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Integrated Analysis and Optimization of Ethylbenzene Dehydrogenation Unit for Styrene Production

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Styrene is an important monomer for the synthesis of polymer materials, and its production consumes a large amount of energy. In this work, the styrene production process is simulated. Based on the simulation results, the exergy loss and exergy efficiency of single equipment are analysed, as well as the distribution of exergy loss in the whole system. The heat exchanger network is analyzed and shows that, based on the integration, the exergy loss of heating and cooling utilities can be reduced by 6,824.12 kW and 5,803.14 kW. The influence of employing the azeotrope’s property in the energy recovery system is analyzed, and its application will reduce the exergy loss of heating and cooling utilities by 1,299.57 kW and 957.27 kW.

1. Introduction

In chemical production, styrene is a basic organic material and one of the important monomers in polymer synthesis. It can be used to produce styrene butadiene rubber, polystyrene, polystyrene foam and a variety of engineering plastics. Its polymer is widely used in electronics, automation, construction, packaging, light industry and other fields. Styrene can be produced based on the ethylbenzene dehydrogenation, and the production process consumes large amount of energy. In order to reduce the energy consumption, its production process should be optimized.

Many experts and scholars studied the optimization of styrene production process. Liu (2008) simulated and optimized a process of ethylbenzene dehydrogenation using PRO/II software, and presented a sensible heat recovery process and tail gas recovery system. Optimising the parameters of dehydrogenation reactor and crude styrene tower can reduce the energy consumption and equipment investment effectively. Dimian and Bildea (2019) studied the process with superheated steam used as the inert gas in ethylbenzene dehydrogenation reactor. With the steam generation device operated under vacuum condition and followed by mechanical vapour recompression (MVR), the cold and hot streams of the process can be matched in the evaporation/condensation zone, which accounts for 40 % of the hot energy input. The disturbances of ±10 % will not affect the stability of the system and the purity of styrene.

Exergy is the maximum shaft work that can be done in a process to bring the system into equilibrium with the environment, and is widely applied to analyse the energy saving from a deeper level. Ali and Hadj-Kali (2018) studied the energy requirements and recovery of styrene production process using Exergy analysis and Heat Integration, and identified 68 % of the exergy loss can be reduced. The study of Damanabi and Bahadori (2018) shows that, the exergy efficiency can increase from 77.45 % to 90.86 % when the pressure of benzene–toluene column is decreased from 220 kPa to 60 kPa, while optimizing the flow rate of oxygen injected into the second reactor can increase the exergy efficiency from 25.76 % to 38.07 %.

In the study introduced above, not all equipment are analyzed in terms of exergy, and the distribution of the system’s exergy loss cannot be identified accurately. In addition, few studies considered the effect of employing the ethylbenzene-water azeotrope. In this paper, the ethylbenzene dehydrogenation to styrene process will be simulated by using the Aspen Plus 10.0 (Aspen Tech., 2015). Then, the exergy loss and exergy efficiency of all devices are calculated. The effect of employing the ethylbenzene-water azeotrope recovering low temperature heat is analyzed in terms of exergy loss.

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2. Simulation of the ethylbenzene dehydrogenation to styrene process

The ethylbenzene dehydrogenation to styrene process is composed of ethylbenzene unit and styrene unit. The former is designed to produce the intermediate product ethylbenzene from benzene and ethylene, and includes two main working zones, the alkylation/anti-alkylation zone and the ethylbenzene distillation zone. The alkylation/anti-alkylation zone includes an alkylation reaction system and an anti-alkylation reaction system. The alkylation reaction is carried out in two reactors (R-4101 and R-4102) in series of benzene, and the ethylene is divided into four equal parts and inlet into two reactors. In addition to ethylbenzene, polyethylbenzene and a small amount of high-boiling substances are generated in the reactor. In order to increase the yield of ethylbenzene, polyethylbenzene and benzene are further reacted in the anti-alkylation reactor (R-4103). The effluents of the alkylation reactor and the anti-alkylation reactor are called the alkylation solution, and are sent to the ethylbenzene distillation zone.

In the ethylbenzene distillation zone, three distillation columns (T-4201, T-4203 and T-4204) are used to separate the alkylation solution into benzene (circulated to the alkylation reactor or anti-alkylation reactor), ethylbenzene, polyethylbenzene (circulated to the anti-alkylation reactor), and by-product ethylbenzene tail oil. In addition, a benzene removal tower (T-4202) is used to separate benzene from the light hydrocarbon generated in the reactor. The specific process is shown in Figure 1.

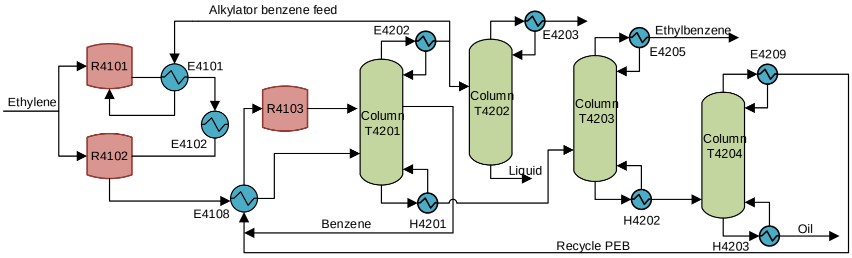


Figure 1: Process flowsheet of ethylbenzene unit

The styrene unit includes two working zones. In the ethylbenzene dehydrogenation zone, ethylbenzene is heated by steam and vaporised in the ethylbenzene evaporator. The vaporised mixture is heated by the reactor effluent in heat exchanger E-5304, and then mixed with steam and inlet into the first-stage reactor. The high-temperature effluent of the reactor is cooled through heating the ethylbenzene/steam mixture and generating steam. D-5305 is an oil-water separator. A portion of its aqueous product (process condensate) is used for desuperheating the reactor's effluent, and the remained process condensate is overheated and sent to T-5301 as stripping steam. The oil phase is separated in the ethylbenzene/styrene tower (T-5401). Ethylbenzene and other light components are obtained at the top of this column. The bottom product includes styrene and more heavy fractions. The distillate of T-5401 is the feed of ethylbenzene recovery tower (T-5402), which separates benzene and toluene from the top. Ethylbenzene is obtained at the bottom and recycled to the dehydrogenation reactor. Benzene and toluene are sent to the benzene/toluene separation tower (T-5404), and benzene is obtained at the top and sent to the tank. Toluene is produced at the bottom and sent to the tank as a by-product. The bottom product of T-5401 is sent to the styrene product tower T-5403. At the top of this tower, the vapour is partially condensed, the non-condensate gas is sent to the vacuum unit, and the styrene are sent to the tank. The specific process is shown in Figure 2.

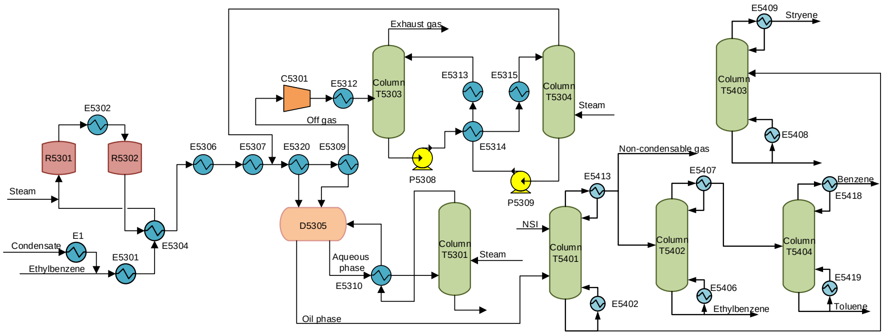


Figure 2: Process flowsheet of styrene unit

According to the flowsheet introduced above, the simulation model is built in Aspen Plus 10; the simulation results are in good agreement with the practical data, and the average error is less than 6 %. Part of the data obtained from the simulation are compared with the practical data in Table 1.

Table 1: The comparison between simulation data and practical data

Unit and Comp.	Outlet flow/ kg·h^{-1}		Components	Product composition of EB unit / kg·h^{-1}		Components	Product composition of SM unit/ kg·h^{-1}	
	Practical	Simulation		Practical	Simulation		Practical	Simulation
EB unit	15,946.9	15,946.3	Benzene	15.8	16.1	Ethylbenzene	3	0.29
SM unit	23,750.6	23,690.7	Toluene	5.8	6	Styrene	14,984.3	14,952.8
Product purity/ wt%			Ethylbenzene	15,736.4	15,740	C8/C9	6	0.02
Styrene	≥ 99.6	99.8	Diethylbenzene	7.4	6.1	Alpha-Methylstyrene	3	24
Toluene	≥ 99.45	99.6	Others	6.1	3.4	Others	3.7	0.39
Benzene	≥ 99.8	99.9	Total	15,771.5	15,771.6	Total	15,000	14,977.5

3. Exergy analysis of the process

3.1 Exergy

In chemical process, there are mainly three types of exergy transfer, which are related to mass flow, heat interaction and work. Exergy related to mass flow (E_M) can be divided into physical exergy (E_{ph}) and chemical exergy (E_{ch}), as shown by Eq(1) (Kotas, 1980).

$$E_M = E_{ph} + E_{ch} = N\left(\overline{E}^{ph} + \overline{E}^{ch}\right) \tag{1}$$

Where $\overline{E}^{ph}$ and $\overline{E}^{ch}$ are the physical exergy and chemical exergy of molar mixture, and can be calculated by Eq(2) and Eq(3).

$$\overline{E}^{ph} = H - H_0 - T_0\left(S - S_0\right) \tag{2}$$

$$\overline{E}^{ch} = \sum x_i \overline{E}^{ch}_{i,ref} + RT_0 \sum x_i \ln x_i \tag{3}$$

Where H is the enthalpy under actual temperature, kJ·mol^{-1}; S denotes the entropy, kJ·mol^{-1}·K^{-1}; x_i is the molar fraction of component i; R is the ideal gas constant, 8.314 kJ·mol^{-1}·K^{-1}; $\overline{E}^{ch}_{i,ref}$ is the molar exergy in the reference state, kJ·mol^{-1}. Subscript 0 indicates the environment/reference state; Szargut model (1989) is used as the reference state (T_0 = 25 °C, P_0 = 101.325 kPa).

The maximum work that can be done by the heat (Q) at temperature T is its thermal exergy, and can be calculated by Eq(4). The closer the temperature to the ambient temperature (T_0), the smaller the exergy.

$$E_q = \left(1 - \frac{T_0}{T}\right) \times Q \tag{4}$$

All the work (W) can be converted into effective energy (E_W), as shown by Eq(5).

$$E_w = W \tag{5}$$

For the steady-state flow, the exergy equilibrium of the ‘i’th term is given by Eq(6).

$$E^{in,i} = \sum_i E_M^{in,i} = E^{out,i} + E^{loss,i} = \sum_i E_M^{out,i} + E_{q,i} + E_{w,i} + E^{loss,i} \tag{6}$$

Exergic efficiency (η_{exergy}) an be expressed by Eq(7).

$$\eta_{exergy,i} = \frac{E^{out,i}}{E^{in,i}} = 1 - \frac{E^{loss,i}}{E^{in,i}} \tag{7}$$

Where $E^{in,i}$ is the exergy inlet into the system, kW; $E^{out,i}$ is the exergy outlet form the system, kW; $E^{loss,i}$ represents the loss of exergy, kW.

3.2 Exergy analysis of equipment

Based on the simulation results of the process and Eqs(1) - (7), the exergy efficiency and exergy losses of each equipment and its utility in the actual production process are calculated and listed in Table 2. From this table, it can be seen that the total exergy loss is 10,515.93 kW; the exergy efficiency of pump and heat exchanger is generally low. The exergy loss in heat recovery process is 6,932.84 kW, accounting for 65.93 % of the total exergy loss. The energy consumption of the tower is mainly due to the utility consumption in the condenser and reboiler.

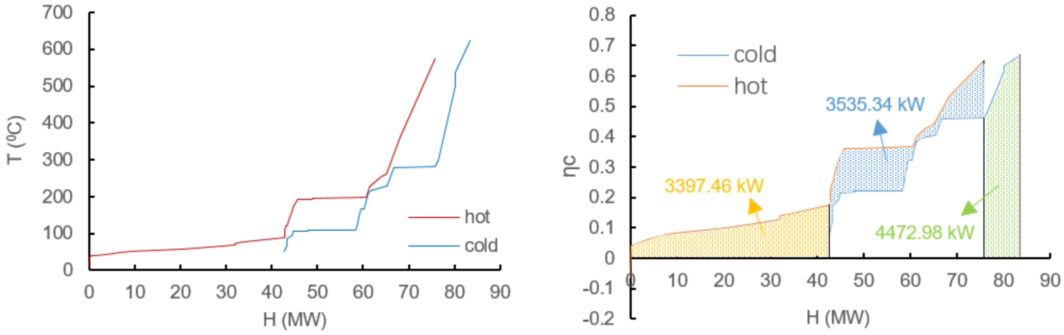
Table 2: Data of exergy loss and exergy efficiency

Equipment	E^{loss} / kW	η_{exergy} / %	E^{loss} of heating(cooling) utilities/ kW	Equipment	E^{loss} / kW	η_{exergy} / %	E^{loss} of heating(cooling) utilities/ kW
R-4101	3.58	95.72		E-5314	5.47	70.58	
R-4102	8.28	82.85		E-5315	4.16	83.76	25.62
R-4103	30.94	76.19		P-5308	1.08	48.94	
E-4101	35.41	91.08		P-5309	0.01	41.94	
E-4102	157.35	68.99	(350.09)	T-5303	6.07	99.86	
E-4108	15.27	91.30		T-5304	84.01	98.52	
T-4201	1,293.37	76.02	4,700.6(4,099.98)	E-5407	58.93	23.82	(18.43)
T-4202	160.74	6.56	(11.28)	E-5409	264.16	20.75	(69.17)
T-4203	305.55	75.27	829.07(930.08)	E-5410	0.29	57.12	0.67
E-4207	30.43	9.04	(3.02)	E-5412	9.64	49.31	9.19
T-4204	25.35	78.25	80.84(91.22)	E-5413	1,253.74	26.60	(454.25)
E-5301	61.44	70.32	206.98	E-5414	1.60	23.99	(0.51)
E-5302	96.54	95.61	2,200.34	E-5418	8.17	23.32	(2.49)
E-5304	789.94	82.82		P-5402	26.23	14.72	
E-5306	3,038.18	37.89	(1,853.69)	P-5403	0.66	33.91	
E-5307	64.16	79.83	(253.94)	P-5404	1.24	24.21	
E-5309	123.02	15.12	(21.91)	P-5406	11.45	4.35	
E-5310	20.11	77.84		P-5417	0.01	5.81	
E-5320	875.80	53.68	(1,015.07)	P-5418	0.02	31.28	
R-5301	310.17	74.67		T-5401	415.09	81.89	2291.66
R-5302	198.51	85.49		T-5402	50.82	79.32	245.72
T-5301	116.51	91.10		T-5403	388.25	43.23	683.94
X-5302	141.78	99.95		T-5404	2.64	82.16	14.8
E-5312	11.10	66.50	(22.04)	Z-5401	0.71	90.73	7.68
E-5313	7.91	30.51	(3.47)	Total	10,515.93		11,297.1(9,200.6)

Note: R stands for reactor; T stands for tower; E stands for heat exchanger; Z stands for flash; X stands for mixer; P stands for pump.

For pumps, the total exergy loss is 40.7 kW, accounting for 0.39 % of the total exergy loss. According to Eq(6) and Eq(7), it can be seen that the exergy loss is caused by the inefficiency of the pump, and there is no space for improving its efficiency through process modification.

Pinch Analysis is an important method for targeting the minimum utility consumption. With the vertical coordinates of the Composite Curve (CC) and the Grand Composite Curve (GCC) changed from temperature to Carnot factor (η_c), the exergy Composite Curve (ECC) and the exergy Grand Composite Curve (EGCC) are constructed (Linnhoff, 1992). The area between the cold/hot Composite Curve and the horizontal axis is the exergy required to be provided by utilities, and the area between two Composite Curves is the exergy loss of the heat recovery process. Based on the simulation data, the Composite Curve is plotted using Aspen Energy Analyser (Aspen Tech., 2015), as shown in Figure 3(a), and the exergy Composite Curve is plotted by using Microsoft Excel 2016, as shown in Figure 3(b).



(a) Composite Curves

(b) Exergy Composite Curves

Figure 3: The Composite Curves (CC) and the exergy Composite Curve (ECC)

Based on the calculation by Origin 2018, the exergy transferred outward by hot streams is 18,802 kW and the amount of exergy required by cold streams is 15,141.33 kW. From Table 2, it can be seen that in the actual production process, the exergy losses of in the cooling process is 9,200.6 kW, and the exergy increment of cold streams in the heating process is 11,297.1 kW. From Figure 3(b), it can be seen that the target exergy loss during heat recovery process is 3,535.34 kW. For hot streams, their low temperature energy should be cooled by the cooling utility, and the exergy loss is 3,397.46 kW, 5,803.14 kW less than the practical value. For cold streams, its minimum exergy increment in the heating process is 4,472.98 kW, 6,824.12 kW less than the practical value.

4. Effect of ethylbenzene-water azeotrope on the system

Under atmospheric pressure, the boiling point of ethylbenzene is 136 °C, and that of water is 100 °C. Ethylbenzene and water form the minimum azeotrope, whose boiling point is 92 °C, lower than that of ethylbenzene and water. The mass ratio of water and ethylbenzene in the azeotrope is about 1:2. The azeotropic mixture can be heated to vaporize by streams with lower temperature. Based on this characteristic, the mixing of ethylbenzene and water can be used to enhance the energy recovery and the utilization of low temperature energy.

In the practical process, 9,255 kg·h^{-1} 350 kPaG superheated steam (148 °C) is mixed with 23,035 kg·h^{-1} ethylbenzene (90 °C). The mixture is evaporated in the evaporator E-5301 and the evaporation temperature is 96 ~ 136 °C. After evaporation, it is heated to 500 °C with the outlet stream of the secondary reactor in heat exchanger E-5304. As shown by mode 1 in Figure 4. To compare with mode 2 under the same reference, the steam is taken as obtained from the condensate, which is heated by heat exchanger E-1.

From the Grand Composite Curve, it can be seen that the system has a lot of low temperature energy. Since ethylbenzene and water need to be mixed and vapourised, ethylbenzene can be mixed with condensate water instead of steam to form the mixture with azeotropic composition, and evaporate at 92 °C to recover the low temperature energy. In mode 2, 9,255 kg·h^{-1} condensate and 23,035 kg·h^{-1} ethylbenzene raw materials are mixed in accordance with the mass ratio of 1:2 to form the azeotrope, and the mixture is evaporated and heated to the target temperature by heat exchangers E-1 and E-2. The remaining ethylbenzene is heated to the target temperature by two other heat exchangers (E-3 and E-4).

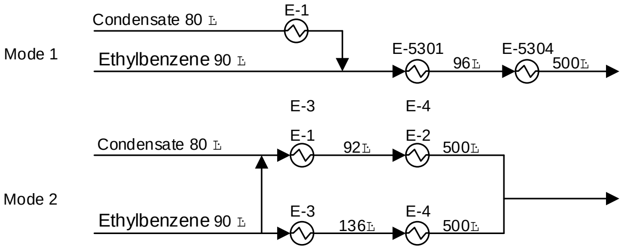


Figure 4: Different feeding modes of ethylbenzene dehydrogenation reactor

When the minimum heat transfer temperature difference (ΔT_{min}) is take as 10 °C, the minimum utility, Pinch temperature and exergy loss under two feed heating modes are compared in Table 3.

Table 3: The Minimum utility consumption under different feeding modes

Mode	Heating utility/ kW	Cooling utility/ kW	Exergy loss/ kW		Pinch temperature/°C
			Heating utility	Cooling utility	
Mode 1	16,482.84	40,687.17	6,872.63	4,264.46	84.3
Mode 2	11,217.58	34,754.58	5,573.06	3,307.19	84.3

Compared with Mode 1, the heating utility consumption decreases by 5,265.26 kW, and the cooling utility consumption decreases by 5,932.59 kW. The exergy loss of heating and cooling processes decrease by 1,299.57 kW and 957.27 kW. This is due to the recovery of the low-temperature heat for vaporising the azeotropic mixture and reducing the utility consumption. Because of the exergy loss in the energy recovery process, the decrement of the exergy loss is significantly less than that of the utility consumption. The results show that the utility consumption and exergy loss of heat exchanger network can be reduced with the characteristic of the minimum azeotrope employed in the energy recovery.

5. Conclusions

In this work, ethylbenzene unit and styrene unit were integrated and simulated, and the exergy loss and exergy efficiency of each equipment and the distribution of exergy loss were calculated. The results show that the exergy efficiency of some pumps and heat exchangers is relatively low, and the exergy loss of heat exchangers accounts for 65.93 % of the total. Optimising the heat exchanger network properly can reduce the exergy loss of heating and cooling utilities by 6,824.12 kW and 5,803.14 kW. With the characteristic of the minimum azeotrope employed in the energy recovery, the consumption of cooling and heating utilities can be reduced by more than 5,000 kW, and the heating utility and cooling utility exergy loss can be reduced by 1,299.57 kW and 957.27 kW.

Acknowledgements

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