

Huang Dan

**SULFUR-IODINE THERMOCHEMICAL CYCLE FOR
HYDROGEN PRODUCTION**

Bachelor Thesis

**CENTRAL OSTROBOTHNIA UNIVERSITY OF APPLIED
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Abstract

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Author: Huang Dan

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Supervisor: Kaj Jansson

The aim of the thesis was to study the Sulfur-Iodine thermochemical cycle for hydrogen production. There were three reactions in this cycle: Bunsen reaction, sulfuric acid decomposition and the hydriodic acid decomposition. The sulfuric acid decomposition required most heat in these three reactions. The thermal efficiency of this cycle mostly affects this section. The HYSYS simulator by Aspen Technologies was used for sulfuric acid decomposition. There were two steps in this section: sulfuric acid concentration and sulfuric acid decomposition. Thus two separate HYSYS simulations, firstly, were built for each of them. Then a whole process simulation was made for analysis. Based on the HYSYS analyses and the statistic of this data, 650°C was found the most suitable temperature for sulfuric acid decomposition with the highest thermal efficiency of 75.11%.

Key words: Sulfur-Iodine cycle, sulfuric acid decomposition, HYSYS simulation

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1 INTRODUCTION

1.1 Background

Energy is always the hot topic around the world. There are many different forms of energy carriers: the solid (e.g. wood, coal), the liquid (e.g. petrol, alcohol) and the gas (e.g. nature gas). For an energy carrier to enter the market, several objectives should be considered. The first one is the efficiency of the energy getting from burning those energy carriers: It is easy to see that the gas should be the most efficient energy carrier. When the distance between the molecules in gas form is the longest and well touched with oxygen, thus gas form burns much better the other two forms (solid and liquid) and gets more efficiency. Moreover the transportation of gas form energy carrier is the easiest one by using the pipelines. From these two objectives, gas form energy carriers should be the best in those three forms. Therefore the applications worldwide are slowly shifting from the solid energy carrier to gas form. Moreover another important objective that should be considered is the pollution. Carbon not well burned gets the toxic gas CO. Burning wood and coal it is easily to form CO. But even when well burned they still gets CO₂, cause of global warming. Thus new energy carriers are needed for the market. For a new energy carrier to enter the market, those objectives must be met. Today hydrogen (H₂) is one of the most widely used new energy sources, and as it is a non-pollution and reproducible gas-form energy carrier, the only product from burning it is water. International cooperation aims at delivering H₂ as a replacement fuel for vehicles. Hydrogen will be used as fuel for transport vehicles instead of gasoline/diesel oil/natural gas as fuel step by step in the future. The worldwide demand for hydrogen is about 50 million tons per year, and it is growing rapidly. Many experts believe that hydrogen will overtake electricity as the preferred energy source. (Thomas 2007.)

There are many ways to produce hydrogen, but not all of the methods can be a compromise between hydrogen economy and safety of environmental. The thermochemical method to produce hydrogen shows a big potential for hydrogen economy. In this method, high temperature heat is used as energy input to a sulfur-iodine water splitting cycle to get hydrogen. The sulfur-iodine cycle process, invented at General Atomics Company in the 1970s, is one such cycle developed for the large scale hydrogen production. The only input

in this cycle is water and the only products are hydrogen and oxygen. Unlike electrolysis, thermochemical cycles for splitting water can convert thermal energy directly into chemical energy by forming hydrogen and oxygen, without any greenhouse gas product. (Huang & T-Raissi 2005, 632.)

The sulfur iodine (S-I) water splitting cycle for hydrogen production consists of three coupled chemical reactions. The first reaction is called the Bunsen reaction. The second reaction is the HI decomposition reaction. The third reaction is the sulfuric acid decomposition reaction. In the S-I cycle, most of the input heat goes into the dissociation of sulfuric acid. The next reaction is the decomposition of water into hydrogen and oxygen. The whole process takes only water and high temperature heat and releases only hydrogen, oxygen and low temperature heat. All reagents are recycled; there are literally no effluents. The S-I cycle does require high temperatures, but offers the prospects for high efficiency conversion of heat energy to hydrogen energy. As the S-I cycle is widely used around the world today, more and more scientists pay attention on this topic. They try to decrease the heat energy used in the cycle and to make the process more efficient. (Patel, Maheshwari, Vijayan & Sinha 2005.)

1.2 Purpose and goals of the project

The purpose of this thesis is to study the S-I cycle flowsheet, the heat transfer in the cycle and the efficiency of the process. The reaction that requires the greatest heat input is the thermal decomposition of H_2SO_4 , typically at temperatures in the range of 800-900°C. Higher temperatures tend to favor greater efficiency. If the high temperature can be decreased to some extent, yet keeping efficiency in the same level, or even higher, then a great deal of sources can be saved. Thus H_2SO_4 decomposition is considered as the most potential step for making the process more efficient and for saving energy.

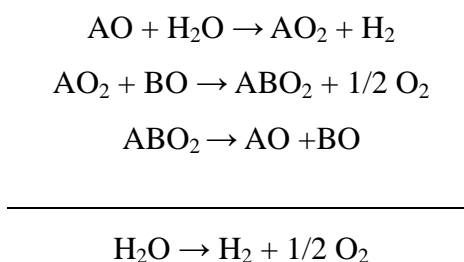
In this thesis the HYSYS chemical process simulator by Aspen Technologies is used for analyzing and increasing the sulfuric acid (H_2SO_4) decomposition efficiency in order to find a new solution for increasing the whole process efficiency. Also the HYSYS simulation based on the Bilgen flowsheet will be the most important aim for this thesis. After constructiong the simulation, five different temperatures of 650°C, 700°C, 750°C,

800°C and 850°C will be used for analyzing for the decomposition of sulfuric acid (H_2SO_4). A suitable temperature for sulfuric acid decomposition with the high efficiency should be found in this thesis. The temperature stability of the Bilgen flowsheet is low. An effort will be made to achieve higher temperature stability in this simulation.

2 THE SULFUR-IODINE THERMOCHEMICAL WATER-SPLITTING CYCLE

2.1 Thermochemical water-splitting cycle

Thermochemical production of hydrogen involves the separation of water into hydrogen and oxygen through chemical reactions at high temperatures (450-1000°C), and all the other chemicals are recycled in the process (Brown 2007a):



A thermochemical water-splitting cycle involves a series of chemical reactions, some at higher temperatures than others. Engineers carefully choose chemicals to create a closed loop system that reacts with water to release oxygen and hydrogen gases. All reactants and compounds are regenerated and recycled. Studies conducted through the Nuclear Energy Research Initiative were identified more than 100 different thermochemical water-splitting cycles. A few of the most promising cycles were 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. (Hydrogen 2008.)

The biggest challenge with thermochemical processes today is corrosion of process reactors and system materials. The reaction that requires the greatest heat input is the thermal decomposition of H_2SO_4 , typically at about 850°C. Higher temperatures tend to favor greater efficiency. (Hydrogen 2008.)

2.2 Inventing and Development of the S-I Cycle process

Since the conception of the first thermochemical cycle in 1960's, a large number of water-splitting cycles have been conceptualized and few of those extensively investigated.

The research collaboration of General Atomics (GA), Sandia National Laboratory (SNL) and University of Kentucky (UK) found 115 unique thermochemical cycles, but just 25 top thermochemical cycles selected to screening. Thermochemical cycles which have been intensively studied include Sulfur-Iodine, UT-3 Univ. of Tokyo, Westinghouse, Ispra Mark. The sulfur-iodine cycle for hydrogen production was invented at General Atomics (GA) in the 1975. Moreover all steps of the process were demonstrated at GA in 1975-1986. Full chemical flowsheets, process equipment sizing and plant cost estimates were generated for fission, fusion and solar powered plants –1980's, 2002, 2005. (Brown 2007a; Thomas 2007.)

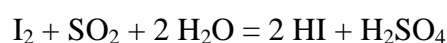
Extensive work was and is being carried out in other countries widely. Phase equilibrium measurements were conducted in Germany in the 1980's. Innovative flowsheets were developed in Canada in the 1980's and 1990's. Closed loop glass demonstration for the S-I cycle process were invented in Japan at the early 2000's. Currently there is experimental S-I programs in the US, France, Japan, China, Korea, India, Italy globally all over the world. (Brown 2007a.)

2.3 Process description

2.3.1 Three main chemical reaction equations in S-I cycle

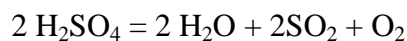
The sulfur-iodine cycle is a prime example of a thermochemical cycle. It consists of three chemical reactions, which sum to the dissociation of water. (Öztürk, Hammache & Bilgen 1995.)

Reaction equation (1) – exothermic (20-120°C, $\Delta H = -75(\pm 15)$ kJ/mol)



Equation (1) is the Bunsen reaction. This is an exothermic reaction. it is spontaneous react at 20°C to 100°C. At certain reactant concentrations, involving an excess of iodine, a phase separation occurs between the two acid products leading to a H₂SO₄ phase principally devoid of HI.

Reaction equation (2) – endothermic (600-900°C, $\Delta H = +186(\pm 3)$ kJ/mol)

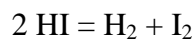


Equation (2) is the sulfuric acid decomposition step, which can be assumed to two reactions:



The first stage (equation 4), occurs at a temperature of 300-400°C, whereas the second stage, given by equation (5), occurs at 600-900°C with some solid catalyst.

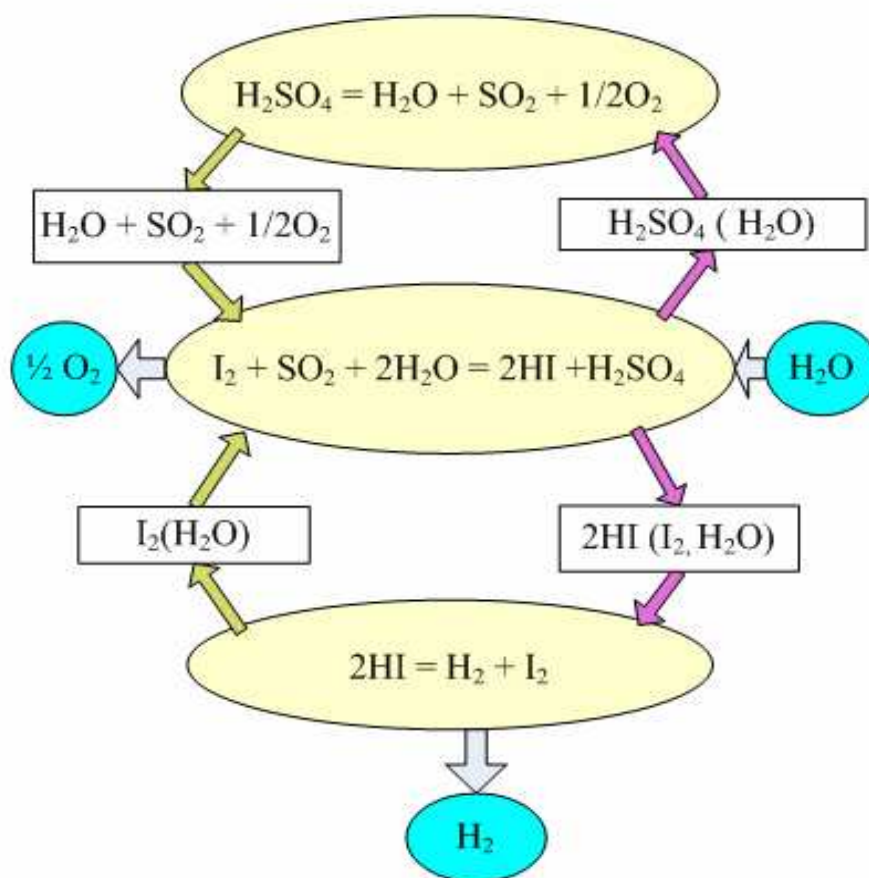
Reaction equation (3) – endothermic (300-450°C, $\Delta H = +12$ kJ/mol)



Equation (3) is the hydriodic acid decomposition reaction. This is a slightly endothermic reaction at the temperature 300-450°C, and it can be conducted in the liquid or gas phase.

2.3.2 Description for the three sections

There are three sections in S-I cycle process. The cycle system is clearly showed in Graph 1. And it easily seen just water in and oxygen and hydrogen out.



GRAPH 1. Overview of the Sulfur-Iodine process

Section I is for the Bunsen reaction, which produce and separate H_2SO_4 and HI for section II and III, and the O_2 is also separated in this step. Recycled I_2 from Sections III reacts with water and SO_2 which comes from section II in a countercurrent reactor. They spontaneously reacted at 20°C to 100°C . It results in the formation of a solution of two acids, H_2SO_4 and HI. This solution contains two phases with different density. The lower density phase 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 contains all the HI with amounts of I_2 in an H_2O solution and also small amount of SO_2 . Both phases are separated. The concentration of H_2SO_4 is increased to be about 57% by weight by reacting the H_2SO_4 phase with molten iodine and SO_2 . Then sulfuric acid with some water is transferred to Section II 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 III for purification and HI separation. And for the oxygen separate. It was mixed

with SO_2 , coming directly from the SO_3 decomposition reaction of Section II, then it 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 is practically the pure oxygen, but there is a small amount of iodine with them. A scrub column is used for removing iodine. Then the pure oxygen leaves the system as a product. (Öztürk et al. 1995, 11.)

Section II is the H_2SO_4 concentration and decomposition step. The concentration is an important part before decomposition. The 57% by weight sulfuric acid is concentrated in a series of flash evaporators and separators. 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 . The nuclear energy is used in this reactor. 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 to Section I. Most heat needed in this section, as it reacts at high temperature about 850°C . (Brown 2007a.)

In Section III there are also two steps: the HI separation step and the HI decomposition step. In the HI separation step: the HI is trying to be separated from the HI- I_2 - H_2O solution which comes from Section I. It is a complex step as there are three compounds that should be separated from HI. In this step a concentrated phosphoric acid is used to separate 95% of the I_2 away from the solution. The solution containing HI, H_2O , H_2SO_4 and some I_2 is transferred to an extractive distillation column, where most of the H_2O remains with the phosphoric acid, and HI, I_2 and a very small amount of H_2O are removed as overhead vapor. The vapor is then cooled to condense and separate. The purified liquid HI at 5 MPa from the HI separation step is pumped into a decomposition reactor. Then it is catalytically decomposed at about 300°C in it. After the reaction another separation should be taken to get the pure hydrogen production. The hydrogen product is separated from most of the I_2 and some HI in a liquid gas separator. Then the gaseous H_2 product is scrubbed with H_2O . Finally, the pure hydrogen is the resulting product in this step and flows out from there. And the I_2 is returned back into Section I. (Öztürk et al. 1995, 12.)

2.4 Advantages and Disadvantages of S-I Cycle

A major advantage of the S-I cycle for hydrogen production is that there are not any harmful by-products or emissions from the process. All the chemical reactions have been

demonstrated. The only out let is hydrogen and oxygen. If it can be heated with a nuclear source, it could prove to be an ideal environmental solution to hydrogen production. And one more important advantage is that it offers the higher efficiency than any other hydrogen production process. (Crosbier & Chapin 2003; also see Brown 2006.)

However there are some disadvantages in this cycle. There are sulfuric acid and hydroiodic acid contained in this cycle, both of them are very corrosive, it is really harmful and must be contained properly. The material of the reactors and all the units in this cycle should be avoided to acid. And Iodine is an expensive material. One more thing is for the controlling of the reaction conditions is a significant hurdle. As a lot of models are just build up from the laboratory. It was in an ideal condition for the reaction. There are coming the operation problems. (Crosbier & Chapin 2003.)

3 HYSYS SIMULATION FOR SULFURIC ACID DECOMPOSITION

3.1 Introduction

Section II (H_2SO_4 concentration and decomposition) needs most heat in the S-I thermochemical water splitting cycle. Thus this section is considered the most investigated part of the process. There is much room for thermodynamic improvement of this section. A lot of scientists work in this section, and it is generally accepted that the efficiency of the whole process depends on the efficiency of H_2SO_4 decomposition. There are lot of possibilities for improvement, using adiabatic equipment, better heat matching and mechanical power generation. (Öztürk, et al. 1995, 12.)

A very high efficient flowsheet was published by Öztürk in 1995 named Bilgen's flowsheet. It reported that thermodynamic evaluation of the process was resulted in 76% first law efficiency and 75.6% exergetic efficiency. In this paper a HYSYS simulation was based on this flowsheet and used its data. (Öztürk, et al.1995, 12.)

In this flowsheet it can be divided into two important parts: sulfuric acid concentration and decomposition. There are two HYSYS simulations for both of the steps in this paper. The concentration part is very important, as the higher purity of the sulfuric acid can be obtained before it enters to the decomposition unit, after this the higher efficiency for the decomposition can be carried out.

3.2 HYSYS simulation code

In the HYSYS simulation for the section II both sulfuric acid concentration and the decomposition there are five chemicals involved: oxygen (O_2), water (H_2O), sulfur dioxide (SO_2), sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4).

Flow package is one of the most important elements for HYSYS simulation. As a non-idealized system is used for this simulation, a PRSV equation of state is used as a fluid package in the sulfuric acid concentration and the decomposition simulation.

Thus reaction and reactor choice is the most important part in the sulfuric acid decomposition part. Once the sulfur trioxide is produced from sulfuric acid decomposition, it will immediately decompose to sulfur trioxide and oxygen. To simplify the process, the decomposition is assumed to be separated into two steps. In the first step, sulfuric acid is assumed to decompose into water and sulfur trioxide ($\text{H}_2\text{SO}_4 = \text{SO}_3 + \text{H}_2\text{O}$). Next the sulfur trioxide decomposes to oxygen and sulfur dioxide ($2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$). Thus two reaction and two reactors should be chosen for both of the two steps.

Firstly because of first reaction ($\text{H}_2\text{SO}_4 = \text{SO}_3 + \text{H}_2\text{O}$) is not a kinetic reaction, the conversion reactor is carried for this step. The conversion is assumed 90% in this simulation. A plug flow reactor model is should be most suitable for this reaction. But the conversion reactor is not suitable for this reactor. Therefore a conversion reactor is carried in this step.

The second reaction ($2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$) is a kinetic reaction. The reaction is taken in this step, where the reaction rate is based on: $r = k * f(\text{basis}) - k' * f'(\text{basis})$, where $k = A \exp\{-E / RT\} * T^\beta$. The activation energy (E) is assumed to be 17.46 kcal/mol/K, and pre-exponential factor (A) is assumed as $2.45 * 10^8 \text{h}^{-1}$. And no heat loss is assumed for all the reactors and heat exchangers for the simulation.

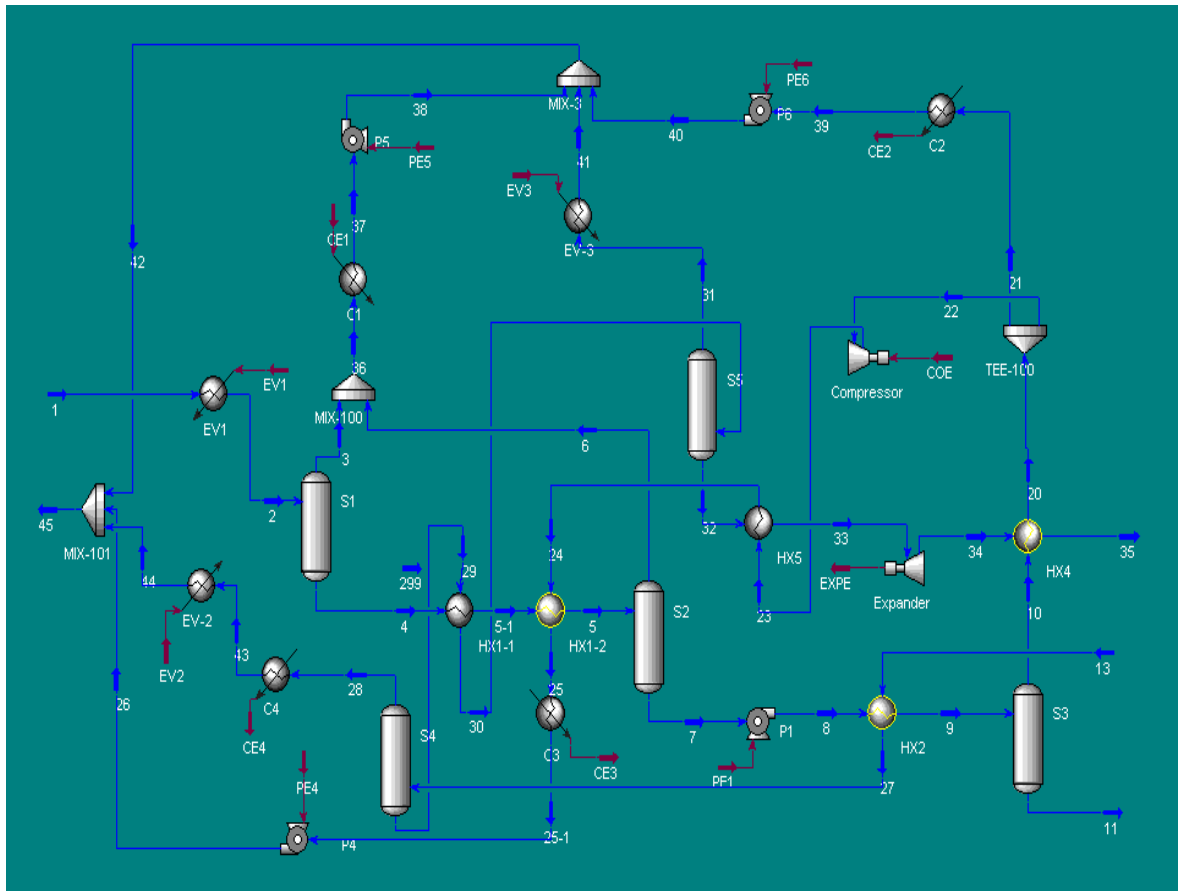
3.3 Description of the simulation

It is a big process simulation. First there are two separate simulations for each step of H_2SO_4 concentration and H_2SO_4 decomposition to make those two steps easily and clearly seen. The connection fluids (11 and 13) between the two steps were assumed for the two separate simulations based on each other's result. Then a whole process simulation of section II was made for the energy analyzing.

3.3.1 H_2SO_4 concentration simulation

Graph 2 shows the HYSYS simulation for H_2SO_4 concentration part in section II. In this

part it can divide into two parts. Fluid 1-11 is actually the concentration part. Fluid 13-45 is carried for the gas separation and heat recovery.



GRAPH 2. HYSYS simulation for H_2SO_4 concentration part in section II

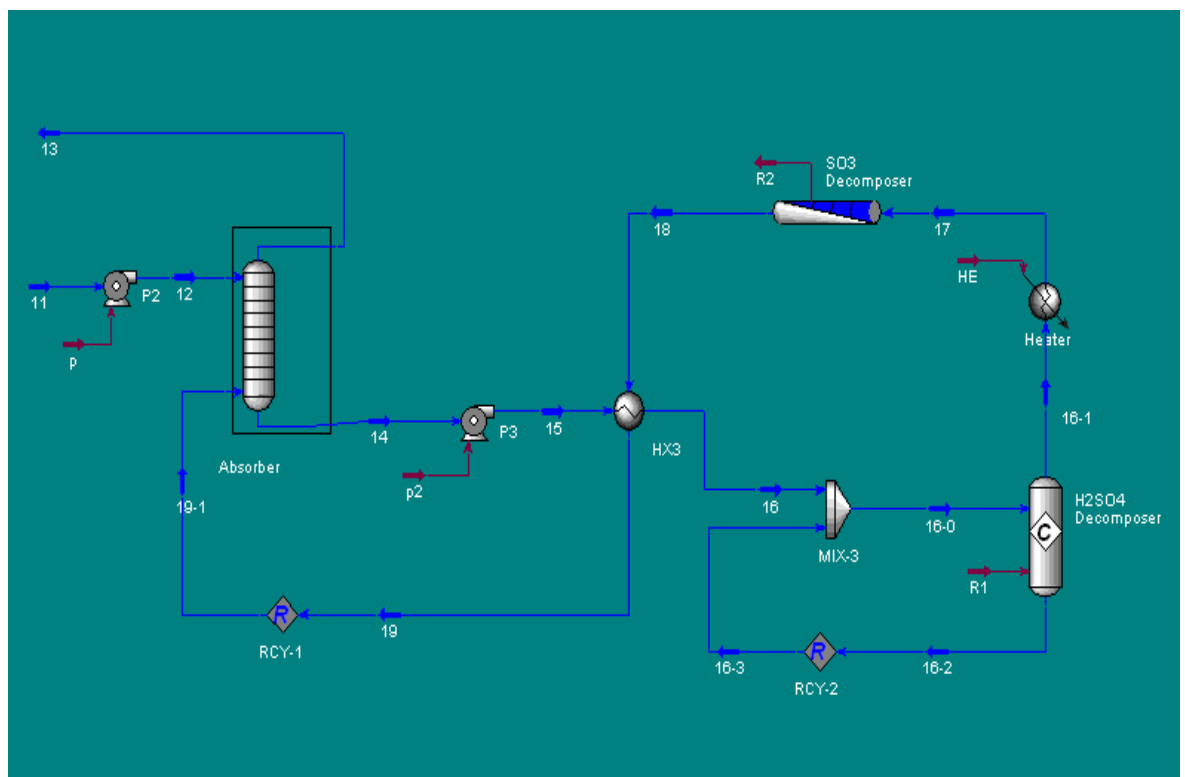
Fluid 1 from section I, contains mostly water (H_2O) and sulfuric acid (H_2SO_4), and a small amount of sulfur dioxide (SO_2), and then decreases the pressure from 180 kPa to 8 kPa and goes through three separators (S1, S2 and S3) to get the H_2SO_4 concentrated. This means fluids 3, 6 and 10 are mostly water vaporized from the separators. After the separation, steam 11 is concentrated to be composition.

Fluid 13 from the H_2SO_4 composition contains gas sulfur dioxide (SO_2), oxygen (O_2) and some water (H_2O). In other part of this simulation two additional separators (S4 and S5) are carried to separate the gas sulfur dioxide (SO_2) and oxygen (O_2) with water (H_2O). Five heat exchangers (HX1-1, HX1-2, HX2, HX4 and HX5) are carried to recycle the heat energy.

Finally fluids 35 and 45 come out from the whole process. It is mainly sulfur dioxide (SO_2) and oxygen (O_2) that come out in fluid 35, and go back to section I. Fluid 45 contains mostly water (H_2O), and it goes back to section I.

3.3.2 H_2SO_4 decomposition simulation

Graph 3 shows about HYSYS simulation for H_2SO_4 decomposition step. All the reactions are in this part.



GRAPH 5. HYSYS simulation for H_2SO_4 composition part of section II

Fluid 11 which comes from the concentration part is pumped into the absorption column to accomplish sulfur acid purification. In the absorption column (Absorber), sulfur trioxide is assumed to be totally reacting back to sulfuric acid as $\text{H}_2\text{O} + \text{SO}_3 = \text{H}_2\text{SO}_4$. Thus fluid 13 which comes out from the absorption column to the concentration part contains only sulfur dioxide (SO_2), oxygen (O_2) and water (H_2O).

High temperature heat is needed for the sulfuric acid decomposition reaction. Nuclear

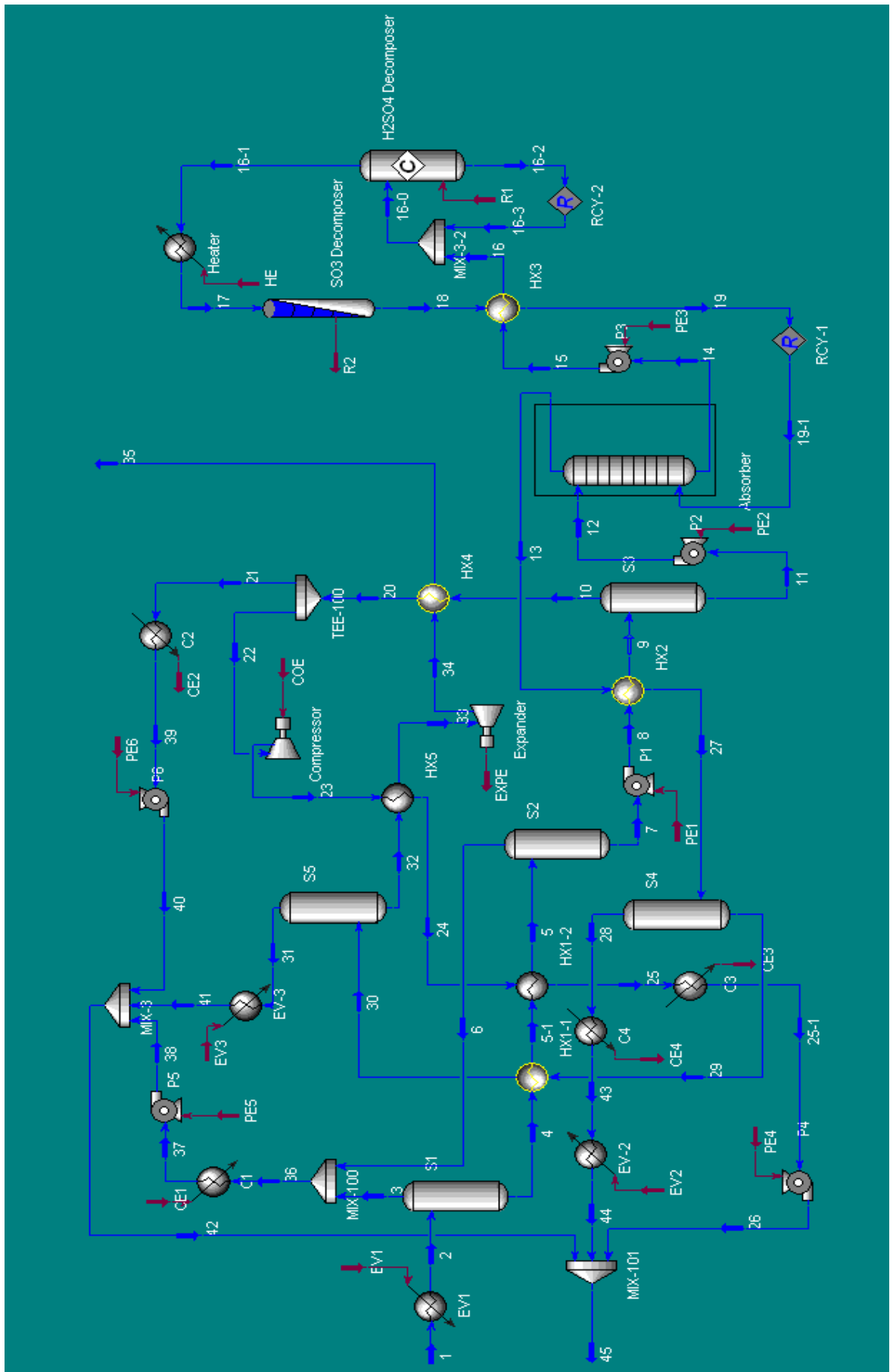
energy is considered the best choice for the high temperature reaction. There are various nuclear reactor types built for this reaction: pressurized water-cooled reactors, organic cooled reactors, alkali metal-cooled reactors, heavy metal-cooled reactors, boiling water-cooled reactors, molten salt-cooled reactors, liquid-core reactors, gas-core reactors and gas cooled reactors. Sandia National Laboratories evaluated the nuclear reactors by their safety, economic and operational issues. The helium gas-cooled reactor was recommended as the most suitable for this reaction. It has been widely used around the world. (Schultz 2003.)

But the helium gas-cooled reactor cannot be found in HYSYS. A common reactor model is taken for H_2SO_4 decomposition ($\text{H}_2\text{SO}_4 = \text{SO}_3 + \text{H}_2\text{O}$) and a plug flow reactor model is taken for SO_3 decomposition ($2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$) instead of the helium gas-cooled reactor. Thus the efficiency of the simulation cannot be as high as using the helium gas-cooled reactor. Actually, the temperature needed in the first step reaction is not very high, the temperature in the common reactor is around 380°C with the high pressure 1200 kPa. A high temperature is required for the second reaction in the plug flow reactor at $650\text{-}850^\circ\text{C}$ and with a high pressure 1200 kPa.

Between the two reactors, there is a heater, which heats up the steam to a higher temperature for further reaction. Actually the two reactions cannot be separated to two reactions. Sulfuric acid (H_2SO_4) is assumed to be decomposed into sulfur trioxide (SO_3) and water (H_2O) at the lower temperature around 380°C , and react in another reactor at higher temperature to decompose trioxide (SO_3).

3.3.3 The whole process simulation

Based on the two separate simulations, the whole process simulation (Graph 4) is easily to build.



GRAPH 4. HYSYS simulation for the whole process of sulfuric acid decomposition

As two separate part simulations are based on assumptive data of fluids 11 and 13. They cannot be used for the further analysis. The whole simulation made for it. The mole flow out of the process and the energy balance is going to be analyzed by HYSYS at the different temperatures from 650 to 850°C. An overview of this simulation clearly shows that the fluid 1 flow into the process, fluid 35 and 45 come out with the production from this process. And the red arrowhead in the graph shows all the heat flow in this simulation.

4 RESULTS AND DISCUSSION

4.1 The workbook of the HYSYS simulation

The workbook of the HYSYS simulation is directly calculated by HYSYS. Table 1 shows the vapor fraction, temperature, pressure, the mole flow and the mole fraction of the five compounds of all the streams flowing in the process at 850°C.

TABLE 1. Mass balance and five compounds mole fraction at 850°C

	Vapour Fraction	T (°C)	P (kPa)	Molar Flow kmol/h	Mole Fraction				
					O ₂	H ₂ O	SO ₂	SO ₃	H ₂ SO ₄
1	0.0019	119.90	180	5.4053	-	0.8036	0.0007	-	0.1957
2	0.7526	74.05	8	5.4053	-	0.8036	0.0007	-	0.1957
3	1.0000	74.05	8	4.0680	-	0.9990	0.0010	-	0.0000
4	-	74.05	8	1.3373	-	0.2092	0.0000	-	0.7908
5	0.1266	94.35	8	1.3373	-	0.2092	0.0000	-	0.7908
5-1	0.1262	94.23	8	1.3373	-	0.2092	0.0000	-	0.7908
6	1.0000	94.35	8	0.1693	-	1.0000	0.0000	-	0.0000
7	-	94.35	8	1.1681	-	0.0946	0.0000	-	0.9054
8	-	94.35	20	1.1681	-	0.0946	0.0000	-	0.9054
9	0.0567	151.90	20	1.1681	-	0.0946	0.0000	-	0.9054
10	1.0000	151.90	20	0.0662	-	1.0000	0.0000	-	0.0000
11	-	151.90	20	1.1019	-	0.0402	0.0000	-	0.9598
12	-	151.85	1,200	1.1019	-	0.0402	0.0000	-	0.9598
13	1.0000	201.28	1,200	2.6882	0.1967	0.4099	0.3934	0.0000	0.0000
14	-	172.55	30	1.0776	0.0000	0.0157	0.0002	0.0000	0.9841
15	-	172.50	1,200	1.0776	0.0000	0.0157	0.0002	0.0000	0.9841
16	-	384.20	1,200	1.0776	0.0000	0.0157	0.0002	0.0000	0.9841
16-0	-	379.40	1,200	1.2010	0.0000	0.0202	0.0001	0.0013	0.9784
16-2	-	335.30	1,200	0.1234	0.0000	0.0590	0.0000	0.0123	0.9288
16-3	-	335.30	1,200	0.1234	0.0000	0.0590	0.0000	0.0123	0.9287
16-1	1.0000	335.30	1,200	2.1352	0.0000	0.5032	0.0001	0.4953	0.0014
17	1.0000	850.00	1,200	2.1352	0.0000	0.5032	0.0001	0.4953	0.0014
18	1.0000	850.00	1,200	2.6640	0.1985	0.4034	0.3971	0.0000	0.0011
19	0.9988	271.12	1,200	2.6640	0.1985	0.4034	0.3971	0.0000	0.0011
19-1	0.9988	271.13	1,200	2.6639	0.1985	0.4033	0.3971	0.0000	0.0011
20	1.0000	60.86	20	0.0662	-	1.0000	0.0000	-	0.0000
21	1.0000	60.86	20	0.0199	-	1.0000	0.0000	-	0.0000
22	1.0000	60.86	20	0.0463	-	1.0000	0.0000	-	0.0000
23	1.0000	243.42	83	0.0463	-	1.0000	0.0000	-	0.0000

TABLE 1. Mass balance and five compounds mole fraction at 850°C (cont.)

	Vapour Fraction	T (°C)	P (kPa)	Molar Flow kmol/h	Mole Fraction				
					O ₂	H ₂ O	SO ₂	SO ₃	H ₂ SO ₄
24	1.0000	135.00	83	0.0463	-	1.0000	0.0000	-	0.0000
25	1.0000	95.00	83	0.0463	-	1.0000	0.0000	-	0.0000
25-1	-	94.34	83	0.0463	-	1.0000	0.0000	-	0.0000
26	-	94.41	570	0.0463	-	1.0000	0.0000	-	0.0000
27	0.8518	139.95	1,200	2.6882	0.1967	0.4099	0.3934	0.0000	0.0000
28	-	139.95	1,200	0.3984	0.0001	0.9739	0.0260	0.0000	0.0000
29	1.0000	139.95	1,200	2.2898	0.2309	0.3117	0.4573	0.0000	0.0000
30	0.8553	124.90	1,200	2.2898	0.2309	0.3117	0.4573	0.0000	0.0000
31	-	124.90	1,200	0.3313	0.0001	0.9666	0.0333	0.0000	0.0000
32	1.0000	124.90	1,200	1.9585	0.2700	0.2010	0.5291	0.0000	0.0000
33	1.0000	127.14	1,200	1.9585	0.2700	0.2010	0.5291	0.0000	0.0000
34	0.9498	70.11	200	1.9585	0.2700	0.2010	0.5291	0.0000	0.0000
35	0.9520	70.40	200	1.9585	0.2700	0.2010	0.5291	0.0000	0.0000
36	1.0000	74.86	8.	4.2372	-	0.9991	0.0009	-	0.0000
37	-	52.17	20	4.2372	-	0.9991	0.0009	-	0.0000
38	-	52.24	570	4.2372	-	0.9991	0.0009	-	0.0000
39	-	59.00	20	0.0199	-	1.0000	0.0000	-	0.0000
40	-	59.07	570	0.0199	-	1.0000	0.0000	-	0.0000
41	0.0008	93.05	570	0.3313	0.0001	0.9666	0.0333	0.0000	0.0000
42	-	55.29	570	4.5885	0.0000	0.9967	0.0033	0.0000	0.0000
43	-	140.02	1,200	0.3984	0.0001	0.9739	0.0260	0.0000	0.0000
44	0.0453	140.00	570	0.3984	0.0001	0.9739	0.0260	0.0000	0.0000
45	-	63.93	570	5.0331	0.0000	0.9949	0.0050	0.0000	0.0000

There are four more different workbooks for the simulation by changing the temperature 850°C in streams 17 and 18 to 650°C, 700°C, 750°C and 800°C. Those five workbooks are the basic data for further statistic.

4.2 Mass balance of the process

Table 2 shows the mole flow in stream 1 from section I, and it is assumed the same mole flows into the process for all decomposition at five different temperatures. Sulfuric acid (H₂SO₄) flows into this process to get hydrogen (O₂), water (H₂O) and sulfur dioxide (SO₂).

TABLE 2. The mole flow in from stream 1

	O ₂ (kmol/h)	H ₂ O (kmol/h)	SO ₂ (kmol/h)	SO ₃ (kmol/h)	H ₂ SO ₄ (kmol/h)
Stream 1	-	4.3437	0.0038	-	1.0578

Streams 35 and 45 are the flow out from this process. They contain hydrogen (O₂), water (H₂O) and sulfur dioxide (SO₂). The data in Table 3 and Table 4 show that the productions from different temperatures are similar. Thus the average mole flow out of the process calculated from those data for streams 35 and 45.

TABLE 3. The mole flow out from stream 35 at different temperatures

stream 35	O ₂ (kmol/h)	H ₂ O (kmol/h)	SO ₂ (kmol/h)	SO ₃ (kmol/h)	H ₂ SO ₄ (kmol/h)
650 °C	0.5287	0.3696	1.0364	-	-
700 °C	0.5287	0.3696	1.0364	-	-
750 °C	0.5287	0.3696	1.0362	-	-
800 °C	0.5287	0.3696	1.0362	-	-
850 °C	0.5287	0.3696	1.0362	-	-
Average	0.5287	0.3696	1.0362	-	-

TABLE 4. The mole flow out from stream 45 at different temperatures

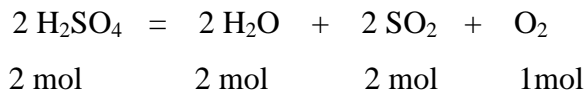
stream 45	O ₂ (kmol/h)	H ₂ O (kmol/h)	SO ₂ (kmol/h)	SO ₃ (kmol/h)	H ₂ SO ₄ (kmol/h)
650 °C	-	4.9969	0.0251	-	-
700 °C	-	5.0071	0.0254	-	-
750 °C	-	5.0091	0.0254	-	-
800 °C	-	5.0086	0.0254	-	-
850 °C	-	5.0077	0.0254	-	-
Average	-	5.0059	0.0253	-	-

However there is 4.3237kmol/h water (H₂O) and 0.0038kmol/h sulfuric acid (H₂SO₄) contained in the inlet flow. For the mass balance it should be subtract from the productions. Hence Table 5 is made for the total mass flow.

TABLE 5. Total mass flow

	O ₂ (kmol/h)	H ₂ O (kmol/h)	SO ₂ (kmol/h)	SO ₃ (kmol/h)	H ₂ SO ₄ (kmol/h)
Flow in 1	-	4.3437	0.0038	-	1.0578
Flow out 35	0.5287	0.3696	1.0362	-	-
Flow out 45	-	5.0059	0.0253	-	-
Total out	0.5287	5.3755	1.0615		
Reactant	-	-	-	-	1.0578
Products	0.5287	1.0318	1.0577	-	-

The mass balance calculation:



From calculation 1.0578mol 1.0578mol 1.0578mol 0.5289mol

From HYSYS 1.0578mol 1.0318mol 1.0577mol 0.5287mol

Compare the data from calculation with HYSYS simulation analysis. The error is not very significant. There is just a little bit difference for the water (H₂O). The error comes from the simulation at 650°C.

4.3 Energy requirement and efficiency

TABLE 6. The energy flow between 650°C to 850°C

	650 °C	700 °C	750 °C	800 °C	850 °C
CE1	- 184,149.80	- 184149.80	- 184,149.80	- 184,149.80	- 184,149.80
CE2	845.80	845.80	845.80	845.80	845.80
CE3	1,899.63	1899.63	1,899.63	1,899.63	1,899.63
CE4	- 2.33	- 2.35	- 2.36	- 2.32	- 2.36
COE	291.41	291.41	291.41	291.41	291.41
EV1	140,101.63	140101.63	140,101.63	140,101.63	140,101.63
EV2	527.26	509.42	507.11	507.74	508.86
EV3	- 769.21	- 795.57	- 799.78	- 798.76	-796.70
EXPE	7,516.66	7515.47	7,515.45	7,515.59	7,515.47
HE	67,796.97	65699.87	64,068.40	62,710.90	64,181.47
PE1	0.93	0.93	0.93	0.93	0.93
PE2	93.01	93.01	93.01	93.01	93.01
PE3	144.35	120.07	103.91	93.97	92.88

TABLE 6. The energy flow between 650°C to 850°C (cont.)

PE4	0.57	0.57	0.57	0.57	0.57
PE5	56.83	56.83	56.83	56.83	56.83
PE6	0.27	0.27	0.27	0.27	0.27
R1	234,160.18	237012.51	239,087.14	240,648.04	239,522.90
R2	102,458.41	102114.91	101,776.86	101,441.21	101,116.19
SUM	370,972.57	371,314.61	371,397.01	371,256.65	371,278.99

Table 6 depicts the energy requirement for various unit operations at temperature raising from 650 to 850°C and the sum of the energy supplied in this process.

The overall thermal efficiency of the process is calculated by the formula:

$$\eta = Q_{\text{reaction}} / \sum Q_i$$

Where η : Thermal efficiency of the process

Q_{reaction} : Overall reaction enthalpy of the sulfuric acid decomposition

$\sum Q_i$: Total thermal energy supplied to the process

The reaction enthalpy of the sulfuric acid decomposition Q_{reaction} is 278.643kJ/mol. The total thermal energy supplied is presented in Table 6. (Öztürk, et al. 1995,16.)

$$\eta_{650^\circ\text{C}} = Q_{\text{reaction}} / \sum Q_i = 278.643 / 370.973 = 75.11\%$$

$$\eta_{700^\circ\text{C}} = Q_{\text{reaction}} / \sum Q_i = 278.643 / 371.315 = 75.04\%$$

$$\eta_{750^\circ\text{C}} = Q_{\text{reaction}} / \sum Q_i = 278.643 / 371.397 = 75.03\%$$

$$\eta_{800^\circ\text{C}} = Q_{\text{reaction}} / \sum Q_i = 278.643 / 371.257 = 75.05\%$$

$$\eta_{850^\circ\text{C}} = Q_{\text{reaction}} / \sum Q_i = 278.643 / 371,279 = 75.05\%$$

From the calculation, the efficiency of the process got the highest value at the temperature 650°C. But the efficiency at each temperature does not change a lot. The efficiency difference from 700 to 850°C is only 0.02%.

5 CONCLUSION

The Sulfur-Iodine thermochemical water-splitting cycle is an effective and reasonable way for hydrogen (H_2) producing. And there are not any harmful byproducts or emissions from the process. Just water (H_2O) in and oxygen (O_2) and hydrogen (H_2) out. Heat is the only thing it needed in this process. It can be heated by nuclear source, and it can be also powered by solar energy. It is considered as the idea environmental solution for hydrogen produce.

The first aim of this thesis was constructing a simulation for sulfuric acid decomposition by HYSYS. In this thesis there were three simulations constructed: Two separate simulations for H_2SO_4 concentration and H_2SO_4 decomposition, and one whole process simulation. It shows a good result. The mass balance is almost the same with that calculated by the reaction equation.

For the thermal efficiency of the process a very good result is reported 75.03-75.11%. Comparing the result with Bilgen's flowsheet with a high thermal efficiency of about 77%, the thermal efficiency reported in this thesis seems not so good. But for the temperature stability of the Bilgen's process is not so high. It can not react under $720^\circ C$. But the stability is much better by this HYSYS simulation, it still gets a high thermal efficiency at the temperature $650^\circ C$. But no heat loss is considered in this whole process. It can not get so high thermal efficiency with for operation.

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