GasProcessingJournal

Vol. 3, No.1 , 2015
http://uijs.ui.ac.ir/gpj

Application of Exergy Analysis and Response Surface Methodology (RSM) for Reduction of Exergy Loss in Acetic Acid Production Process

Vafa Feyzi[1], Masoud Beheshti*[2]

[1] Department of Chemical Engineering, University of Isfahan, Isfahan, Iran
[2] Process Engineering Institute, University of Isfahan, Isfahan, Iran

Abstract: Exergy analysis and response surface methodology (RSM) is applied to reduce the exergy loss and improve energy and exergy efficiency of acetic acid production plant. Exergy analysis is run as a thermodynamic tool to assess exergy loss in reactor and towers of acetic acid production process. The process is simulated in Aspen Plus(v.8.4) simulator and the necessary thermodynamics data for calculating exergy of the streams is extracted from the simulation. By applying exergy balance on each one of the equipment, exergy losses are calculated. Response Surface Methodology (RSM) is a well-known statistical optimization method adopted in optimizing and modeling chemical processes, and operational parameters in reactor and towers. In this optimization framework the objective is to minimize exergy loss as objective function, subject to engineering and operational constraints. One of the modifications made on the reaction section is consumption of hot effluent stream from the reactor to produce steam. This modification prevents wasting the generated heat in the reactor and leads to improving exergy efficiency in reactor. All tunable operation parameters regarding reactor and towers and their upper and lower limits are specified and optimized through the RSM method. As a result, by optimization, exergy loss is reduced by 11365.8 Mj/hr and 2496.1Mj/hr in reactor and towers, respectively.

Keywords: Acetic Acid, Exergy analysis, Exergy loss, Optimization, RSM method.

1. Introduction

Acetic acid is one of the most consumed chemicals as the raw material in production of vinyl acetate monomer (VAM), anhydride acetic and many other chemical solvents (Othmer, 1980). One of the most popular manners in acetic acid production is through the reaction between methanol and carbon monoxide, known as methanol carbonylation reaction (Ullmann & Elvers, 1991). Acetic acid production process mainly consists of the three: reaction, purification and light ends recovery sections. In the reaction section acetic acid is produced as a result of reaction between methanol and carbon monoxide in a slurry reactor. Purification section has two main duties: catalyst recovery and extracting pure and dry acetic acid as the ultimate product of this process from the stream at the bottom of drying column. In the light ends recovery section the methyl iodide is recovered from gas stream before it is burned in the flare(Forster, 1979). For this process, reactor, distillation columns and one reactive distillation column are involved. Assessment of energy efficiency and optimization of energy consumption is very important. By optimizing operating variables for unit operations, loss of energy in this process can be reduced significantly.

---

* **Corresponding Author.**

Authors' Email Address:
[1] **Vafa Feyzi** (vafafaizi@yahoo.com),[2] **Masoud Beheshti** (m.behshti@eng.ui.ac.ir)

ISSN (On line): 2345-4172, **ISSN (Print):** 2322-3251

Exergy analysis is an applied method in design and optimization of chemical processes (Ratkje & Arons, 1995). The principles of this method is based on the second law of thermodynamics, adopting applying this method the bottleneck points of energy consumption in a process could be specified and could be found the reasons for energy loss in different equipment of the process (Bejan & Kestin, 1983; Dincer & Cengel, 2001; Kotas, 1985; Moran, 1982). Exergy is defined as the maximum theoretical work obtainable from the interaction of a system with its environment until the equilibrium state between both is reached (Moran, Shapiro, Boettner, & Bailey, 2010), and considered as the departure state of one system from that of the reference environment as well (Bejan & Tsatsaronis, 1996). Another application this method is optimization of operating parameters according to minimizing the exergy loss in a process (Tsatsaronis, 1999). Shin et al adopted the exergy method in order to reduce energy consumption in natural gas liquids recovery processes(Shin, Yoon, & Kim, 2015), they calculated the amount of exergy loss for the process and then developed an optimization framework to minimize the exergy loss subject to product specifications and engineering constraints. One of the common methods in exergy analysis of chemical processes is the blocks method (Nimkar & Mewada, 2014), where each process equipment is considered as a separate block and exergy balance is established around that blocks. Prins and Ptasinski analyzed the oxidation and gasification of carbon by exergy method (Prins & Ptasinski, 2005), they divided the process into different blocks and evaluated the exergy loss for each process. Results of that study reveals that gasification process is more efficient than combustion process from the energy consumption viewpoint and exergy loss in gasification process is lower than exergy loss in combustion process.

Due to chemical exergy degradation through a chemical reaction, sizable volume of exergy in a chemical process returns to the chemical reactions proceed in the reactor instead of being lost (Kotas, 1985). Simpson and Lutz analyzed the hydrogen production through steam methane reforming (SMR) adopting the exergy method (Simpson & Lutz, 2007), the results obtained reveal that the main reason of exergy loss in the process is due to the chemical reactions in the reactor. They assessed the effects of the different operational parameters: operating temperature, operating pressure and steam to carbon molar ratio in the reactor feed on the exergy loss in the reactor.

Response surface methodology (RSM) consists of a set package of mathematical and statistical techniques applicable in developing the experimental models where optimization of the response that is affected by some independent variables is the objective (Bruns, Scarminio, & de Barros Neto, 2006; Gilmour, 2006). RSM is one of the most popular optimization methods with a wide application in chemical and biochemical processes(Baş & Boyacı, 2007). The effect of the independent variables on the objective function, alone or in combination can be defined by this method. RSM has the ability to generate a mathematical model for the objective function (Myers, Montgomery, & Anderson-Cook, 2016).

Despite the importance of applying the exergy analysis in designing chemical processes, acetic acid production process exergy analysis has not been reported on. In this study applied the exergy analysis method is applied in an acetic acid production plant in order to assess the exergy loss volume in the reactor and the towers. Then response surface methodology (RSM) applied to optimize operational parameters and reduce exergy loss in the reactor and the towers. It is expected that this proposed modifications would lead to enhancing the energy efficiency of such process.

2. Exergy Analysis

Exergy is defined as the maximum obtainable work from a mass of fluid through a reversible process from existing state to zero exergy state or environmental state. The exergy of a stream in general consists of physical exergy, chemical exergy, potential exergy and kinetics exergy, however, the potential and kinetics exergies are usually neglected.

$$Ex = Ex^{ph} + Ex^{CH} \tag{1}$$

The physical component of exergy is defined as the maximum work obtained during a pure mechanically and thermally that brings the stream from present temperature and pressure (T, P) to the dead state (T_0, P_0). That is, the reference state in definition of physical exergy is to find thermal and mechanical equilibrium with the surrounding environment. According through the presented definition, amount of physical exergy for a stream can be calculated by equation (2)

$$Ex^{ph} = (h-h_0)-T_0(S-S_0) \tag{2}$$

Where, h_0 and S_0 are the enthalpy and entropy of the stream at the dead state (T_0, P_0), respectively.

Chemical exergy is defined as the amount of work obtained from a reversible reaction that converts the components of the stream into the compounds that normally exist in the environment. That is, in the definition of the chemical exergy of stream in addition to thermal and mechanical equilibrium, chemical equilibrium with the environment is necessary, as well.

$$Ex^{CH} = \sum x_i \varepsilon_i + RT_0 \sum x_i \ln(\gamma_i x_i) \qquad (3)$$

where, ε_i and γ_i are the standard chemical exergy and activity coefficient of components present in stream, respectively. The standard chemical exergy volumes of different components present in this process are tabulated in Table1.

Table 1. Standard Chemical Exergy Volumes of Different Components Present in the

Component	Standard Chemical Exergy (Mj/kmol)
H_2	227.9
CH_4	826.8
CO	271.6
CO_2	24.7
CH_3OH	702.8
CH_3I	787.5
Methyl Acetate	1609.3
Acetic Acid	887.4
HI	147.9
Propionic Acid	1593
C_2H_5OH	1350

Exegy can be exchanged between the system and the environment in the forms of heat transfer, mass transfer and work. The amount of exergy transferred to or from the system is equal to the amount of transferred work. The amount of exergy transferred as a result of heat exchange between the system and a heat source at temperature T_r is calculated through Eq. 4:

$$Ex^Q = Q(1 - T_0/T_r) \qquad (4)$$

For a steady state open system, the amount of exergy loss can be evaluated through exergy balance equation.

$$\sum (\dot{m}Ex)_{in} - \sum (\dot{m}Ex)_{out} + \dot{w} = \sum Ex^Q + Irr \qquad (5)$$

where, Irr is the exergy loss.

3. Process Description and Simulation

Acetic acid production process run by methanol carbonylation consists of three sections. In the reaction section acetic acid is produced through continuous reaction of carbon monoxide and methanol in a mechanically agitated gas-liquid reactor at approximately 185 °C and 28.6 bar. A soluble catalyst system consisting of a rhodium complex (catalyst) and methyl iodide-hydrogen iodide (the promoter) make the reaction to occur at a reasonable rate.

There are three primary reactions which occur in the acetic acid process:

1) Carbonylation reaction.

$$CO + CH3OH \longrightarrow CH3COOH \qquad (6)$$

Rate's equation for this reaction is (Haynes et al., 2004):

$$Rate = 156664276 \times \exp\left(-\frac{71407}{RT}\right) [I]^{1.055} [Rh]^{1.0096} \qquad (7)$$

2) Water gas shift equation.

$$CO + H2O \longrightarrow CO2 + H2 \qquad (8)$$

Rate's equation for this reaction is (Haynes et al., 2004):

$$Rate = 146664 \times \exp\left(-\frac{71407}{RT}\right) [I]^{1.055} [Rh]^{1.0096} \qquad (9)$$

[I] and [Rh] in equations 7 and 9 are molar concentration of methyl iodide and rhodium in $kmol/m^3$, respectively.

3) By-products reaction.

$$CH3CH2OH + CO \longrightarrow CH3CH2COOH \qquad (10)$$

$$CH3COOH + 2H2 \longrightarrow H3CH2OH + H2O \qquad (11)$$

The conversion of the carbonylation reaction is high (99.4%) and completely converts the methanol. The acetic acid process does not produce significant volumes of by-products. The major by-product is propionic acid. The simulation of the process is made based on the design data of an acetic acid production plant in Fanavaran Petrochemical Plant, Industrial Complex, Mahshahr- Iran. Due to non-ideal nature of the solutions present in this process, different thermodynamic methods: NRTL, NRTL-RK, UNIFAC and CHAO-SEADER are adopted for simulation of this process. The reactor is simulated with RCSTR model which is a model for mixed flow reactors simulation in Aspen Plus simulator. The outlet stream, after passing through a throttling valve, turns into liquid phases which are separate in the 03-D 2103 drum. The catalyst returns to the reactor together with the liquid phase stream. A simple schematic of reaction section is shown in Fiqure1.

In order to validate the simulation, the results of outlet streams from the reactor are compared with the design data for these streams. As observed in Table2, Aspen Plus works reasonably well in predicting the design data.

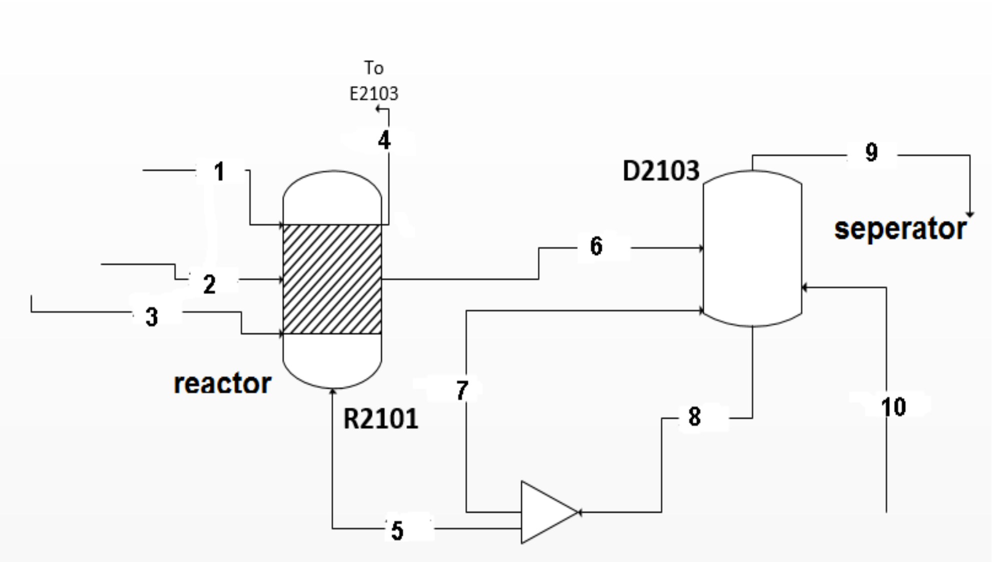

Figure 1. A Schematic of Reaction Section in Acetic Acid Production Plant

Table 2. Validation of Reactor's Outlet Streams Results Obtained from the Simulation

Stream name	6 Distillate reactor			4 Bottom		
	Simulation	Design	Deviation (%)	Simulation	Design	Deviation (%)
Temperature (°C)	185	185	0	185	185	0
Pressure (bar)	28.6	28.6	0	28.6	28.6	0
Flow (kmol/hr)	4472.4	4474.1	0.15	60.1	60.9	1.3
Mole percent						
H2	0	0	0	0.05	0.04	2
N2	0.0003	0.008	6.5	0.07	0.065	7.6
CO	0.0022	0.0024	0.83	0.4	0.42	5
CO2	0.001	0.0008	20	0.0143	0.017	15.8
CH3OH	0.001	0.0006	40	0.008	0.006	3.3
CH3I	0.035	0.035	0	0.13	0.138	5.7
CH3COOCH3	0.0059	0.006	1.6	0.008	0.01	2
CH3COOH	0.558	0.558	0	0.132	0.125	5.6
H2O	0.382	0.383	0.26	0.165	0.169	2.3
HI	0.011	0.011	0	0.0012	0.002	4

The purification section is fed with vapor from flash tank (03-D2103). It consists of two columns: 1) light ends column. where most of the methyl iodide and some water overhead and most of the hydrogen iodide out of the bottom and acetic acid as a side stream are recovered and 2) drying column dries the acid and reduces the hydrogen iodide are dried. The hydrogen iodide can be removed overhead as methyl iodide by reacting with methanol, and the water, remaining light ends and a portion of acetic acid go overhead. A simple schematic of purification section is shown in Fiqure 2.

In order to validate the simulation, the results of outlet and inlet streams of the drying column are compared with the design data for these streams in Table 3.

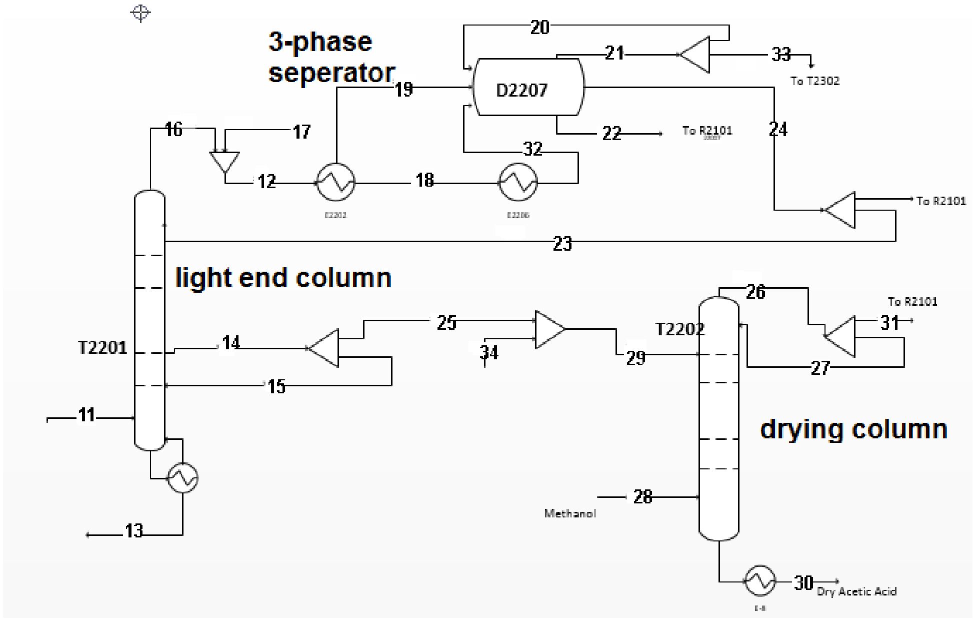

Figure 2. A schematic of Purification Section in Scetic Scid Production Plant

Table 3. Validation of Drying Column's Outlet Streams Results Obtained from the Simulation

Stream name	Distillate			Bottom		
	Simulation	Design	Deviation (%)	Simulation	Design	Deviation (%)
Temperature (°C)	133	130	2.3	46	47	2
Pressure (bar)	2.73	2.7	1.1	28.6	28.6	0
Flow (kmol/hr)	622.5	629.5	1.1	25.5	26	2
Mole percent						
CO2	0	0	0	0	0	0
CH3OH	0.0015	0	100	0	0	0
CH3I	0.015	0.0145	3.4	0	0	0
CH3COOCH3	0.008	0.013	3.8	0	0	0
CH3COOH	0.2287	0.2145	6.5	0.9954	0.9968	0.14
H2O	0.747	0.7577	1.4	0.0015	0.0016	6
HI	0	0	0	0.006	0.006	0
C2H5COOH	0	0	0	0	0	0

Light ends recovery section consists of a high pressure absorber, a low pressure absorber and a stripper. Acetic acid is the absorbing medium consumed in both the absorbers. Here the methyl iodide (catalyst promoter) is recovered from gas stream before it is burned in the flare. The results for outlet streams from stripper are compared with that of the design data

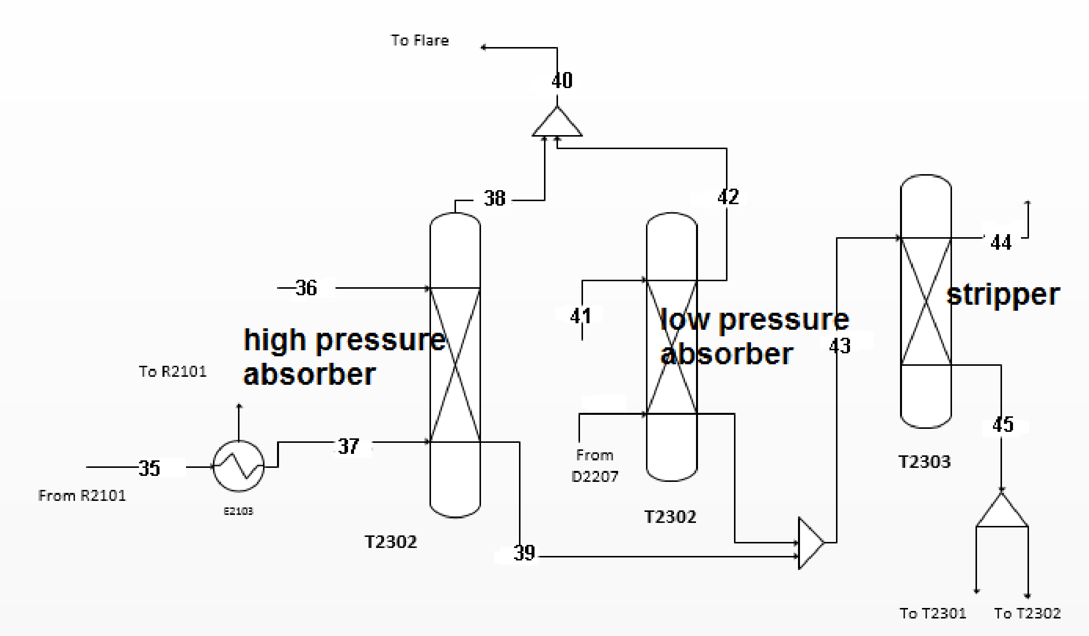

Figure 3. A schematic of Light Ends Recovery Section in Acetic Acid Production Plant

Table 4. Validation of Stripper's Outlet Streams Results Obtained from the Simulation

Stream name	Distillate			Bottom		
	Simulation	Design	Deviation (%)	Simulation	Design	Deviation (%)
Temperature (°C)	121	117	3.3	185	185	0
Pressure (bar)	2.1	2.1	0	28.6	28.6	0
Flow (kmol/hr)	11	10.3	6.3	60.1	60.9	1.3
Mole percent						
H2	0.00168	0.00171	1.7	0	0	0
N2	0.0087	0.00885	1.7	0	0	0
CO	0.046	0.0451	2.2	0	0	0
CO2	0.08	0.0804	0.5	0	0	0
CH3OH	0.0018	0.00175	3	0.00006	0.00006	0
CH3I	0.508	0.511	0.5	0	0	0
CH3COOCH3	0.013	0.015	13	0.0005	0.00056	10
CH3COOH	0.312	0.307	1.6	0.98247	0.98022	0.23
H2O	0.027	0.0283	4.6	0.017	0.0191	11
HI	0	0	0	0	0	0

4. Exergy Analysis Results

Based on the data extracted from this simulation, exergy value for each of the streams is calculated and the amount of exergy loss for unit operations is calculated through the exergy balance equation. In order to evaluate the volume of exergy for streams, based on the procedure proposed by (Szargut, Morris, & Steward, 1987) for calculating the chemical and the physical exergy the codes written with visual basic and attached to Aspen HYSYS are applied. Through these attached codes Aspen HYSYS is able to calculate the chemical and the physical exergy for streams in an automated manner. These cods are written in accordance with the method proposed by Demneh et al (Abdollahi-Demneh, Moosavian, Omidkhah, & Bahmanyar, 2011). The unit operations analyzed by the exergy method are the towers and reactor. Amount of the exergy loss for each of the columns is presented in Fiqure4.

Among the columns the highest exergy loss occurs in the drying column. Drying column is a reactive distillation column and the reaction that occurs here increases the exergy loss. In chemical processes a significant volume of exergy is wasted in the columns and the primary causes for these phenomena are (Kotas, 1985):

- Finite temperature differences in reboiler and condenser
- Mass transfer among different phases present in column
- Pressure drop
- Heat loss from the column's wall
- Mixture of streams with different properties in feed tray

The exergy analysis result for the reactor reveals that the volume of the exergy loss for the reactor is 27713.1 Mj/hr. The exergy loss in the reactor is much more than that of the columns. During a chemical reaction materials with high chemical exergy convert to materials that have lower chemical exergy, hence a significant exergy waste.

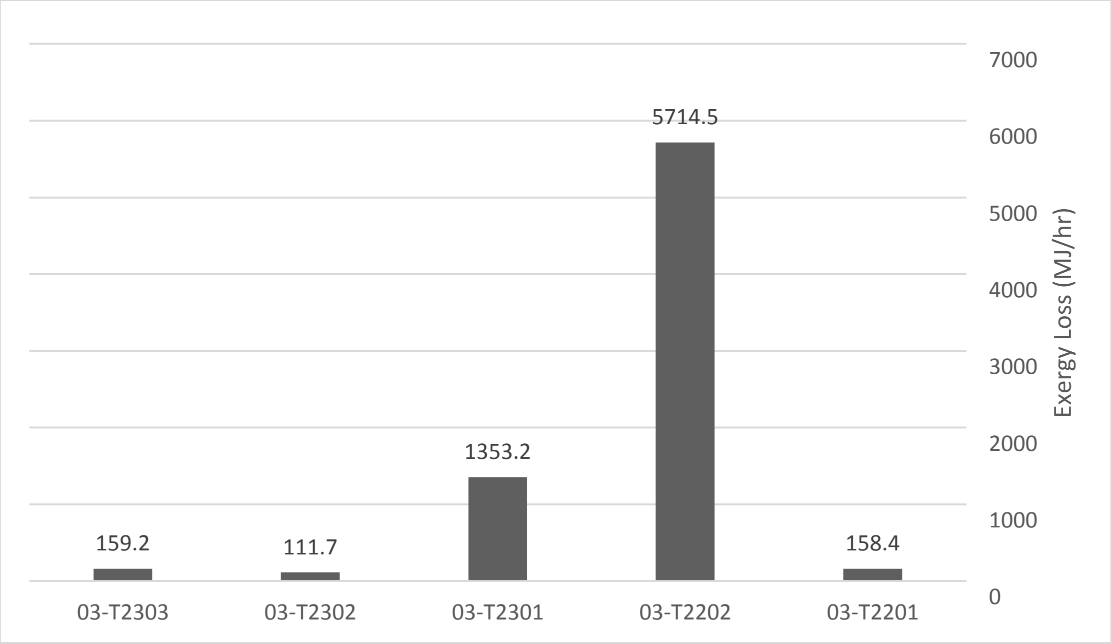

Figure 4. Amounts of the Exergy Loss for Columns in Acetic Acid Production Process

5. Optimization

5.1. Steps in Optimization by RSM Method

Response surface methodology is developed by Box and? In the 50s (Baş & Boyacı, 2007; Bruns et al., 2006; Gilmour, 2006; Myers et al., 2016). This method consists of a set of statistical and mathematical techniques for developing a mathematical model for the objective function by the means of the results obtained from the experimental designs The results of experiment design to model the objective function (the exergy loss) with a linear or second order polynomial function from operating parameters are applied in thi smethod. Through this developed mathematical model the operating parameters will be optimized due to minimization of the exergy loss (Baş & Boyacı, 2007). Stages in applying RSM as an optimization technique are as follows: 1) specifying the operating parameters that may affect the objective function (the exergy loss) and the lower and the upper limits of this parameters according to operational and process constraints, 2) designing an appropriate set of experiments (runs) according to the specified ranges for operating parameters and running the simulation at each of these specified points to calculate the exergy loss, 3) fitting the experiment design with a polynomial design, 4) the examination of the model's fitness, 5) verification of the necessity and possibility of performing a displacement orientated towards the optimal region subject to specified constraints; and 6) obtaining the optimum values for each one of the operating parameters. The calculations for optimization by RSM method is made through Minitab 16 software. The optimization algorithm in RSM method is shown in Fiqure 5.

5.2. Operating Parameters Selection

The first step in optimization by RSM method is the selection of the tuning parameters that may affect the objective function. The units studied in this method include: reactor, light ends column, drying column, absorbers and the stripper. Selected operational parameters and the upper and the lower limits are shown in Table10.

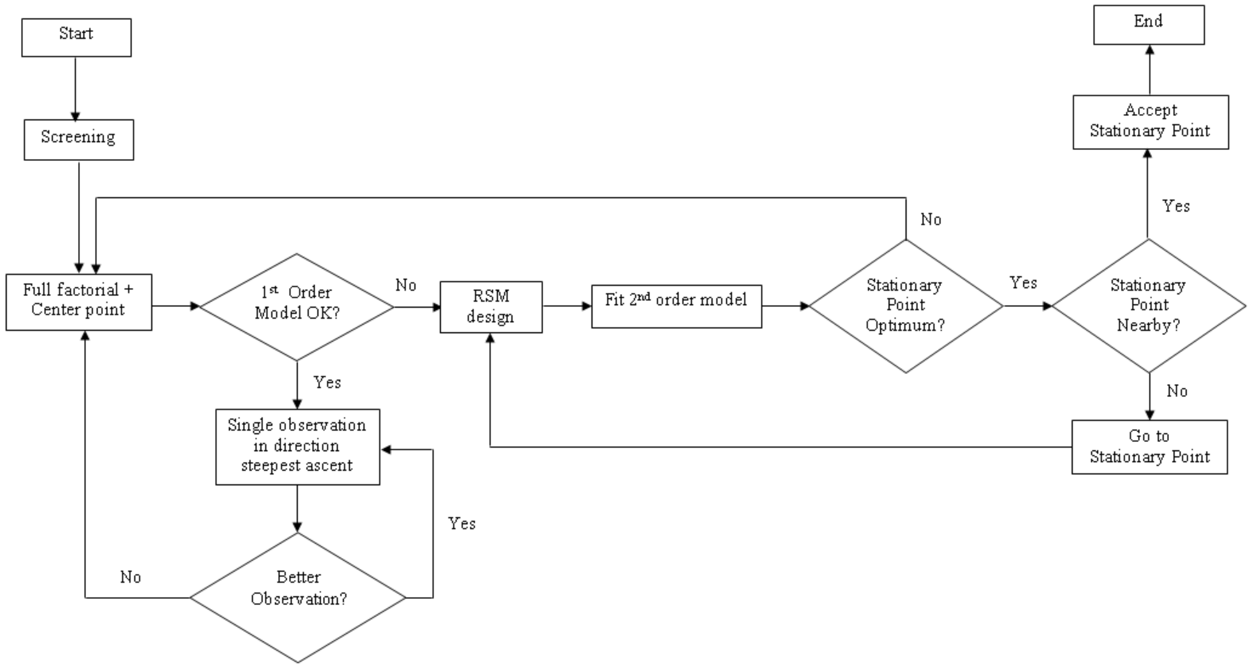

Figure 5. Optimization Algorithm in RSM Method

5.3 Exergy Loss Modelling by RSM Method

One of the main features in RSM method is its ability to show the curvature in the data and interaction between parameters (Bezerra, Santelli, Oliveira, Villar, & Escaleira, 2008). In order to consider the curvature and the effect of interaction between parameters it is necessary that this proposed mathematical model be in a quadratic polynomial form. In addition to the terms for each individual parameter, the relation must contain terms for interaction of the parameters. In order to determine a critical points the (maximum, minimum and saddle), it is necessary for the polynomial function to contain quadratic terms according to the following equation:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i \beta_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j \qquad (12)$$

In equation, $\beta$and$x$ are the polynomial constants and independent operational parameters, respectively. In RSM method the experiments are designed so intelligently that the results of experiments can be fitted through equation 12. Since in this study the preparation of simulations of the process is of concern, each experiment represents one of the runs in this simulation in Aspen Plus. So, after running the simulation at specified conditions the results of each run on exergy loss is calculated. The set of experiments (runs) designed for reactor and the results of exergy analysis are tabulated in the Table 5. That is, by running the simulation in different operational parameters, the volume of exergy loss in each run is calculated and the results are inserte in equation 12. It must be mentioned that the values of parameters in the runs is specified by the Minitab software, an applied software for RSM applications.

Table 5. Amounts of the Operating Parameters and the Results in each Run for Reactor

Run#	Operating temperature (°C)	Operating pressure (bar)	steam temperature (°C)	Co to Methanol malar ratio	Exergy loss (Mj/hr)	Methanol conversion
1	200	27.5	160	1	18231.3	0.998
2	180	27.5	160	1	16781	0.979
3	180	27.5	160	2	18048	0.992
4	160	40	140	0.5	8948.4	0.48
5	180	27.5	160	1	16781	0.979
6	180	27.5	160	1	16781	0.979
7	140	27.5	160	1	6054.3	0.324
8	180	27.5	160	1	16781	0.979
9	200	40	140	0.5	10407.4	0.497
10	200	40	140	1.5	19068.2	0.999
11	180	27.5	160	1	16781	0.979
12	160	40	180	1.5	14863.3	0.909
13	160	15	180	0.5	8431.6	0.495
14	200	40	140	1.5	21230	0.873
15	160	27.5	140	1	16330.3	0.909
16	180	15	160	1.5	16781	0.979
17	200	27.5	180	1	19608.6	0.998
18	180	15	200	1.5	15320.1	0.979
19	160	27.5	140	1	16444.9	0.903
20	180	40	120	0.5	18488.1	0.979
21	160	27.5	180	1	8225.7	0.48
22	180	40	160	0.5	16781	0.979
23	200	15	180	1.5	9849.7	0.497
24	160	27.5	180	0	4594.4	0
25	180	40	160	1.5	15022.6	0.903
26	200	52.5	180	1	115800	0.999
27	200	15	180	0.5	37781.4	0.999
28	180	2.5	160	1	36998	0.966
29	160	15	140	1.5	184.7	0.437

This developed model for the exergy loss in reactor is presented below:

$$Exergy\ Loss = -25318.083 + 3.657T^2 + 2.702P^2 + 4377.589(Mole\ Ratio)^2 - 0.013T^3 - 14.537T_{Steam} + 14.296T * Mole\ Ratio + 6.526P * Mole\ Ratio - 22.983T_{steam} * Mole\ Ratio. \quad Mj/hr\ [R^2] = 0.998 \tag{13}$$

RSM method has the ability to determine the degree of importance of each term in the model by two parameters of P-Value and F-Value. If the amount of P-Value for a term is less than 0.05 it indicates that this term is important. The lower the P-Value is for a term, the more its effect on objective function. The amounts of the P-Value and F-Value for the terms present in model obtained for the exergy loss of reactor are tabulated in Table 6.

Terms with P-Value greater than 0.05 have no significant effect on the exergy loss in reactor, while terms with small P-Value have more effect. Therefore, factors like generated steam temperature, interaction between operating pressure and mole ratio are not very important.

As for columns, the experiments designed for drying column and for the reactor and their results on. exergy analysis are tabulated in the Table 7.

Table 6. P-Value and F-Value for Studied Parameters in Reactor

Term	P-Value	F-Value
(Operating temperature) ^{2}	0	257
(Operating pressure) ^{2}	0.000517	25
(Mole ratio) ^{2}	0.000317	29
(Operating temperature) ^{3}	0	268
(Steam temperature)	0.088938	4
(Operating temperature) * (Mole ratio)	0.004592	13
(Operating pressure) * (Mole ratio)	0.5925617	0
(Steam temperature) * (Mole ratio)	0.010172	10
(Operating pressure) * (Operating temperature)	0.000119	37

Table7. Volumes of the Operating Parameters and the Results in each Run for Drying Column

Run#	Feed temperature (°C)	Methanol Flowrate (kmol/hr)	Methanol entrance tray	Feed entrance tray	Boilup ratio	Reflux ratio	Exergy loss (Mj/hr)	Acetic acid flowrate (kmol/hr)
1	130	1.05	27	27	4.35	0.5	533321.8	260.45
2	130	1.05	27	5	3.65	0.5	53092	310.88
3	130	1.95	27	27	3.65	0.5	53110	310.97
4	110	1.05	27	49	3.65	0.5	54101.9	279.30
5	115	1.05	27	27	3.65	0.5	53002.4	310.34
6	120	0.15	27	27	3.65	0.5	52896	309.71
7	120	1.05	27	27	3.25	0.5	50493.2	332.64
8	115	1.05	27	27	3.65	0.46	47658.8	277.31
9	115	1.05	5	27	3.65	0.5	50030	291.97
10	130	1.05	49	27	3.65	0.5	50032.8	291.89
11	130	1.05	27	27	3.65	0.54	52643.4	308.12
12	115	1.05	27	27	3.65	0.5	53002.4	310.34
13	120	1.5	38	16	3.3	0.52	49307.1	319.25
14	120	1.5	16	38	3.3	0.52	49311.6	319.12
15	115	0.6	38	38	4	0.48	50419.7	267.66
16	115	0.6	38	16	4	0.52	53079.5	282.70
17	120	0.6	38	38	3.3	0.52	49211.8	318.47
18	120	1.5	16	38	4	0.48	50520.7	268.21
19	115	1.05	27	27	3.65	0.5	53002.4	310.34
20	130	1.5	16	16	3.3	0.48	47005.2	303.46
21	130	0.6	16	16	3.3	0.52	49207	318.60
22	115	1.5	38	38	3.3	0.48	47009.5	303.32
23	115	1.05	27	27	3.65	0.5	53002.4	310.34
24	120	0.6	16	38	4	0.52	53080.9	282.62
25	115	1.05	27	27	3.65	0.5	53002.4	310.34
26	120	1.5	16	16	4	0.52	53185.4	282.62
27	115	1.05	27	27	3.65	0.5	53002.4	310.34
28	120	0.6	16	16	4	0.48	50417.8	267.72
29	115	1.05	27	27	3.65	0.5	53002.4	310.34
30	120	0.6	16	38	3.3	0.48	46915.3	302.71
31	120	0.6	38	16	3.3	0.48	46910.7	302.84

This developed model for the exergy loss in drying column is presented below:

$$\begin{aligned}
&Exergy\ Loss\\
&= 16352.009 + 3.7187MF - 10.455MS\\
&- 4.512FS + 840.135BR - 81425.917RR\\
&+ 0.507(MF) * (MS) - 0.282(MF) * (FS)\\
&+ 1.749(MF) * (BR) - 71.799(MF) * (RR)\\
&+ 0.007(MS) * (FS) - 0.021(MS) * (\mathrm{BR})\\
&- 5.212(MS) * (\mathrm{RR}) + 0.40(FS) * (\mathrm{BR})\\
&+ 3.536(\mathrm{FS}) * (RR) + 3364.669(\mathrm{BR}) * (RR)\\
&- 7.616(MF)^2 + 0.232(MS)^2 + 0.026(FS)^2\\
&+ 66838.827RR^2\ kj/hr\ [R^2]\\
&= 0.981 \qquad (14)
\end{aligned}$$

where, MF, MS, FS, BR, RR and FT are the methanol flow rate, methanol entrance stage, feed entrance stage, boilup ratio, reflux ration and feed stage, respectively.

The P-Value and F-Value for each of the terms present in equation 14 are tabulated in Table 8. The parameters that have the most effect on exergy loss in drying column include: methanol entrance tray, feed entrance tray, boilup ratio and reflux ratio are tabulated in Table 8. The methanol flow rate has no significant effect on the exergy loss in drying column. Among parameter's interactions, interaction between feed entrance and boilup ratio is the most important one.

Table8. P-Value and F-Value for Studied Parameters in Drying Column

Term	P-Value	F-Value
(Methanol flow rate)	0.093167	4
(Methanol stage)	0	166
(Feed stage)	0.000435	29
(Boilup ratio)	0	1286
(Reflux ratio)	0	14643
(Feed temperature)	0.000003	3452
(Methanol flow rate)* (Methanol stage)	0.000435	60
(Methanol flow rate)* (Feed stage)	0.001936	19
(Methanol flow rate)* (Boilup ratio)	0.416222	1
(Methanol flow rate)* (Reflux ratio)	0.076632	4
(Methanol stage)* (Feed stage)	0.022343	8
(Methanol stage)* (Boilup ratio)	0.804131	0
(Methanol stage)* (Reflux ratio)	0.006239	13
(Feed stage)* (Boilup ratio)	0.000921	23
(Feed stage)* (Reflux ratio)	0.039446	6
(Reflux ratio)* (Boilup ratio)	0	5311
(Methanol flow rate)^2	0.000215	35
(Methanol stage)^2	0	11713
(Feed stage)^2	0.000225	35
(Reflux ratio)^2	0	10645

As mentioned, the objective of this optimization is to minimize the exergy loss in each studied unit operation. According to the function of each unit operation, one constraint is considered per unit while the exergy loss for that unit operation is minimized in order to guarantee the product specifications; these optimization constraint for all unit operations are tabulated in Table9.

Values of operating parameters in reactor and column after optimization are tabulated in Table 10.

Table9. Constraints for Optimization in Each Unit Operation

Equipment	Constraint
Reactor	Methanol convertion$\geq$0.994
Light Ends Column	Acetic acid flow rate in stream 22023$\geq$394 kmol/hr
Drying Column	Acetic acid flow rate in stream 22020$\geq$336 kmol/hr
Absorber Columns	CH3I Concenteration in stream 23002$\leq$100 PPM
Stripper	Acetic acid Makeup $\leq$8 kmol/hr

Table10. Upper and Lower Limits and Optimum Values of Parameters

Equipment	Parameter	Upper limit	Lower limit	Value
Reactor	CO to Methanol Molar ratio in Feed	1.5	0.5	1.2
	Operating Temperature (°C)	200	160	180
	Operating Pressure (bar)	40	15	38
	Generated Steam Temperature (°C)	180	140	165
Light Ends column	Feed Stage	14	6	14
	Feed Temperature (°C)	145	125	135
	Split Fraction in Splitter SP	0.11	0.091	0.098
	Reflux Ratio	0.388	0.3	0.39
	Boilup Ratio	20	12.5	15.5
Drying column	Feed Stage	38	16	12
	Feed Temperature (°C)	135	115	120
	Methanol flowrate (kmol/hr)	1.5	0.6	2
	Methanol stage	38	16	3
	Reflux Ratio	0.54	0.48	0.52
	Boilup Ratio	4	3.3	3.15
Absorber columns	High pressure absorber feed stage	4	2	4
	Low pressure absorber feed stage	8	4	8
	Feed Temperature (°C)	30	15	29
	Split Fraction in Splitter SP2	0.3	0.2	0.2
	Split Fraction in Splitter SP3	0.8	0.3	0.2
	Split Fraction in Splitter SP4	0.8	0.3	0.2
Stripper column	Boilup Ratio	0.54	0.45	0.54
	Feed Temperature (°C)	38	27	28

By applying the RSM optimization method, the optimum values for operating parameters in studied unit operations are specified. The amount of each parameter is changed to its optimum value and the exergy loss for unit operations is re-calculated. Results indicate that the exergy loss is reduced significantly. The results show that by applied modification and optimization of operating parameter in reactor, exergy loss for reactor is reduced by 0.41%. The exergy losses in the columns before and after optimization are illustrated in figure 6. Maximum reduction in exergy loss among columns relates to column 03-T2202.

As a result of this optimization the exergy loss in reactor is reduced significantly to about 11365.8Mj/hr. The optimization in columns was effective such that the exergy loss is reduced by 2496.1 Mj/ hr in columns, Fig (6)

6. Conclusions

In order to understand the existing irreversibility in the process and improve energy efficiency in acetic acid production process, exergy analysis is applied. This process is simulated based on design data for acetic acid production plant in Fanavaran Petrochemical Plant. This simulation results are validated by comparing them to design data with simulation results of outlet streams from several unit operations, where a reasonable closeness is observed. Through Aspen HYSYS program, the total volume of the exergy for streams is calculated. The exergy loss in the reactor and the columns is calculated by applying exergy balance equation around this pertrochemical apparatus (facilities). The obtained results indicate that the maximum exergy loss isthe reactor. The RSM method is adopted to optimize the operating variable and minimize the exergy loss in reactor and columns, subject to operational and engineering constraints that guarantee the production specifications. The results here indicate that the exergy loss for studied unit operation reduced significantly in reactor and columns by 11365.8 Mj/hr and 2496.1 Mj/hr, respectively.

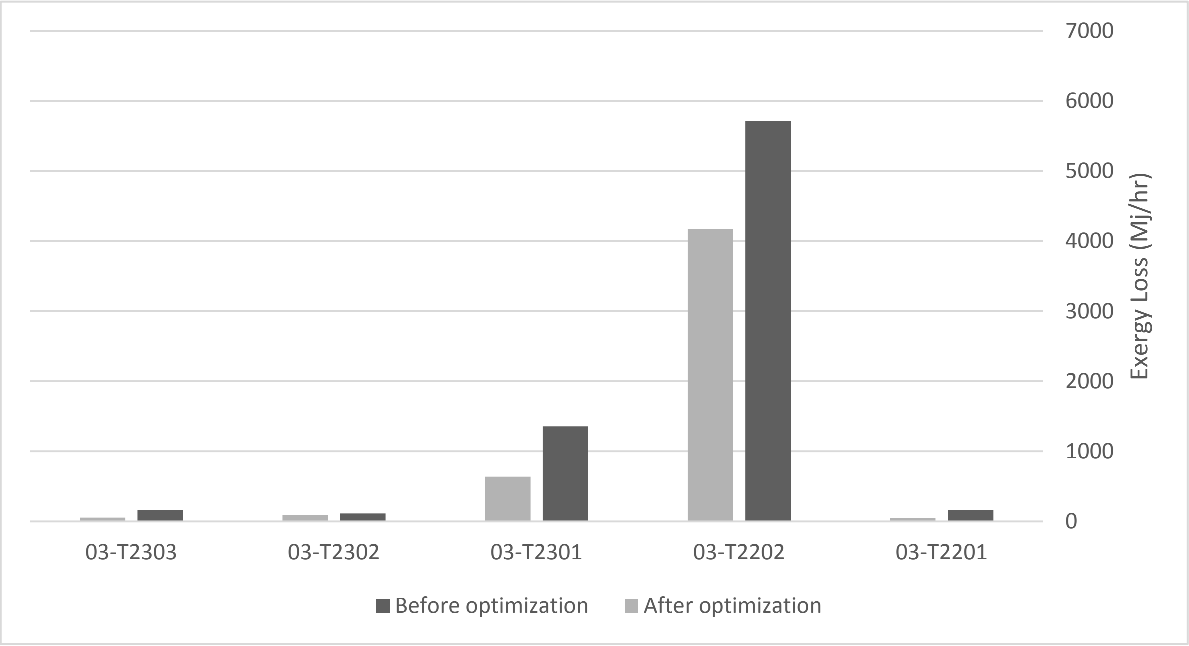

Figure 6. Comparison of the Exergy Loss for Columns before and after Optimization

Nomenclature

Ex	exergy [kj/hr]
Ex^{CH}	chemical exergy [kj/hr]
Ex^{ph}	physical exergy [kj/hr]
Ex^{Q}	heat exergy [kj/hr]
h	enthalpy [kj/hr]
h_0	enthalpy at environmental state [kj/hr]
Irr	exergy loss [kj/hr]
$\dot{m}$	molar flow rate of stream [kmol/hr]
Molar Ratio	CO to methanol molar ratio in the reactor's feed [-]
P	pressure [kpa]
P_0	surrounding pressure [kpa]
Q	heat [kj/hr]
S	entropy [kj/hr.k]
S_0	entropy at environmental state [kj/hr.k]
T	temperature [k]
T_0	surrounding temperature [k]
T_r	heat source temperature [k]
T_{steam}	generated steam temperature [k]
$\dot{w}$	shaft work [kj/hr]
x_i	i-component's mole fraction in mixture [-]
ε_i	i-component's standard chemical exergy [kj/kmol]
γ_i	i-component's activity coefficient [-]

References

Abdollahi-Demneh, F., Moosavian, M. A., Omidkhah, M. R., & Bahmanyar, H. (2011). Calculating exergy in flowsheeting simulators: A HYSYS implementation. Energy, 36(8), 5320-5327.

Baş, D., & Boyacı, İ. H. (2007). Modeling and optimization I: Usability of response surface methodology. Journal of Food Engineering, 78(3), 836-845.

Bejan, A., & Kestin, J. (1983). Entropy generation through heat and fluid flow. Journal of Applied Mechanics, 50, 475.

Bejan, A., & Tsatsaronis, G. (1996). Thermal design and optimization: John Wiley & Sons.

Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., & Escaleira, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta, 76(5), 965-977.

Bruns, R. E., Scarminio, I. S., & de Barros Neto, B. (2006). Statistical design-chemometrics (Vol. 25): Elsevier.

Dincer, I., & Cengel, Y. A. (2001). Energy, entropy and exergy concepts and their roles in thermal engineering. Entropy, 3(3), 116-149.

Forster, D. (1979). by Rhodium and iridium Complexes. Advances Organometallic Chemistry, 17, 255.

Gilmour, S. G. (2006). Response surface designs for experiments in bioprocessing. Biometrics, 62(2), 323-331.

Haynes, A., Maitlis, P. M., Morris, G. E., Sunley, G. J., Adams, H., Badger, P. W., Ghaffar, T. (2004). Promotion of iridium - catalyzed methanol carbonylation: Mechanistic studies of the cativa process. Journal of the American Chemical Society, 126(9), 2847-2861.

Kotas, T. (1985). The exergy method of thermal plant analysis.

Moran, M. J. (1982). Availability analysis: a guide to efficient energy use.

Moran, M. J., Shapiro, H. N., Boettner, D. D., & Bailey, M. B. (2010). Fundamentals of engineering thermodynamics: John Wiley & Sons.

Myers, R. H., Montgomery, D. C., & Anderson-Cook, C. M. (2016). Response surface methodology: process and product optimization using designed experiments: John Wiley & Sons.

Nimkar, S. C., & Mewada, R. K. (2014). An overview of exergy analysis for chemical process industries. International Journal of Exergy, 15(4), 468-507.

Othmer, K. (1980). Ency. of Chem. Tech., 2, 218.

Prins, M., & Ptasinski, K. (2005). Energy and exergy analyses of the oxidation and gasification of carbon. Energy, 30(7), 982-1002.

Ratkje, S. K., & Arons, J. D. S. (1995). Denbigh revisited: Reducing lost work in chemical processes. Chemical engineering science, 50(10), 1551-1560.

Shin, J., Yoon, S., & Kim, J.-K. (2015). Application of exergy analysis for improving energy efficiency of natural gas liquids recovery processes. Applied Thermal Engineering, 75, 967-977.

Simpson, A. P., & Lutz, A. E. (2007). Exergy analysis of hydrogen production via steam methane reforming. International Journal of Hydrogen Energy, 32(18), 4811-4820.

Szargut, J., Morris, D. R., & Steward, F. R. (1987). Exergy analysis of thermal, chemical, and metallurgical processes.

Tsatsaronis, G. (1999). Strengths and limitations of exergy analysis Thermodynamic optimization of complex energy systems (pp. 93-100): Springer.

Ullmann, F., & Elvers, B. (1991). Encyclopedia of industrial chemistry: VCH.

HIGHLIGHTS

- Application of exergy analysis for acetic acid production process
- Application of RSM optimization method to optimize operating variables in reactor and columns
- Minimization of exergy loss for improving energy efficiency