CHEMICAL ENGINEERING TRANSACTIONS
VOL. 81, 2020

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Qiuwang Wang, Min Zeng, Panos Seferlis, Ting Ma, Jiří J. Klemeš

ISBN 978-88-95608-79-2; **ISSN** 2283-9216

DOI: 10.3303/CET2081185

Study on Energy Saving of Epichlorohydrin Unit Based on Entransy Theory

Li Xia[a], Jianyang Ling[a], Zhen Xu[a], Zhixiang Zhang[a], Xiaoyan Sun[a], Xiaorong Cao[b], Shuguang Xiang[a,*]
[a]State Key Laboratory Base for Eco-Chemical Engineering, College of Chemical Engineering, Qingdao University of Science and Technology, Zhengzhou Road No.53, Qingdao 266042, China
[b]Chemistry and Chemical Engineering Faculty, Qilu Normal University, Jinan, 250013, Shandong, China
xsg@ qust. edu. cn

The mathematical models for calculating the energy utilization efficiency of heat exchanger networks (HENs) based on entransy analysis method was built. The energy utilization efficiency of HENs for epichlorohydrin unit were calculated by exergy analysis and entransy analysis. Aiming at the maximum energy recovery, the entransy analysis of epichlorohydrin unit's HENs was done. By taking three different $\triangle T_{\min}$, 10 K, 15 K and 20 K, the results show that the exergy efficiencies are 61.01 %, 59.28 % and 57.27 %. The entransy transfer efficiency is 42.81 %, 42.13 % and 41.00 %. Using the entransy analysis method, utilities were saved by 19.41 %, 18.01 % and 15.70 %. Using the exergy analysis method, utilities were saved by 16.59 %, 14.86 % and 12.02 %.

The results of different methods were analysed and compared. Exergy is more complicated than entransy in the calculation process. The exergy analysis method can not complete HENs Synthesis. But the entransy analysis method not only can complete HENs synthesis, but also can calculate the energy utilization efficiency of HENs. The entransy analysis method is more suitable for analyzing the energy utilization of epichlorohydrin unit.

1. Introduction

With the increase of global energy consumption and carbon emissions, the problem of global resource shortage and environmental pollution is becoming more and more serious. Energy consumed by industry accounts for about 53 % of the total global energy consumption. About 72 % of the energy sources are consumed in the manufacturing process (Xia et al., 2019). Saving energy and reducing carbon emissions is of great significance to promote the sustainable development of global economy.

The first law of thermodynamics can reflect the conservation of energy, but does not reflect energy utilization efficiency. Rant (1956) introduce a new thermodynamic parameter which was called “exergy” to solve this problem. Ahern (1980) proposed exergy analysis method which can effectively reflect energy utilization efficiency by analyzing the value, cause and location of the exergy loss. Linnhoff (1990) proposed the concept of exergy loss into HENs. After years of development, the exergy analysis methods were used for HENs synthesis of petrochemical industry, such as graphic method (Stijepovic et al., 2014), formula method (İpeka et al., 2017), and objective function method (Miladiet et al., 2016). However, because the exergy calculation process is too complicated, the application of exergy analysis method to HENs of petrochemical industry is limited.

A new physical quantity named “entransy” was proposed by Guo et al. (2007). Entransy dissipation is described the heat transfer process irreversibility by analyzing the characteristics of the heat transfer process. Hu and Guo (2011) defined entransy transfer efficiency to analyze heat transfer of exchangers. Chen et al. (2012) proposed the temperature-heat flow diagram to intuitively describe the change rule of entransy in the process of heat transfer. Cheng et al. (2014) made use of the temperature-heat flow rate diagram (T-Qdiagram) to research the entransy dissipation rates of chemical processes. Xia et al. (2017b) proposed a method based on entransy for setting energy targets of heat exchanger network. The entransy transfer

Paper Received: 30/04/2020; Revised: 11/06/2020; Accepted: 17/06/2020
Please cite this article as: Xia L., Ling J., Xu Z., Zhang Z., Sun X., Cao X., Xiang S., 2020, Study on Energy Saving of Epichlorohydrin Unit Based on Entransy Theory, Chemical Engineering Transactions, 81, 1105-1110 DOI:10.3303/CET2081185

efficiency can indicate the reasonable heat utilization of heat exchanger network. Xia et al. (2018) proposed the design method of HENs based on entransy theory.

In this work, the mathematical models for calculating the energy utilization efficiency of heat exchanger networks (HENs) based on entransy analysis method was built. Aiming at the maximum energy recovery, the entransy analysis of epichlorohydrin unit's HENs was done. The optimal energy utilization efficiency for heat exchanger networks of epichlorohydrin unit was determined.

2. The entransy transfer efficiency for heat exchanger networks

The entransy is defined as,

$$E_{vh} = \frac{1}{2}Q_{vh}U_h = \frac{1}{2}Q_{vh}T = \frac{1}{2}mc_vT^2 \tag{1}$$

where Q_{vh} is thermal capacity of an object with constant volume, c_v is specific heat capacity at constant volume, U_h represents the thermal potential.

Assume heat exchanger containing two streams is operated in steady state. The temperature drop of the stream is d_T, and the heat flow generating is d_Q (Xia et al., 2017a). The quality of entransy for the heat exchanger output is,

$$\mathrm{d}E_{vh} = TdQ_{vh} \tag{2}$$

T is a state quantity. δ_Q is a process quantity. So entransy $T{\cdot}\delta_Q$ is obviously a process quantity. The quality of entransy for HENS can be obtained by the integration of the cold and hot Composite Curves with the Q - axis in the T - Q diagram (Xia et al., 2017d). For the heat exchanger networks, the entransy of all the hot streams is:

$$E_H = \sum_{i=1}^{n} E_{h,i} \tag{3}$$

$$E_{h,i} = \frac{1}{2}\cdot Q_{h,i}\cdot T_{h,i} = \frac{1}{2}\cdot CP_{h,i}\cdot (T^2_{h,i,inlet} - T^2_{h,i,outlet}) \tag{4}$$

where E_H denotes the entransy of all the hot streams in heat transfer network, $E_{h,i}$ denotes the entransy of the i hot stream, $Q_{h,i}$ denotes heat of the i hot stream, $CP_{h,i}$ denotes heat capacity flowrate of the i hot stream.

The entransy of cold streams for the heat exchanger networks is：

$$E_C = \sum_{i=1}^{n} E_{c,i} \tag{5}$$

$$E_{c,i} = \frac{1}{2}\cdot Q_{c,i}\cdot T_{c,i} = \frac{1}{2}\cdot CP_{c,i}\cdot (T^2_{c,i,outlet} - T^2_{c,i,inlet}) \tag{6}$$

Where E_C denotes the entransy of all the cold streams in a heat transfer network，$E_{c,i}$ denotes the entransy in the i cold stream, $Q_{c,i}$ denotes heat of the i cold stream, $CP_{c,i}$ denotes heat capacity flowrate of the i cold stream.

The entransy dissipation ΔE is:

$$\begin{aligned}\Delta E &= \sum_{i=1}^{n} E_{h,i} - \sum_{i=1}^{n} E_{c,i} = \frac{1}{2}\cdot Q_{h,i}\cdot T_{h,i} \\ &= \frac{1}{2}\cdot\sum_{i=1}^{n} CP_{h,i}\cdot\left(T^2_{h,i,inlet} - T^2_{h,i,outlet}\right) - \frac{1}{2}\cdot\sum_{i=1}^{n} CP_{c,i}\cdot(T^2_{c,i,outlet} - T^2_{c,i,inlet})\end{aligned} \tag{7}$$

The entransy transfer efficiency is：

$$\eta = \frac{E_C}{E_H} = \frac{\sum_{i=1}^{n} CP_{c,i}\cdot(T^2_{c,i,outlet} - T^2_{c,i,inlet})}{\sum_{i=1}^{n} CP_{h,i}\cdot\left(T^2_{h,i,inlet} - T^2_{h,i,outlet}\right)} \tag{8}$$

According to the different temperature differences, make use of the Eq (8) to the calculate the entransy transfer efficiency of HENs. The maximum heat transfer capability of hot streams of HENs is determined. It can be seen from Eq(8) that the greater the heat transfer temperature difference between cold and hot streams, the greater the entransy dissipation, the greater the entransy transfer efficiency, and the worse the energy utilization effect.

3. Comparison of entransy analysis and exergy analysis in HENs of epichlorohydrin unit

The epichlorohydrin was produced with propylene and chlorine as raw materials. The process diagram of epichlorohydrin produced by the high temperature chlorination method is shown in Figure 2 - 1, Figure 2 - 2, Figure 2 - 3, Figure 2 - 4 of the master thesis Liu X. (2018). The hot and cold stream data of HENs is shown in Table 1 and Table 2.

3.1 Entransy analysis of existing HENs

According to the data of Table 1, the cold and hot Composite Curves of epichlorohydrin unit are plotted in the T-Q diagram, as shown in Figure 1.

The entransy of cold streams and hot streams of epichlorohydrin unit are 8.27×10^6 kW·K and 1.17×10^7 kW·K. The entransy of cold utilities and hot utilities is 6.44×10^6 kW·K and 4.66×10^6 kW·K. The entransy recovery is 3.62×10^6 kW·K. The entransy dissipation is 1.62×10^6 kW·K. The efficiency of entransy transfer is 30.98 %.

3.2 Exergy analysis of existing HENs

Set the pressure as 0.1013 MPa, the ambient temperature T_0 = 298.15 K.

The exergy of cold streams and hot streams for epichlorohydrin unit are 4,028.30 kW and 5,163.72 kW. The exergy loss is 1,970.8 kW, the exergy efficiency of epichlorohydrin unit is 61.83 %. The total rate of exergy loss is 38.17 %.

Table 1: The data for hot streams

Stream	Stream description	Supply Temperature / K	Target Temperature / K	CP / kW·K^{-1}
1	propylene	380	331	6.45
2	propylene	404	355	7.17
2A	propylene	355	313	35.10
3	inert gases	313	303	0.00
4	propylene	313	283	9.74
6	the gas product of the reaction	743	303	8.07
8	heat conduction oil	477	391	13.61
9	the gas product of the reaction	303	263	19.41
11	propylene	283	263	2.58
12	crude chloropropene	342	313	2.25
13	chloropropene	318	318	3,396.32
13A	chloropropene	318	313	5.69
14	crude D-D mixture	392	313	0.34
15	low boiling point mixture	318	316	746.38
16	chloropropene	344	308	1.86
21	dilute hydrochloric acid	341	313	6.72
22	dilute hydrochloric acid	323	309	12.03
23	washing water	361	309	55.03
24	washing water	348	303	58.44
27	epoxy wastewater	358	338	193.51
28	epoxy Steam	371	357	591.13
28A	epoxy Steam	357	313	15.53
29	the top of prefractionator's low boiling point mixture	360	328	17.03
29A	the top of prefractionator's low boiling point mixture	328	313	1.86
32	epichlorohydrin	327	327	13,150.50
32A	epichlorohydrin	327	313	6.14
34	low boiling point mixture	353	313	3.60
36	epichlorohydrin	400	313	0.09
37	epichlorohydrin	355	313	1.38
38	high boiling point mixture	366	313	0.18

3.3 The maxium energy recover HENs

According to the data of Table 1 and Table 2, minimum approach temperature ⊿T_{min} is given as 10 K, 15 K and 20 K, the results of exergy analysis and entransy analysis are shown in Table 3 and 4. Synthesis of epichlorohydrin unit HENs based on entransy theory is shown in Figure 2. From the results, it was seen that the quantity of entransy varies with the variation of minimum approach temperature. When ΔT_{min} is given as 10 K, 15 K and 20 K, the exergy efficiency of epichlorohydrin unit are 61.01 %, 59.28 %, 57.27 %, saving utilities are 16.59 %, 14.86 %, 12.02 %. It is indicated that the greater the temperature difference, the lower quality of exergy. When ΔT_{min} is 10 K, 15 K and 20 K, the entransy transfer efficiency of epichlorohydrin unit are 42.81 %, 42.13 %, 41.00 %, saving utilities is 19.41 %, 18.01 %, 15.70 %. It is obvious that the greater the minimum approach temperature difference, the larger entransy dissipation, and the lower entransy transfer efficiency.

Table 2: The data for cold streams

Stream	Stream description	Supply Temperature / K	Target Temperature / K	CP / kW·K^{-1}
5	propylene	283	286	352.30
5A	propylene	286	553	6.41
7	heat conduction oil	391	477	13.61
10	the top gas of prefractionator	230	291	5.50
17	the tower bottoms of prefractionator	270	303	10.55
18	the tower bottoms of propylene stripping tower	340	342	158.46
19	the tower bottoms of D-D separation tower	389	392	500.57
20	the tower bottoms of M-C separation tower	343	347	461.64
25	the tower bottoms of propylene absorber	360	378	311.49
26	dichloropropanol aqueous solution	319	353	171.72
30	the tower bottoms of hydrogen chloride absorber	383	384	1,563.17
33	the tower bottoms of fractionating tower	394	395	1,178.61
35	the tower bottoms of propylene absorber	400	401	1,504.78
39	the tower bottoms of propylene scrubber	365	366	50.01
40	water	363	418	16.13

Table 3: The results of exergy analysis method for epichlorohydrin unit

Items	⊿T_{min} = 10 K	⊿T_{min} = 15 K	⊿T_{min} = 20 K
Hot streams exergy / kW	4,811.63	4,631.73	4,449.20
Cold streams exergy / kW	4,234.98	4,331.42	4,426.63
Hot utilities exergy / kW	2,106.93	2,150.19	2,220.92
Cold utilities exergy / kW	1,591.43	1,624.66	1,680.17
Exergy loss / kW	1,875.90	1,885.90	1901.10
Exergy efficiency / %	61.01	59.28	57.27
Saving exergy / %	16.59	14.86	12.02

Table 4: The results of entransy analysis method for epichlorohydrin unit

Items	⊿T_{min} = 10 K	⊿T_{min} = 15 K	⊿T_{min} = 20 K
Hot streams entransy / kW·K	11,670,394	11,670,394	11,670,394
Cold streams entransy / kW·K	8,274,245	8,274,245	8,274,245
Hot utilities entransy / kW·K	3,277,686	3,357,630.23	3,489,182
Cold utilities entransy / kW·K	5,663,815	5,739,316.464	5,864,135
Entransy recovery / kW·K	4,996,559	4,916,614.77	4,785,063
Entransy dissipation / kW·K	1,010,020	1,014,462.766	1,021,196
Entransy transfer efficiency / %	42.81	42.13	41.00
Saving entransy / %	19.41	18.01	15.70

In the entransy analysis, the calculations of entransy and entransy dissipation are not affected by ambient temperature. But in the exergy analysis, calculations of exergy and exergy loss must take into account ambient temperature and pressure. The calculation process of exergy is also complex, considering physical and chemical exergy, as in other cases.

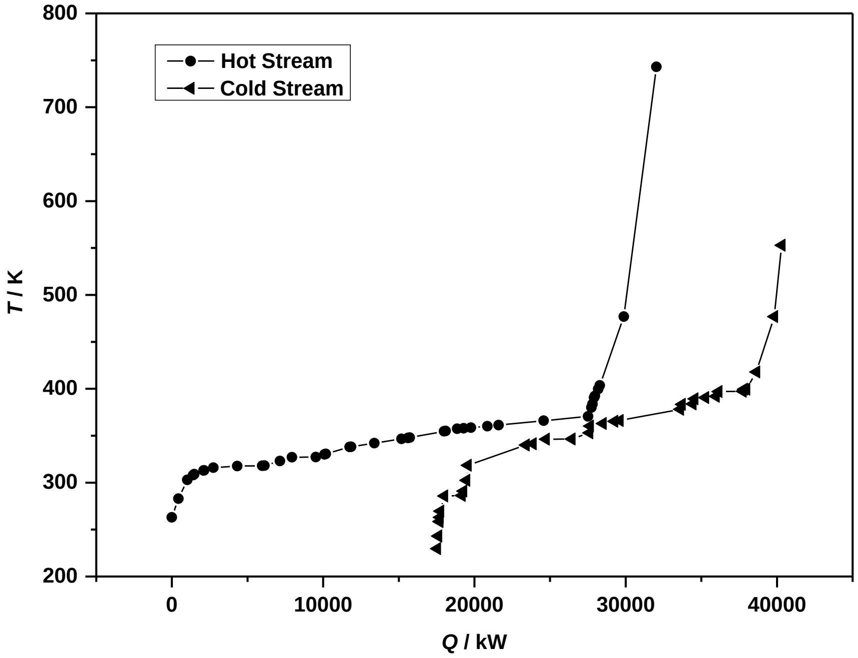

Figure 1: Composite Curves diagram of epichlorohydrin unit

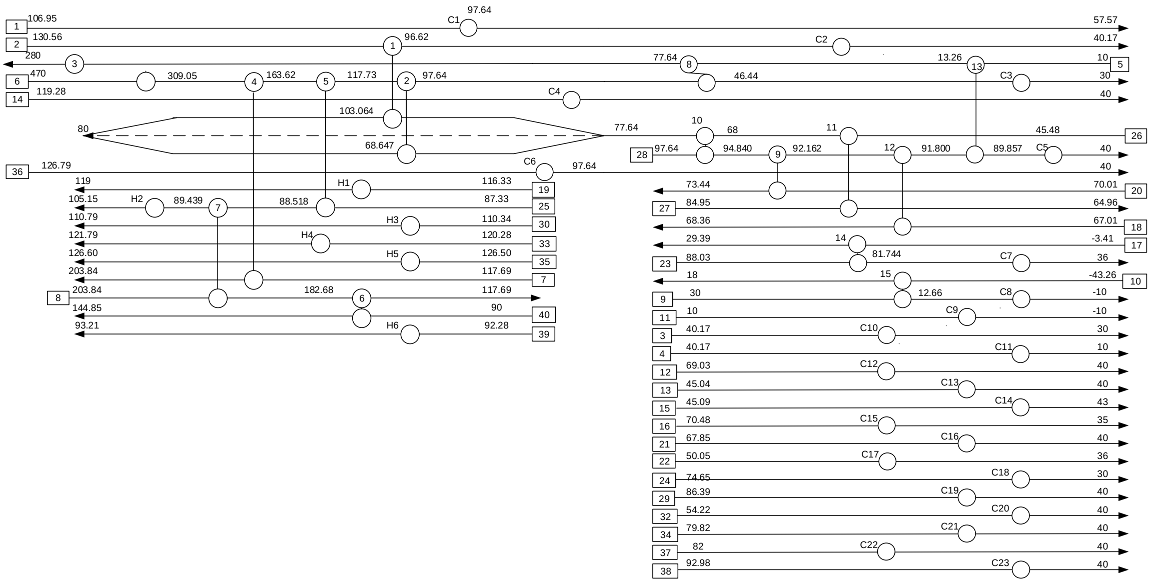

Figure 2: Synthesis of epichlorohydrin unit HENs based on entransy theory

The variation trend of entransy transfer efficiency is same as exergy efficiency. But saving utilities of entransy analysis is more than exergy analysis. To sum up, entransy analysis and exergy analysis can calculate the energy utilization efficiency of the HENs of epichlorohydrin unit. Compared with exergy analysis method, entransy analysis is simpler and more efficient.

4. Conclusion

The mathematical models for calculating the energy utilization efficiency of heat exchanger networks (HENs) based on entransy analysis method was built.The energy utilization efficiency of epichlorohydrin unit's HENs was calculated by entransy analysis method. Aiming at the maximum energy recovery, the entransy analysis of epichlorohydrin unit's HENs was done. Synthesis of epichlorohydrin unit HENs based on entransy theory was done. By taking three different $\triangle T_{min}$, 10 K, 15 K and 20 K, the entransy transfer efficiency is 42.81 %, 42.13 % and 41.00 % , the utilities are saved by 19.41 %, 18.01 % and 15.70 %. The greater the minimum approach temperature difference, the larger entransy dissipation, and the lower entransy transfer efficiency.

The results of entransy analysis method was compared with the exergy analysis method. By taking three different $\triangle T_{min}$, 10 K, 15 K and 20 K, the exergy efficiency are 61.01 %, 59.28 % and 57.27 %. Exergy analysis method is calculated under certain ambient temperature and pressure, but entransy analysis method cannot need reference state. Exergy is more complicated than entransy in the calculation process. Besides, the entransy analysis method not only can complete HENs synthesis of epichlorohydrin unit, but also can calculate the energy utilization efficiency of HENs.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (21406124) and Major science and technology innovation project of Shandong province (2018CXGC1102).

References

Ahern J.E., 1980. Exergy method of energy systems analysis. New York, Country of Publication, USA, OSTI ID: 6148569.

Chen Q., Xu Y.C., Guo Z.Y., 2012. The property diagram in heat transfer and its applications. Chinese Science Bulletin, 57 (57), 4646-4652.

Cheng, X., Liang, X., 2014. T-q diagram of heat transfer and heat-work conversion. International Communications in Heat and Mass Transfer, 53, 9-13.

Guo Z.Y., Zhu H.Y., Liang X.G., 2007. Entransy - A physical quantity describing heat transfer ability. International Journal of Heat Mass Transfer, 50 (13), 2545 – 2556.

HU G.J., Guo Z.Y., 2011. The efficiency of heat transfer process. Journal of Engineering Thermophysics, 32 (6) , 1005-1008.

İpeka O., Kılıçb B., Gürela B., 2017. Experimental investigation of exergy loss analysis in newly designed compact heat exchangers. Energy, 124, 330 - 335.

Linnhoff B., Ahmad S., 1990. Cost optimum heat exchanger networks: 1. minimum energy and capital using simple models for capital cost. Computers Chemical Engineering, 14 (7), 729 - 750.

Liu X., 2018. The process simulation and optimization of epichlorohydrin. Master Thesis, Qingdao University of Science and Technology, Qingdao, China.

Miladiet R., Frikha N., Gabsi S., 2016. Exergy analysis of a solar-powered vacuum membrane distillation unit using two models. Energy, 120, 872 - 883.

Rant Z., 1956. Exergy, a new word for technical available work. Forsch Ingenieurwes, 22 (1), 22 - 36.

Stijepovic M.Z., Papadopoulos A.I., Linke P., Grujic A.S., Seferlis P., 2014. An exergy Composite Curves approach for the design of optimum multi - pressure organic rankine cycle processes. Energy, 69 (5), 285 - 298.

Xia L., Liu R.M., Zeng Y.T., Zhou P., Liu J.J., Cao X.R., Xiang S.G., 2019. A review of low-temperature heat recovery technologies for industry processes. Chinese Journal of Chemical Engineering, 27 (10), 2227-2237.

Xia L., Feng Y.L., Sun X.Y.,Xiang S.G., 2017a. A novel method based on entransy theory for setting energy targets of heat exchanger network. Chinese Journal of Chemical Engineering, 25 (8), 1037-1042.

Xia L., Feng Y. L., Sun X.Y., Xiang S.G., 2018. Design of heat exchanger network based on entransy theory. Chinese Journal of Chemical Engineering, 26 (8), 1692-1699.

Xia L., Feng Y.L., Xiang S.G., 2017b. Comparative study of adaptability for s-zorb unit based on exergy analysis and entransy analysis. Chemical Engineering Transactions, 61 (10), 1825-1830.