

Heat Exchanger Network Integration of a Hydrogenation Process of Benzene to Cyclohexene Considering the Reactor Conversion

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In chemical industrial processes, reactor is the core of the whole system and influences other units and the utility consumption. To reduce the energy consumption, it is necessary to consider the reactor design and heat exchanger network (HEN) simultaneously, and optimize the reactor parameters based on the HEN integration. A graphical method is proposed to optimise a selective hydrogenation process of benzene to cyclohexene. Since the selectivity of benzene to cyclohexene is affected by the reaction rate of the main reaction and the side reaction in CSTR, the relationship among reaction temperature, the conversion and selectivity of benzene is deduced based on the kinetic equations. Based on this, the HEN's Composite Curve diagram is extended with the conversion-temperature-energy curve accommodated, and the relation between the reactor and the HEN is analysed. In the analysis process, the temperature variation of the source is accommodated by shifting the corresponding inflection point of the composite curve. By this method, optimal reaction temperature, conversion, and the minimum energy consumption of the process are identified simultaneously.

1. Introduction

Cyclohexene with active double bond is widely applied as important chemical material. It is of great synthetic and industrial interest for selective hydrogenation of benzene to cyclohexene. In recent years, many researchers have conducted the study on the selective hydrogenation of benzene to cyclohexene. In 1934, Truffault (1934) proposed that cyclohexane was the intermediate product for the hydrogenation of benzene to cyclohexene and suggested producing cyclohexene through this process. In 1963, the liquid-phase selective hydrogenation of benzene to cyclohexene on Ru/Rh catalyst was put forward by Hartog (1963). Until now, different catalysts with high selectivity and yield, such as Ru-M-B/ZrO₂ has been developed and applied in industry (Wang, 1991). The catalyst was made of RuCl₃·H₂O, FeSO₄·7H₂O and KBH₄ and carried by ZrO₂.

The production process of cyclohexene from benzene is highly energy-consuming; large amount of cooling utility is consumed to keep the temperature of the hydrogenation reactor stable. The temperature of inlet feed, outlet product and the coolant stream, which are sinks or sources of the heat exchanger network (HEN), are all affected by the kinetic and thermodynamic parameters. The supply or target temperature of some sinks and sources will change with the reaction parameters, and this influences the integration of the whole system as well as the energy consumption. On the other hand, the reactor parameters, such as temperature, pressure, residence time, outlet temperature and the product flowrate are all related to the conversion. It is necessary to study the reactor conversion together with the HEN first.

Glavič et al. (1988) first proposed the integration of reactors and energy network with Pinch by placing the reactor appropriately in a process and optimising the integration of the reactor into the process. Thereafter, they developed the utility concept tool which treat chemical reactors as hot/cold utilities in HEN (Kravanja et al., 1989), and solved the problem by the computerized program (Glavič et al., 1990). However, these studies only focused on the investigation of the reactor network and start with a thermodynamic decomposition and the influence of reaction parameters on the reactor profile instead of the influence on the HEN. Then, a new method was proposed by extending to the integration between chemical reactors network (Lavric et al., 2006) and HEN or even the integration of wastewater treatment (Klemeš, 2012). In recent years, some researchers applied the

heat integration with other parameters of the process. Chew et al. (2015) extended the graphical pinch-based methodology of total site heat integration to consider the pressure drop factor during the minimum energy requirement targeting stage. However, there is no research on the integration between reactors and HEN.

For the selective hydrogenation process of benzene to cyclohexene, a graphic method will be proposed to analyse the integration of HEN with the effect of reactor conversion considered. In this method, the Conversion-Temperature-Energy Consumption Curve is constructed and combined with the Composite Curve of the HEN. The variation of the cold and heating utilities can be identified directly without complex calculation.

2. The selective hydrogenation process of benzene to cyclohexene

The simplified flowsheet of a selective hydrogenation of benzene to cyclohexene is shown in Figure 1. There are 5 reactors, 7 distillation columns and 22 heat exchangers (A-E811 and A-E861 are in the wastewater treatment unit, and are not shown in this figure). Reactor R104 is the hydrogenation reactor producing cyclohexene; its parameter will be optimized together with the HEN. For this reactor, the processing ability, $F_{BZ,0}$, is 982 mol/min; residence time, τ , is 15 min and the reactor volume, V_R , is 640 L. There are 13 hot streams and 9 cold streams in the HEN and the data of each stream is listed in Table 1. With the approach temperature taken as 10 K, the Composite Curve is plotted, as shown by Figure 2, and main inflection points are marked with letters. It is identified that the minimum hot and cold utility consumptions and the Modified Pinch Temperature are 7,162.88 kW, 5,371.87 kW and 375 K. Among the hot streams, H1 is the feed stream while H2 is the product stream of R104. H4 is the coolant stream which removes the heat of the reactor and is cooled by cooling water.

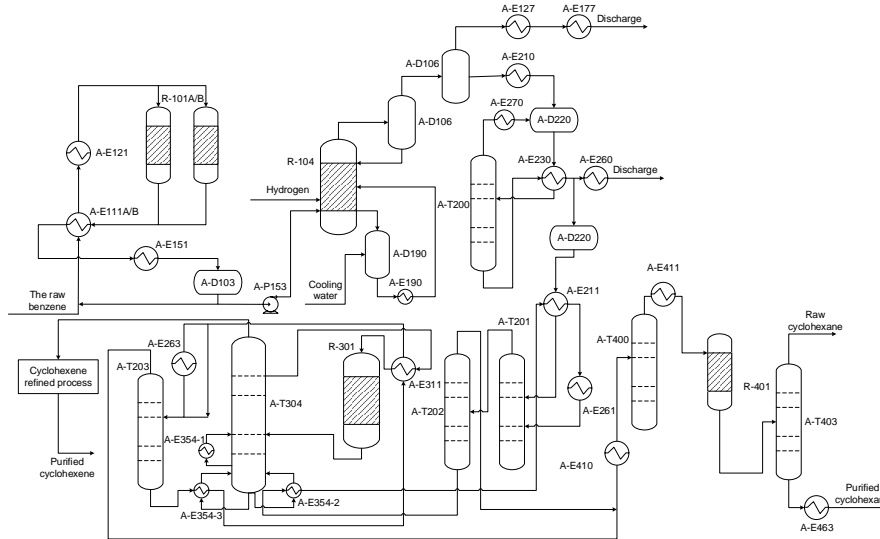


Figure 1: The flowsheet of benzene to cyclohexene process

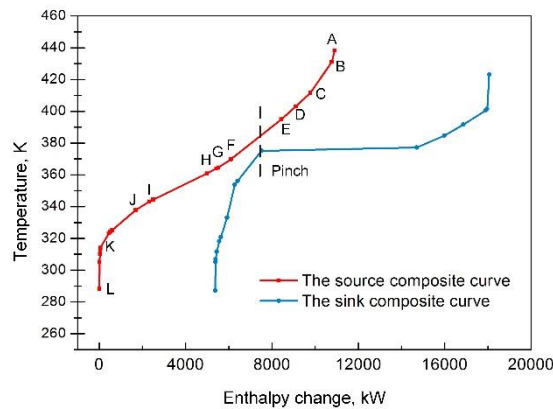


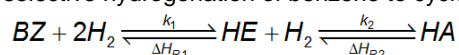
Figure 2: The Composite Curve

Table 1: The data of streams

Streams	Heat exchanger	T_s , K	T_T , K	ΔH , kW	CP , kW·K ⁻¹
H1	A-E111A/B,A-E151	411.65	314.15	2,767.80	28.38
H2	A-E127	403.15	305.15	359.88	3.67
H3	A-E177	305.15	288.15	9.87	0.58
H4	A-E190	364.65	323.15	1,197.64	28.85
H5	A-E210	394.95	313.15	827.18	10.11
H6	A-E354-2,A-E211, A-E261	431.15	337.85	2,982.40	31.97
H7	A-E230 , A-E260	360.85	324.15	285.80	7.79
H8	A-E263	369.65	343.15	1,021.21	38.54
H9	A-E270	313.15	288.15	4.38	0.18
H10	A-E354-3,A-E311	438.35	369.95	1,286.34	18.81
H11	A-E410	310.45	310.15	0.19	0.63
H12	A-E463	363.95	313.15	45.79	0.90
H13	A-E811,A-E861	344.35	325.15	116.68	6.08
C1	A-E111A/B,A-E121	305.15	423.15	574.44	4.87
C2	A-E211	318.15	391.65	856.71	11.66
C3	A-E230	306.95	333.15	156.83	5.99
C4	A-E311	353.85	384.75	1,286.34	41.63
C5	A-E411	287.15	356.15	45.64	0.66
C6	A-E354-3	375.15	400.65	1,227.15	48.12
C7	A-E354-2	375.15	401.55	1,651.33	62.55
C8	A-E354-1	375.15	377.15	6849.11	3424.55
C9	A-E811	311.65	320.85	50.57	5.50

3. The integration of reactor and HEN

Please do not use footnotes. It has been reported (Struijk et al., 1992) that the reaction of the liquid-phase selective hydrogenation of benzene to cyclohexene is a series reaction which can be represented as



Where, BZ is benzene, HE is cyclohexene and HA is cyclohexane. k_1 and k_2 are the reaction rate constants of the positive and reverse reaction in the standard condition (298.15 K, 1.0 bar), ΔH_{R1} and ΔH_{R2} are the heat of reaction of these two reactions and equal -95 k J/mol and -120 kJ/mol. At high temperature and high pressure, the reaction rate only depends on the concentration of benzene (C_{BZ}) and reacting temperature (T), as shown by Eq(1) and (2) see Liu et al. (2003).

$$-r_{BZ} = k_1 C_{BZ} \quad (1)$$

$$r_{HA} = k_2 \quad (2)$$

Where, $-r_{BZ}$ is the reaction rate of benzene while r_{HA} is the generation rate rate of cyclohexane. Based on this, the production rate of HE is obtained, and is shown by Eq(3).

$$r_{HE} = k_1 C_{BZ} - k_2 \quad (3)$$

Where r_{HE} is the generation rate of cyclohexene and (Yang, 2003) ,

$$k_1 = 734.95(\text{min}^{-1}) \exp\left[-32630(\text{kJ}\cdot\text{mol}^{-1})/RT\right] \quad (4)$$

$$k_2 = 478.33(\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}) \exp\left[-21130(\text{kJ}\cdot\text{mol}^{-1})/RT\right] \quad (5)$$

For the CSTR reactor with given reaction volume, the reaction rate is distributed evenly, and the relationship among flow rate of the transformed reactant, reaction rate and reaction volume for the two steps can be clearly indicated by the following design equations.

$$-r_{BZ} = F_{BZ} / V_R \quad (6)$$

$$r_{HE} = F_{HE} / V_R \quad (7)$$

Where, F_{BZ} is the mole flow rate of transformed benzene and F_{HE} is that of generated cyclohexene. In this process, hydrogen is sent dispersedly to the bottom of CSTR, and the benzene and cyclohexane only exist in liquid-phase of this gas-liquid catalytic reaction. What's more, according to the literature, the reaction rate is not affected by the pressure of hydrogen at high pressure and high temperature. The reaction can be simplified as a homogeneous liquid-phase reaction. Consequently, F_{HE} and F_{BZ} can be defined as

$$F_{BZ} = F_{BZ,0} \cdot X \quad (8)$$

$$F_{HE} = XYF_{BZ,0} \quad (9)$$

Where, $F_{BZ,0}$ is the inlet mole flowrate of benzene. X is the conversion of benzene, while Y is the selectivity of cyclohexene and is defined by Eq(10).

$$Y = (k_1 c_{BZ} - k_2) / k_1 c_{BZ} \quad (10)$$

Based on Eq(1), Eq(4) and Eq(8), the outlet concentration of benzene is

$$c_{BZ} = c_{BZ,0} \cdot (1 - X) \quad (11)$$

Where $C_{BZ,0}$ is the inlet concentration of benzene. Then the relation between temperature T and conversion X is deduced and shown by Eq(12).

$$734.95(\text{min}^{-1}) \exp[-32630(\text{J} \cdot \text{mol}^{-1}) / RT] = \frac{F_{BZ,0}}{V_R \cdot c_{BZ,0}} \cdot \frac{X}{1 - X} \quad (12)$$

Besides, in CSTR, the inlet volume flow, v_0 , and the residence time, τ , can be defined as

$$v_0 = F_{BZ,0} / c_{BZ,0} \quad (13)$$

$$\tau = V_R / v_0 \quad (14)$$

Then, Eq(12) can be transformed into Eq(15).

$$734.95(\text{min}^{-1}) \exp[-32630(\text{J} \cdot \text{mol}^{-1}) / RT] = \frac{X}{1 - X} \cdot \frac{1}{\tau} \quad (15)$$

Based on the first law of thermodynamics, the energy balance of the reactor can be represented by Eq(16)

$$Q - F_{BZ,0} \cdot Cp_{BZ} \cdot (T - T_0) + V_R r_{BZ} [\Delta H_{R1} + \Delta Cp_1 (T - 298.15)] + V_R (-r_{HA}) [\Delta H_{R2} + \Delta Cp_2 (T - 298.15)] = 0 \quad (16)$$

Where

$$\Delta Cp_1 = \Delta Cp_{HE} - 2\Delta Cp_{H_2} - \Delta Cp_{BZ} = -38.91 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad (17)$$

$$\Delta Cp_2 = \Delta Cp_{HA} - \Delta Cp_{H_2} - \Delta Cp_{HE} = -23.09 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad (18)$$

$$Q = 28.85(\text{J} \cdot \text{min}^{-1} \cdot \text{K}^{-1})(T_{CT} - 323.15) \quad (19)$$

Where, Q is the energy supplied by cooling water and T_{CT} is the outlet temperature of the coolant.

Based on Eq(15), the reacting temperature, T , can be obtained with certain conversion X . Then keeping the temperature difference of inlet and outlet stream at 89K, the outlet temperature of coolant, T_{CT} , is solved by Eq(16).

Assuming that the CP of each stream stays unchanged when changing the conversion, the energy consumption depends on the variation of relative sources' supply or target temperature. The cooling utility, ΔQ_C , and the heating utility, ΔQ_H , are given as

$$|\Delta Q_C| = 5371.87 + C_{p_{H4}}(T_{CT} - 364.15) - C_{p_{H1}}(T_0 - 314.15) \tag{20}$$

$$\Delta Q_H = 7162.88 + C_{p_{H2}}(T - 403.15) \tag{21}$$

Hence, the unit consumption, S, is presented by Eq(22).

$$S = \frac{a|\Delta Q_C| + b\Delta Q_H}{F_{HE}} = \frac{a|\Delta Q_C| + b\Delta Q_H}{XYF_{BZ,0}} \tag{22}$$

Where, a and b are the conversion coefficients of the hot and cold utilities.

Based on the above analysis, the curve of unit consumption, the inlet and outlet temperature of reactor and the outlet temperature of the coolant against X can be shown in the same diagram with Composite Curve, as shown by Figure 3. The original conversion is 0.4, and the corresponding temperatures T, T₀ and T_{CT} correspond to points O₁, O₂ and O₃. The lowest point in unit consumption curve, O₄, corresponds conversion 0.56, and the minimum unit consumption is 68 kW·min·mol⁻¹. At this conversion, T, T₀ and T_{CT} correspond to points O₁′, O₂′ and O₃′, and are 431 K, 375 K and 342 K.

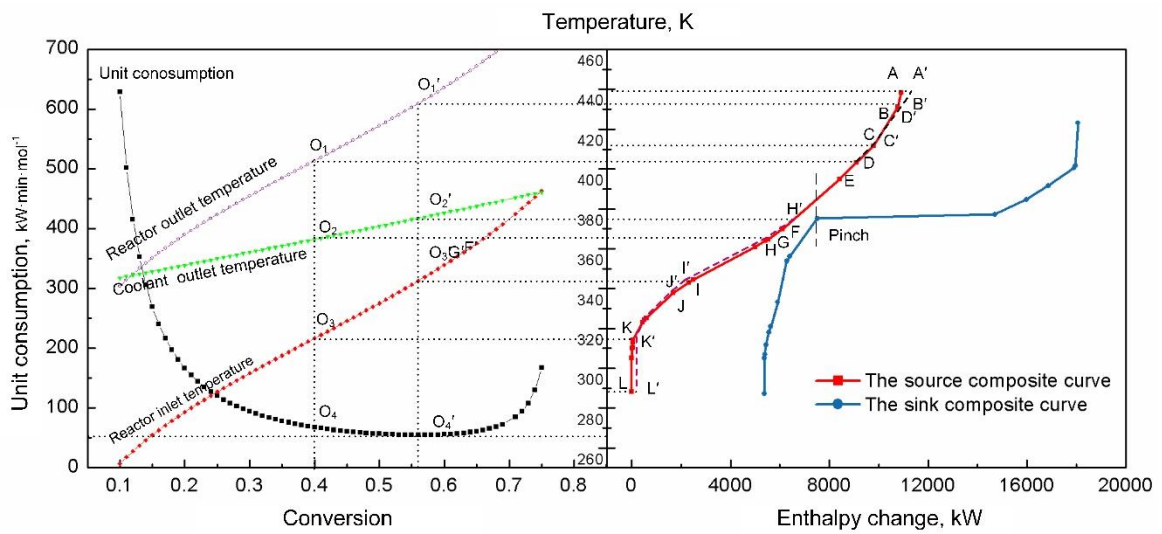


Figure 3: The integration of reactor and HEN

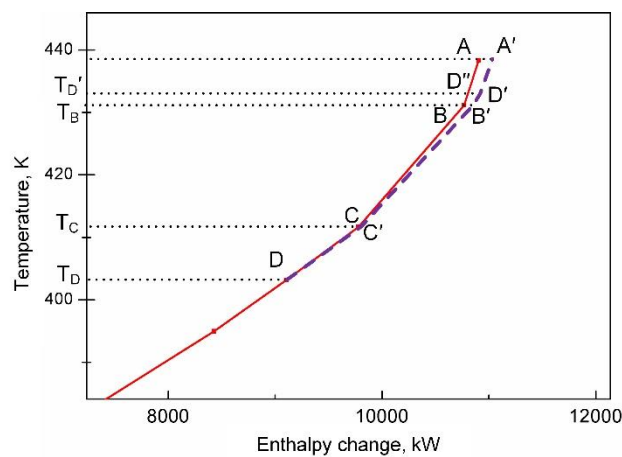


Figure 4: The variation of Source Composite Curve above the Pinch

When the conversion increases from 0.4 to 0.56, the Composite Curve will change correspondingly. To illustrate the variation of Composite Curve clearly, the Source Composite Curve above the Pinch shown in Figure 3 is plotted in Figure 4. When the supply temperature of H₂ increases to T_D′, a horizontal line can be plotted and

intersects the Source Composite Curve at D". There is be one more source in temperature interval $[T_B, T_D]$, $[T_C, T_B]$ and $[T_D, T_C]$ and the increment of CP equals to that of H2. Hence, point C, B, D" and A move rightward to C', B', D' and A'. The distance of AA' is the decrement of minimum heating utility which can be calculated by Eq(21) and equals 7,060.67 kW.

With the same approach, the Source Composite Curve below the Pinch can be analysed, as shown in Figure 3. Consequently, A'B'D'C'DEH'F'G'I'J'K'L' is the Composite Curve when the conversion changes to 0.56. The unit energy consumption is 54.93 kW·min·mol⁻¹.

4. Conclusion

A graphical method is proposed to analyze the integration of the reactor and HEN of the selective hydrogenation process of benzene to cyclohexene. By this method, the relation of the inlet and outlet temperature of the reactor as well as the outlet temperature of coolant with the conversion can be studied respectively based on the mole balance and energy balance in CSTR. In this method, the deduced equation can clearly denote the relation among reaction temperature, the conversion and selectivity of benzene, and can be applied to construct the Conversion-Temperature-Energy Consumption Curve. The Combined Composite Curve and Conversion-Temperature-Energy Consumption Curve can visibly show the effect of the reactor conversion on the reactor temperature and the utility consumption of the HEN. In the studied process, the energy for cooling hydrogenation reactor accounts for 22.23 % of the cooling utility. When the conversion increases from 0.4 to 0.56, the unit consumption decreases from 68 kW·min·mol⁻¹ to 54.93 kW·min·mol⁻¹, accounting for 19.22 % of the unit energy consumption.

In this manuscript, the effect of conversion on the heat exchanger network is studied. Based on this, the effect of other reactor parameters can be analysed, and this will be studied in the future work.

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