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Research Article

The Energy and Exergy Analysis of the Reactor Unit of Boric Acid Production Process with ChemCAD Simulation

Hakan Kızıltaş*,

Department of Chemical Engineering, Faculty of Engineering, Ataturk University, Erzurum, Turkey

Keywords

Boric Acid,
Energy and Exergy Analysis,
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Abstract

Energy and exergy analysis of systems are of great importance to enhance the energy and exergy efficiency of industrial production facilities. With the energy and exergy analyses performed, the energy dependency of the production facilities and their energy consumption can be reduced, the price of the product can decrease, and the profit margin can increase. Additionally, it is ensured that the energy produced based on fossil fuels is used in a controlled way. In the present study, the analysis of energy and exergy has been performed for the production reactor unit of the Boric Acid from Colemanite. The first law of thermodynamics and ChemCAD simulation program was used for energy analysis calculations, and the calculations of exergy analysis were carried out by using the second law of thermodynamics. The total energy loss of the reactor unit and the calculated energy loss per 100 kcal input steam were calculated as 110880 kcal/h and 3.724%, and the losses of total exergy in the reactor units and the losses of exergy calculated per 100 kcal input steam were calculated as 225058.86 kcal/h and 30.095%, respectively. Exergy efficiency for the reactor unit has been determined as 3.3 %. Some suggestions were given for the reactor units of boric acid production plants to minimize system losses.

1. Introduction

In recent years, the continuous increase of the world population and technological developments have greatly increased the energy requirement [1]. The increase in energy demands will, on the other hand, cause the reserves of traditional energy resources to diminish soon, as a result, energy will become very expensive. Due to these reasons, the more efficient use of existing energy resources and the development of alternative energy resources have become increasingly studied topics in recent years [2, 3]. Today, the majority of industrial energy needs are provided by fossil fuels in most countries. The difficulties of transporting fossil fuels to different regions and environmental pollution problems such as the greenhouse effect and toxic gases released into the environment resulting from its burning can limit the use of these types of fuels [4]. For this reason, towards the end of the 20th century, the studies on the effective use of the resources of existing energy and the research for alternative energy sources have completely raised [5, 6].

Exergy term and exergy analysis are of great importance for humanity because of the intensive use of energy, the limited reserves of fossil fuels, which are one of our main energy resources, and cause environmental pollution [7, 8]. The laws of thermodynamics play an important role in defining these terms [9]. The analysis of energy and exergy is a form of analysis that uses together with the first and second laws of thermodynamics and provides the use of the most efficient energy [10]. Especially, while the first law of thermodynamics is used for energy analysis, the second law provides for exergy analysis as it determines the reversible and irreversibility [11]. The purpose of exergy analysis is to enable the development of new technologies that leave less waste to the environment and use less natural resources [12].

The studies on the analyses of energy and exergy are carried out for industrial plants in different countries [13]. The studies on the analyses of energy and exergy, important for developing countries such as Turkey, are frequently carried out for industrial plants in different countries [14, 15]. Because the use of energy in industrial areas and the resulting energy losses can be minimized by energy and exergy modeling, thus strengthening the economy of countries and reducing the environmental pollution [16].

Boron, the 51st element commonly found in the earth, is never found free and it is known that there are approximately 230 types of boron minerals [17]. Boric acid (H_3BO_3), which has many production methods, is a boron intermediate used in many industries [18]. Some of these methods are involving the reactions of ulexite mineral with hydrochloric acid (HCl) [19], tincal with sulfuric acid (H_2SO_4) [20], colemanite with sulfuric acid (H_2SO_4) [21], tincal with nitric acid (HNO_3) [22]. In Turkey, the manufacturing of boric acid has been carried out from the colemanite method [23]. The boric acid production reaction from colemanite by sulfuric acid treatment is as follows. [24]:

$$Ca_2B_6O_{11}.5H_2O+2H_2SO_4+6H_2O \rightarrow 2CaSO_4.2H_2O+6H_3BO_3$$

The reaction of the colemanite mineral, sulfuric acid, and dilute boric acid solution occurs in the reaction unit, as shown in Figure 1. For 100 m^3 dilute boric acid solution, 4 m^3 H_2SO_4 and 16 tons of colemanite minerals are used [25]. The concentrated sulfuric acid and the dilute boric acid solution are mixed in a static mixer and fed into the reactor. The reaction time is about 4 hours and the reaction temperature is in the range of 80-100°C. In the manufacturing of boric acid, four reactors are isolated and reinforced with external heating to prevent heat losses in the reaction unit. Since the reaction in the first reactor is exothermic, a heater is not used [26].

*Corresponding Author: h.kiziltas@atauni.edu.tr
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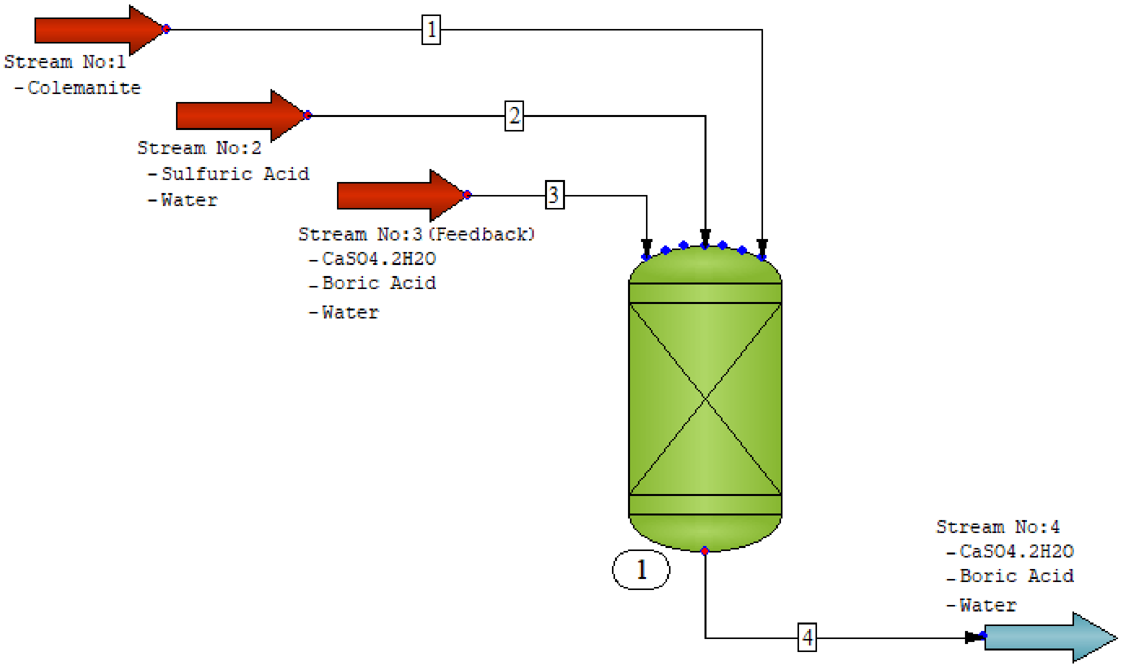

Figure 1. The reaction unit of the boric acid production

The pH values of the first three reactors are kept constant between 1.5 and 1.8. The reaction takes place in the first reactor by using almost all of the sulfuric acid with colemanite, while colemanite and sulfuric acid remaining unreacted in the first stage complete the reaction in other reactors. Reactors are designed to overflow from one to the other. The 2nd, 3rd, and 4th reactors are equipped with heating spirals and the tank temperatures are kept constant. In the 4th reactor, the pH value should be in the range of 3-4 to remove Fe and As impurities [27]. Mixers are used in the reactors to ensure that gypsum sludge is suspended with the same characteristics at every point.

In this study, the mathematical model of the Boric Acid Production Plant was created and the model of the reactor unit, which has the highest energy loss, was designed with the ChemCAD simulation program and the results were obtained. The losses of energy and exergy in the units are calculated by performing energy and exergy analysis based on the first and second law of thermodynamics on the process, respectively.

2. Thermodynamic design equations for Energy and Exergy Analysis

In accord with the law of conservation of mass, the amount of matter inflow and outflow of a system must be equal. Although there are different definitions for the concept of exergy, the most general and basic definition is as follows: It is the amount of maximum beneficial work that can be achieved from the initial state to steady-state in a system with a constant flow of matter [28].

The main parameters of exergy include the terms chemical, physical, potential, and kinetic energies when specific study subjects such as electrical, magnetic, nuclear, and interfacial effects were disregarded [29]. In this case, the obtained equation of exergy could be editable as follows.

$$e = (h - h_0) - (s - s_0)T_0 + \frac{v^2}{2g} + (z - z_0)g + e_{ch} \qquad (1)$$

where e is specific exergy ($J.kg^{-1}$), h is specific enthalpy ($J.kg^{-1}$), s is specific entropy ($J.kg^{-1}.K^{-1}$), T is the temperature (K), υ is the average velocity of flowing materials ($m.s^{-1}$), g is the gravitational acceleration ($m.s^{-2}$), z is the height above sea level (m), and e_{ch} is chemical exergy ($J.kg^{-1}$). The potential and kinetic terms are generally negligible in exergy analysis of chemical processes [30]. The calculation of chemical exergy of solid, liquid and gas flows for pure components and mixtures have been presented with different studies [31]. The definition of chemical exergies for heterogeneous (liquids or solids) flows is as follows:

$$e_{ch} = \sum_j^n w_j . c^{\circ}_{ch,j} \qquad (2)$$

where j is component, n is a number of components, w is the weight fraction of materials, and c°_{ch} is the chemical exergy of each pure component. The chemical exergy expression can be written as follows for solid or liquid materials [32].

$$e_{ch} = \left(\sum x_j e^{\circ}_{ch,j} + RT_0 \sum x_j \ln(a_j)\right)/M_j \qquad (3)$$

where x is a molar fraction, a is activity, and M_j is mean molecular weight.

Since the conservation of exergy can be used for reversible systems, it is necessary to add the loss term (E_{loss}) to include irreversibilities in the study of real systems [33]. With the addition of the loss term, the exergy equation in steady-state-flow systems is as follows:

$$\sum_{in} m.e + \sum_{in} E_Q + W_{in} = \sum_{out} m.e + \sum_{out} E_Q + E_{loss} \qquad (4)$$

where, E_Q is the exergy of heat transferred (Q_h) from a heat source.

$$E_Q = Q_h \left(\frac{T_H - T_0}{T_H}\right) \qquad (5)$$

The exergy performance of the systems can be evaluated by considering the different conditions. According to a defined definition, the exergy performance is the proportion of the total exergy of beneficial products to the total exergy obtained by the feeding substances into the system and is expressed as follows [34]:

$$\mu = \frac{\sum(\text{Exergies of beneficial products})}{\text{Feeding exergies}} \qquad (6)$$

$$\mu = \frac{\sum_{out}(m.e)_P}{\sum_{in}(m.e)_r + m_f e_f + \sum_{in} E_Q + W_{in}} \qquad (7)$$

μ is a measure of exergy performance used for processes in which products or products are produced with one or more chemical reactions. According to another definition, exergy performance is the proportion of the total exergy of the beneficial products to the total exergy obtained by the substances fed into the system for systems where chemical exergy is eliminated and more heat exchange is experienced and is expressed as follows [35]:

$$\eta = \frac{\text{Effect of beneficial exergy}}{\text{Driving exergy}} \quad (8)$$

$$\eta = \frac{\sum_{out}(m.e)_P - \sum_{in}(m.e)_r}{m_f e_f + \sum_{in} E_Q + W_{in}} \quad (9)$$

η is a measure of exergy performance used for systems involving more thermal and separation processes.

The values of enthalpy and entropy for chemicals used in the process of producing boric acid were calculated using the Shomate equations given below [36]:

$$\bar{h} - \bar{h}_0 = A.t + B\frac{t^2}{2} + C\frac{t^3}{3} + D\frac{t^4}{4} - E\frac{1}{t} + F - H \quad (10)$$

$$\bar{s} = A.\ln(t) + B.t + C\frac{t^2}{2} + D\frac{t^3}{3} - E\frac{1}{2.t^2} + G \quad (11)$$

where t is the temperature(K)/1000 and the constant values of A, B, C, D, E, F, H, and G for each component.

For colemanite (($\bar{h}_f^0$(kJ/mol) = -6939.6, $\bar{s}_0$(J/mol.K) = 383.7) [37]:

$$\bar{h} = 51.32456t - 58.5312\frac{t^2}{2} + 111.4752\frac{t^3}{3} - 34.53968\frac{t^4}{4} + 0.054876\frac{1}{t} - 12.35976 \quad (12)$$

$$\bar{s} = 51.32456\ln(t) - 58.5312\,t + 111.4752\frac{t^2}{2} - 34.53968\frac{t^3}{3} + 0.054876\frac{1}{2.t^2} + +276.4583 \quad (13)$$

For H_2SO_4 ($\bar{h}_f^0$(kJ/mol) = -735.13, $\bar{s}_0$(J/mol.K) = 298.78) [38]:

$$\bar{h} = 47.28924t + 190.3314\frac{t^2}{2} + -148.1299\frac{t^3}{3} + 43.86631\frac{t^4}{4} + 0.740016\frac{1}{t} - 758.9525 \quad (14)$$

$$\bar{s} = 47.28924\ln(t) + 190.3314t - 148.1299\frac{t^2}{2} + 43.86631\frac{t^3}{3} + 0.740016\frac{1}{2.t^2} + 301.2961 \quad (15)$$

For H_2O ($\bar{h}_f^0$(kJ/mol) = -241.83, $\bar{s}_0$(J/mol.K) = 188.84) [38]:

$$\bar{h} = 30.092t + 6.832514\frac{t^2}{2} + 6.793435\frac{t^3}{3} - 2.534480\frac{t^4}{4} - 0.082139\frac{1}{t} - 250.8810 \quad (16)$$

$$\bar{s} = 30.092\ln(t) + 6.832514\,t + 6.793435\frac{t^2}{2} - 2.534480\frac{t^3}{3} - 0.082139\frac{1}{2.t^2} + 223.3967 \quad (17)$$

For Boric Acid ($\bar{h}_f^0$(kJ/mol) = -992.28, $\bar{s}_0$(J/mol.K) = 295.23) [38]:

$$\bar{h} = 22.91803.t + 182.0312\frac{t^2}{2} - 125.7518\frac{t^3}{3} + 34.68749\frac{t^4}{4} + 0.145463\frac{1}{t} - 1006.649 \quad (18)$$

$$\bar{s} = 22.91803.\ln(t) + 182.0312.t - 125.7518\frac{t^2}{2} + 34.68749\frac{t^3}{3} + 0.145463\frac{1}{2.t^2} + 273.1524 \quad (19)$$

For Calcium Sulfate Dihydrate (($\bar{h}_f^0$(kJ/mol) = -2021.1, $\bar{s}_0$(J/mol.K) = 193.97) [38]:

$$\bar{h} = 35.056t - 182.5852\frac{t^2}{2} + 290.1912\frac{t^3}{3} - 65.91123\frac{t^4}{4} + 0.246782\frac{1}{t} - 346.5864 \quad (20)$$

$$\bar{s} = 35.056\ln(t) - 182.5852t + 290.1912\frac{t^2}{2} - 65.91123\frac{t^3}{3} + 0.246782\frac{1}{2.t^2} + +225.8765 \quad (21)$$

3. Results and Discussion

To perform the thermodynamic analysis for the reactor unit of the boric acid production system, the first law of thermodynamics was firstly analyzed. The energy inputs, outputs, and losses of the reactor unit for boric acid production, determined by the calculation and the ChemCAD simulation program (as shown in Figure 2), were given per 100 kJ/h of input energy (enthalpy) in Table 1, and the energy band diagram was given in Figure 3.

Table 1. The energy inputs, outputs, and losses of the reactor unit

Steam	Material	Enthalpy (kJ/h)	per 100 kJ/h of input enthalpy (kJ)	Percent age (%)
Steam 1 (input)	Colemanite	26400	0.887	0.887
Steam 2 (input)	Sulphuric Acid (96%)	18934	0.636	0.636
Steam 3 (input)	Boric Acid + Calcium Sulfate Dehydrate + Water	1062182	35.675	35.675
Heating (Q)	Saturated vapor at 8 bars	1869847	62.802	62.802
Total (input)		***2977363***	***100***	***100***
Steam 4 (output)	Boric Acid + Calcium Sulfate Dehydrate + Water	2866483	96.276	96.276
Heat loss (Q_{loss})		110880	3.724	3.724
Total (output)		***2977363***	***100***	***100***

Table 2. The exergy inputs, outputs, and losses of the reactor unit

Steam	Material	Exergy (kJ/h)	per 100 kJ/h of input exergy (kJ)	Percen-tage (%)
Steam 1 (input)	Colemanite	768	0.09062	0.09062
Steam 2 (input)	Sulphuric Acid (96%)	617.3	0.07284	0.07284
Steam 3 (input)	Boric Acid + Calcium Sulfate Dehydrate + Water	70051.8	8.26564	8.26563
Heating (Q)	Saturated vapor at 8 bars	776069.3	91.5709	91.57091
Total (input)		***847506.4***	***100***	***100***
Steam 4 (output)	Boric Acid +Calcium Sulfate Dehydrate + Water	592447.5	69.9048	69.90478
Heat loss (Q_{loss})		225058.9	30.0952	30.09522
Total (output)		***847506.4***	***100***	***100***

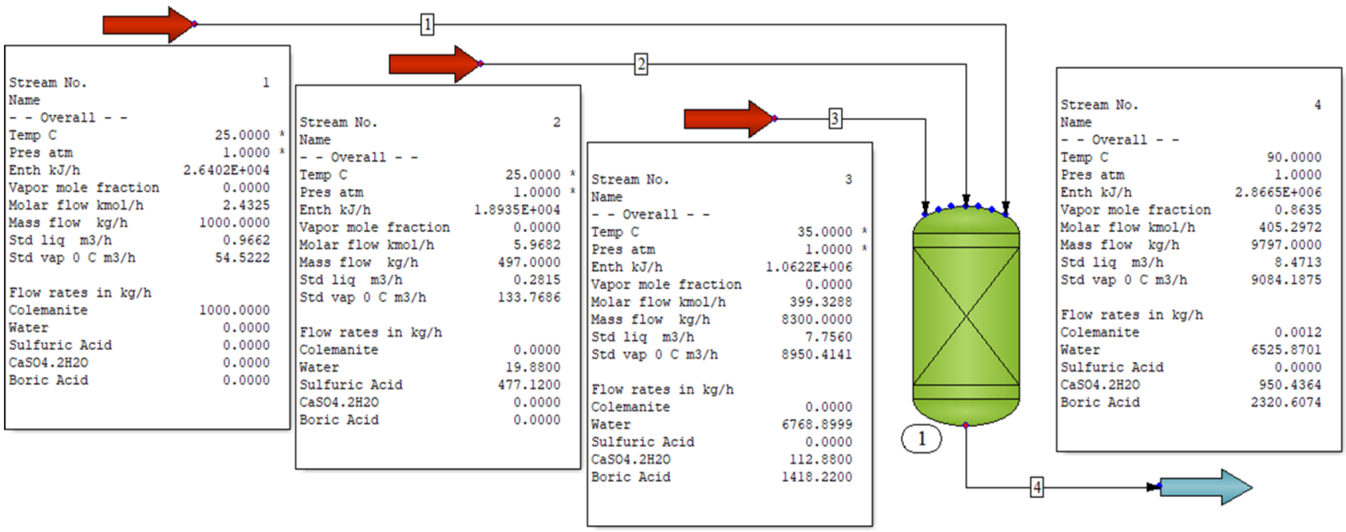

Figure 2. The ChemCAD simulation of the reactor unit and streams

As can be seen from the Table 1 and the Figure 3, it is seen that the stream with the highest enthalpy percentage is the heating water. Besides, the ascending sort of enthalpy amounts is the 1st, 2nd, and 3rd streams, respectively. In addition, approximately 96.3% of the total input enthalpy is the output stream enthalpy (4th stream), while 3.7% of the enthalpy is heat lost despite a heat insulation.

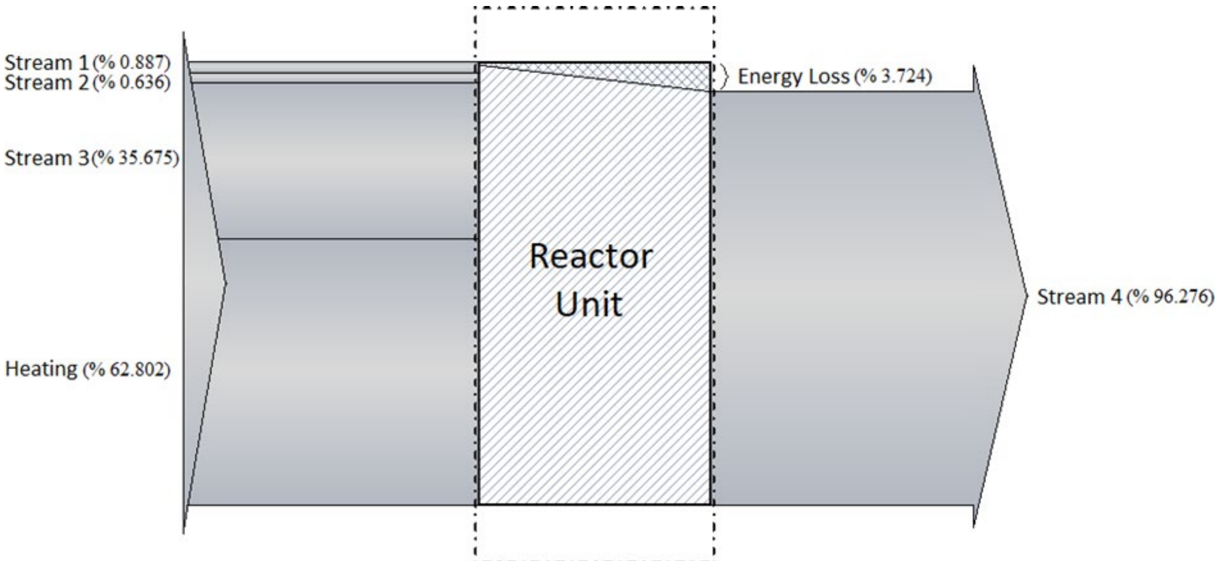

Figure 3. The energy band diagram of the reactor unit

To determine the exergy analysis the reactor unit of the boric acid production system, the second law of thermodynamics was analyzed. Table 2 and Figure 4 show the exergy inputs, outputs, and losses of the reactor unit for boric acid production calculated by using Equation 1.

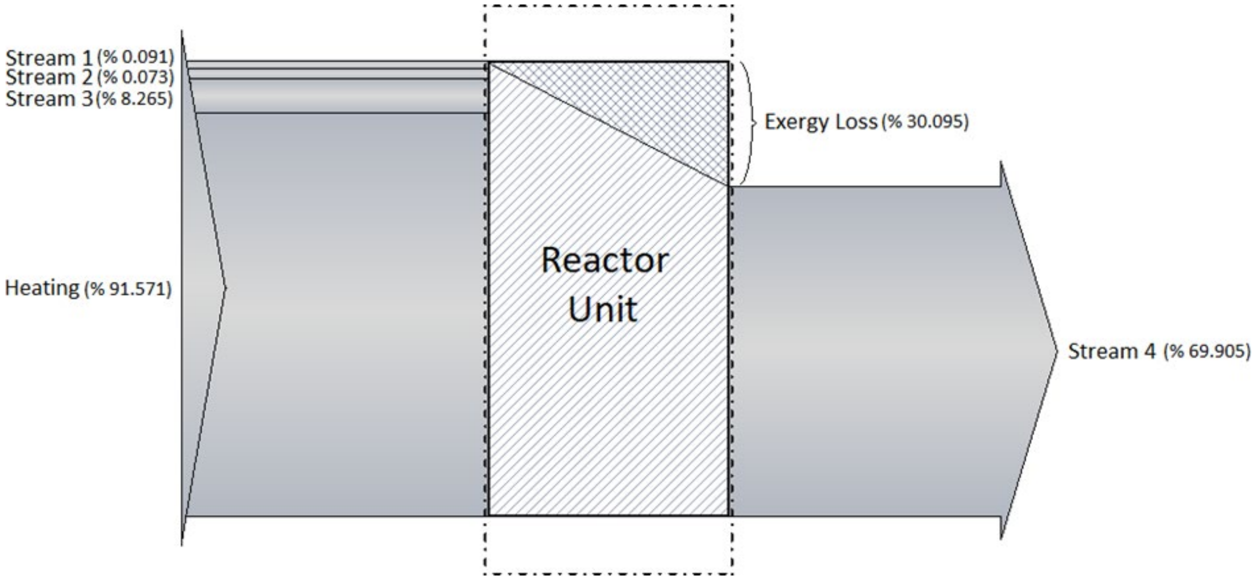

Figure 4. The exergy band diagram of the reactor unit

Exergy values are similar to the enthalpy values, it can be comprehensible in Table 2 and Figure 4 that the highest exergy input (91.571%) is the heating system. Input exergy for 1st, 2nd, and 3rd streams are about 0.091%, 0.073%, and 8.266% respectively. Additionally, while the exergy percentage of the output stream (4th stream) is approximately 69.905, the lost exergy amount is approximately 30.095%.

The exergy performance of the reactor system was calculated by accepting boric acid as a useful product and colemanite and sulfuric acid as feeding material. The exergy performance of the system was calculated to be 0.033 by using Equation 7.

4. Conclusion

In this study, according to the first law of thermodynamics, the total energy loss of the reactor unit and the energy loss calculated per 100 kcal of input currents were calculated as 110880 kcal/h and 3.724%, respectively. In accord with the second law of thermodynamics, the exergy losses in reactor units and exergy losses calculated per 100 kcal of input flows were calculated as 225058.86 kcal/h and 30.09522%, respectively.

To prevent the loss of heat to the environment as a result of the reaction, good insulation can be made to the reaction tanks and lines and a new design can be created. These losses occurring in the reaction unit are due to the irreversible exergy losses of the reactions.

A system cannot work with 100% efficiency by eliminating all exergy losses according to thermodynamic laws. During the process, the energy transmitted to the system as heat or work is transmitted from the system to its environment as energy or stored as internal energy. Energy cannot be consumed or produced but transforms into different forms of energy during the process. The common result of the first and second laws of thermodynamics is that what is consumed in thermal systems is the ability of energy to do work and that the ability of energy to do work is reduced or lost during the process. For this reason, improvements and modernizations to be made in the reactor system do not eliminate all exergy losses. However, even a small increase in efficiency to be achieved as a result of the improvements to be made will bring high profitability in total.

Declaration of Conflict of Interests

The author declares that there is no conflict of interest. They have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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