary for this cycle.
- Simulation models have been developed based on the experimental setup and data.
- Process heat will be supplied from a concentrated solar heat source which will be mainly needed for the steps where O_2 and HCl are generated.
- Though one of the reactions is electrochemical, this cycle poses advantages over the S-I cycle because of its operating temperature ($550^\circ C$).
- Efficiency has been found to be 29% for this cycle. The efficiency calculated by ANL based on the thermodynamics of this cycle is 41%. More reliable efficiency values can be obtained after the chemistry of the cycle is well defined.
- It is important to note that the energy required for compression and separation, and for any inefficiencies and irreversibilities, has not been included in the efficiency calculation. Nevertheless, the efficiency estimates indicate that further development is justified.

- Though the simulation model presented for this cycle is preliminary, it will be very helpful for producing insights for future improvement of this cycle.
- The cost analysis of Cu-Cl cycle has not been done. But it is very necessary to conduct cost analysis and estimation for the economic feasibility of the cycle.
- The solar input must be matched to the chemical process such that high thermal efficiency is obtained, but not at the expense of sacrificing the operability of the combined plant.
- The matching must be done in a way that promotes operational stability of the chemical process.
- Significant research should continue to fully characterize cycles to realistically estimate cost and efficiency, demonstrate the feasibility of the processes to produce significant amounts of hydrogen, and understand tradeoffs between different thermochemical cycles.

REFERENCES

- [1] Jericha, H.; Starzer, O.; Theissing, M., Towards a solar-hydrogen system, 1991 ASME COGEN-TURBO; 5th International Symposium and Exposition on Gas Turbines in Cogenerations, Repowering, and Peak-Load Power Generation, 6 (1991), 435-442.
- [2] Nicoletti, G., Hydrogen option for energy; a review of technical, environmental and economic aspects, International Journal of Hydrogen Energy, 20 (1995), 759-765.
- [3] Huang, C.; Raissi, A., Analysis of sulfur-iodine thermochemical cycle for solar hydrogen production. Part-I: decomposition of sulfuric acid, Solar Energy 2004 (article in press-available online from March 2004).
- [4] Ozturk, I.T.; Hammache, A.; Bilgen, E., An improved process for H_2SO_4 decomposition step of the sulfur-iodine cycle, Energy Conversion Management, 36 (1995), 11-21.
- [5] Roth, M.; Knoche, K. F., Thermochemical water splitting through direct HI-decomposition from $H_2O/HI/I_2$ solutions, International Journal of Hydrogen Energy, 14 (1989) 545-549
- [6] Normana, J. H.; Myselsb, K. J.; Sharpa, R.; Williamsonc, D., Studies of the Sulfur-Iodine thermochemical water splitting cycle, International Journal of Hydrogen Energy, 7 (1982), 545-556.

- [7] Bilgen, C.; Bilgen, E., An assessment on hydrogen production using central receiver solar systems, International Journal of Hydrogen Energy, 9 (1984) 197-204.
- [8] Brown, L.C.; Besenbruch, G. E.; Lentsch, R.D.; Schultz, K.R.; Funk, J. F.; Pickard, P.S.; Marshall, A.C.; Showalter, S.K., High efficiency generation of hydrogen fuels using nuclear power, Final Technical Report, August 1, 1999 through September 30, 2002, General Atomics Report GA – A24285 (2003).
- [9] Sakurai, M.; Miyake, N.; Tsutsumi, A.; Yoshida, K., Analysis of a reaction mechanism in the UT-3 thermochemical hydrogen production cycle, International Journal of Hydrogen Energy, 21 (1996), 871-875.
- [10] Aihara, M.; Umida, H.; Tsutsumi, A.; Yoshida, K., Kinetic study of UT-3 thermochemical hydrogen production cycle, International Journal of Hydrogen Energy, 15 (1990), 7-11.
- [11] Tadokoro, Y.; Yamaguchi, T.; Sakai, N.; Yoshida, K.; Kameyama, H.; Aochi, T.; Nobue, M.; Aihara, M.; Amir, R.; Kondo, H.; Sato, T., A simulation study of the UT-3 thermochemical hydrogen production process, International Journal of Hydrogen Energy, 15 (1990), 171-178.
- [12] Lewis, M. A.; Serban, M.; Basco, J., Hydrogen production at 550°C using a low temperature thermochemical cycle, Proceedings of the OECD/NEA Meeting, Argonne National Laboratory, 2003.
- [13] Lewis, M. A.; Serban, M.; Basco, J., Kinetic study of the hydrogen and oxygen production reactions in the Copper-Chlorine Thermochemical Cycle, AIChE 2004 Spring National Meeting, New Orleans, LA, April 25-29, 2004.

- [14] Seo, Y.-S.; Shirley, A.; Kolaczowski, S.T., Evaluation of thermodynamically favorable operating conditions for production of hydrogen in three different reforming technologies, Journal of Power Sources, 108 (2002) 213-225.
- [15] Kalogirou, S. A., Solar thermal collectors and applications, Progress in Energy and Combustion Science, 30 (2004) 231-295.
- [16] Thomas, A., Solar steam generating systems using parabolic trough concentrators, Energy Conversion and Management 37 (1996) 215-245.
- [17] Steinfeld, A., Solar thermochemical production of hydrogen- a review, Solar Energy, 2004 (article in press).
- [18] Kameyama, H.; Funk, J. E., Simulation study of the UT-3 solar driven thermochemical hydrogen production process, 10th WHEC Conference 1994, Cocoa Beach, Florida.
- [19] ASPEN PLUS 12.1 Help Documentation from ASPEN Tech.
- [20] Khoshnoodi, M.; Lim, Y.S., Simulation of partial oxidation of natural gas to synthesis gas using ASPEN PLUS, Fuel Processing Technology, 50 (1997), 275-289.
- [21] Heinzl, A.; Vogel, B.; Hubner, P., Reforming of natural gas-hydrogen generation for small scale stationary fuel cell systems, Journal of Power Sources 105 (2002) 202-207.
- [22] Monnerat, B.; Kiwi-Minsker, L.; Renken, A., Hydrogen production by catalytic cracking of methane over nickel gauze under periodic reactor operation, Chemical Engineering Science, 56 (2001) 633-639

- [23] Moller, S.; Buck, R. T.; Epstein, M.; Liebermann, D.; Meri, M., Steam reforming of methane rich gas in a solar reactor, German Aerospace Center, Pfaffenwaldring, Stuttgart, Germany.
- [24] Wylen, G. V.; Sonntag, R. E., Fundamentals of Classical Thermodynamics, Second Edition, John Wiley and Sons Inc, 1993.
- [25] Vilim, R.B. (Argonne National Laboratory); Miron, A.; Feldman, E.; Bauer, T.; Farmer, M., Nuclear-chemical plant for low temperature hydrogen co-production, Global 2003: Atoms for Prosperity: Updating Eisenhower's Global Vision for Nuclear Energy, Global 2003: Atoms for Prosperity: Updating Eisenhower's Global Vision for Nuclear Energy, 2003, p 676-680.

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