Heat Integrated Pressure Swing Distillation for Separating Pyrolysis Products of Phenol Tar

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In order to separate phenol-acetophenone azeotrope in pyrolysis products of phenol tar, a process of heat integrated pressure swing distillation (PSD) is proposed for environmental protection and energy saving, where the overhead vapor of high-pressure column is taken as the heat source of low-pressure column reboilers. An activity coefficient model, i.e. universal quasi chemical (UNIQUAC), is chosen as the physical property method for simulation, the feasibility of PSD is studied by the thermodynamic analysis tool of ASPEN, and the pressure of each column was determined too. A general convergence strategy was proposed for PSD process simulation, which can also decouple the interaction between the convergence of recycle stream and the optimization of process parameters. To converge the heat integrated PSD process, a design specification was set to satisfy the mass balance requirement of the process. The simulation results show that 78,236 t/y condensate and 5,397 t/y steam are saved, and total annual cost is reduced by 9.4 % compared with conventional pressure swing distillation.

1. Introduction

Phenol tar is a by-product of the process of coking, petrochemical and phenol producing (Zou et al., 2013), which is a complex mixture of phenol, acetophenone, 4-cumylphenol, α-methylstyrene and other organics, as well as a small amount of salt and the coke with unknown structure (Gai et al., 2015). Phenol tar involved in this paper comes from the residue of distillation column's bottom when producing phenol with cumene.

The pyrolysis products of phenol tar include high value-added chemical products, such as phenol, acetophenone and α-methylstyrene (Schmidt, 2005). The pyrolysis methods of phenol tar mainly include thermal cracking (Dyckman, 2000), hydrocracking (Tao et al., 2011) and catalytic pyrolysis (Han et al., 2014). The products of pyrolysis include azeotropes of phenol-acetophenone, and α-methylstyrene-acetophenone. It is unfeasible to separate them by simple distillation (Luo et al., 2016). At present the existed methods for separating the pyrolysis products of phenol tar mainly include sodium salt method (Ye et al., 2016), pressure swing distillation (PSD) (Lqbal and Ahmad, 2016) and the combination of sodium salt method and PSD (Wang et al., 2016). Sodium salt method can separate the products well, while it has the disadvantages of large equipment investment and large amounts of waste water being produced. The PSD can be used to separate azeotrope whose azeotropic composition is obviously influenced by pressure without introducing impurities (Luyben, 2012), but the cycling stream between the high and low-pressure columns increases energy consumption of the process (Kiran and Jana, 2015). In order to decrease the energy consumption of conventional PSD process, the overhead vapor of the high-pressure column is taken as the heat source of the low pressure columns, so a heat integrated PSD process (Li et al., 2016) was proposed. According to the authors' best knowledge, it's the first time for the phenol-acetophenone being separated via the heat integrated PSD method, which is environmentally friendly and energy efficient. Because of the well-known coupling effect between the units of the PSD process, a general convergence strategy was proposed to simulate the process, which decouples the interaction between the process units and so each column's parameters can be optimized independently. Since the convergence strategy for the heat integrated PSD was rarely mentioned in the literature, the detail analysis for converging this complex and strong coupling process was discussed in this work too.

2. The separation of pyrolysis products of phenol tar

2.1 The pyrolysis products of phenol tar

A factory producing phenol from cumene produces 15,000 t/y phenol tar, whose product of catalytic pyrolysis contains cumene, α-methylstyrene, acetophenone, phenol, 4-cumylphenol, a little of unknown organics and residual viscous fuel oil. The light components such as α-methylstyrene and cumene are removed by a pre-distillation column from the product and sent back to phenol reactor (Ulyev et al., 2016), the bottom discharge of the column is taken as the feed in this paper, whose composition is obtained with high performance liquid chromatography (Wang et. al., 2004) and shown in Table 1.

Table 1: The feed information of the pressure swing distillation

Mass Flow (kg/h)	Temperature (K)	Pressure (MPa)	Component Mass Fraction			
			C_6H_6O	C_8H_8O	$C_{12}H_{10}$	$C_{15}H_{16}O$
462	402.93	0.05053	0.491	0.148	0.188	0.173

2.2 Pressure swing distillation separation

2.2.1 Feasibility analysis

Due to the high boiling point components contained in the feed, vacuum distillation should be selected to prevent coking. In order to analyze the feasibility of PSD, universal quasi chemical (UNIQUAC) was chosen as the physical property method (Simoni et al., 2008) and the azeotropic situations of phenol-acetophenone at different pressures were obtained through azeotrope search function of ASPEN, which is shown in Table 2.

Table 2: Azeotropic composition at different pressures

Pressure (MPa)	Azeotropic temperature (K)	Azeotropic composition (wt%)	
		C_6H_6O	C_8H_8O
0.005	385.21	28.51	71.49
0.01	401.82	25.45	74.55
0.02	420.55	21.28	78.72
0.03	432.69	18.15	81.85
0.04	441.92	15.54	84.46
0.05	449.48	13.26	86.74

It can be seen from Table 2 that the azeotropic composition changes more than 10 % when the pressure is changed from 0.005 MPa to 0.04 MPa, so the PSD is feasible (Zhang et al., 2016).

2.2.2 PSD process

Figure 1 shows the proposed process of recovering phenol and acetophenone by PSD under vacuum, where the information of feed stream, i.e. FEED in Figure 1, is listed in Table 1.
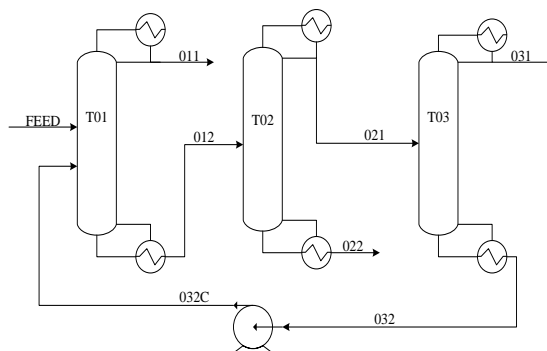

Figure 1: PSD process for the separation of phenol tar's catalytic pyrolysis products

Stream FEED is fed to the high-pressure column T01 whose top pressure is 0.04 MPa, the purity of phenol in its distillate is not less than 99 %. Other heavy components such as biphenyl, 4-cumylphenol and azeotrope of phenol-acetophenone are withdrawn from the column's bottom, i.e. stream 012, which enters to column T02 whose top pressure is 0.001 MPa. Heavy components in stream 012, such as biphenyl and p-cumylphenol are

withdrawn from the column's bottom, while phenol and acetophenone in stream 012 are distillated from T02, i.e. stream 021. The overhead discharge of T02 is fed to the low-pressure column T03 whose overhead pressure is 0.005 MPa. Acetophenone is recovered from T03's distillate, i.e. stream 031, where its purity is more than 99 % and phenol-acetophenone azeotrope at the column pressure is withdrawn from the column's bottom, i.e. stream 032, and sent back to the column T01.

2.2.3 Process simulation

The composition of the recycle stream 032 was chosen as the tear stream, whose composition is different with FEED of T01, so the flowrate of 032 influences the composition profile of column T01 when converging the tear stream. It is important to estimate an initial value close to its real value for 032. The theoretical tray number, i.e. N_T, and feed stage, i.e. N_F, of each column need to be determined before simulation. In the following, initial value of recycle stream flow, theoretical tray number and feed stage of each column will be determined.

The basic principle of PSD is to recover components in azeotrope from high and low-pressure column respectively via the difference in azeotropic composition at different pressure. According to this principle, boiling points of the components and azeotropic situations, the streams of the process shown in Figure 1 have following characteristics: (1) phenol in stream FEED is completely recovered from the distillate of column T01 and acetophenone from the distillate of column T03, (2) acetophenone in FEED, phenol and acetophenone in the recycled stream 032 must form an azeotrope at the overhead pressure of column T01, and (3) recycled stream 032 contains phenol and acetophenone only, whose composition equals to the azeotropic composition at the low pressure. Eq(1) can be listed according to the above characteristics.

$$\frac{F_{032} \cdot x_{LAZ,PH}}{F_{FEED} \cdot x_{FEED,AC} + F_{032} \cdot x_{032,AC}} = \frac{x_{HAZ,PH}}{x_{HAZ,AC}} \tag{1}$$

In the Eq(1), F_{032} and F_{FEED} are the flow rate of stream 032 and FEED, $x_{LAZ,PH}$ and $x_{LAZ,AC}$ represent the content of phenol and acetophenone in the low pressure azeotrope, $x_{FEED,AC}$ is the content of acetophenone in feed, $x_{HAZ,PH}$ and $x_{HAZ,PH}$ represent the content of phenol and acetophenone in the high pressure azeotrope respectively. According to the flow rate, composition of the feed and azeotropic composition at different pressures shown in Table 2, F_{032} is 103.89 kg/h by solving Eq(1). As the simulation converged, F_{032} is 108.11 kg/h, which is slightly larger than the calculated value, because stream 011 and 031 inevitably contain little heavy components.

The feed and separation requirements of each column are known through above calculation, therefore optimal N_T and N_F value for each column can be determined independently. In this paper, the following general method was proposed to optimize the parameters of each column, i.e. theoretical tray number, the feed stage and reflux ratio: (1) adjusting reflux ratio with the design specification of Aspen to satisfy the overhead product purity with different N_T and NF values, (2) with N_T fixed, find optimal N_F by sensitivity analysis of ASPEN, where optimal means the minimum energy consumption of the reboiler, thus the optimal value of N_F/N_T is obtained, and (3) with the calculator function of ASPEN, the value of N_F/N_T for each column can be fixed when varying N_T, then the sensitivity of reboiler duty to N_T was studied, and the optimal N_T is determined considering the investment cost. For feed stages of T01, optimal N_{F1}/N_T and N_{F2}/N_T, where N_{F1} and N_{F2} represent feed stage of stream FEED and 032C in Figure 1, are obtained by optimizing them sequentially and iteratively.

Table 3: The simulation and optimization results of the distillation columns

Column number	T01		T02	T03
Reflux ratio	1.1		2	2.2
Feed stage	16	23	30	25
Column diameter (m)	0.4		0.5	0.3
Theoretical tray number	60		60	90
Condenser duty (kW)	-68.19		-54.41	-25.26
Reboiler duty (kW)	82.97		40.24	27.94
Column top pressure (MPa)	0.04		0.001	0.005
Column overhead temperature (K)	424.6		349.82	381.26
Column bottom temperature (K)	457.64		396.7	385.19

3. Heat integrated pressure swing distillation

It can be seen from Table 3 that the overhead temperature of T01 is much higher than the bottom temperature of T02 and T03, and the condensing duty of T01 is also a little larger than the sum of reboiler duties of T02 and T03. So, a heat integrated PSD process was proposed, which is shown in Figure 2 and described below.
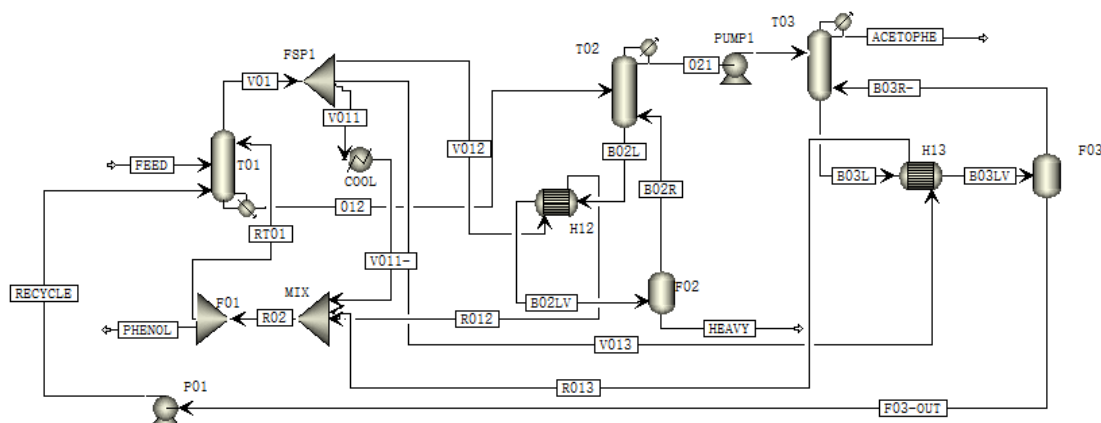

Figure 2: Diagram of heat integrated PSD process for separating the pyrolysis products of phenol tar

The overhead vapor of T01, i.e. stream V01, is divided into three-ply: stream V011, which is condensed directly with cooling water and represents the excess latent condensing heat of V01; stream V012, which exchanges heat with T02's bottom liquid, i.e. B02L, through heat exchanger H12 to produce a vapor-liquid mixture stream, i.e. B02LV, whose vapor part B02R return to T02's bottom tray and liquid part is taken as the bottom discharge of T02; stream V013 works in the similar way with V012. After V011, V012 and V013 are liquefied as V011-, R012 and R013, they are mixed as stream R02, which is split as the overhead product stream PHENOL and the reflux stream RT01 of column T01 respectively. The heavy components in the feed of the process are withdrawn as liquid discharge of flash unit F02, i.e. stream HEAVY, and acetophenone is withdrawn as stream ACETOPHE from overhead of T03. In the real-life process, unit F02 is not necessary because B02R and HEAVY can be withdrawn directly with heat exchanger H12 being a kettle reboiler.

It is obvious that the heat integrated PSD process shown in Figure 2 is complex and the coupling effect between the units is strong, which causes the convergence difficulty for simulation. To converge the process, RT01, B02R and B03R- are selected as the tear stream. The initial values of each tear stream are derived from the profiles of the conventional PSD process simulated in section 2.2.3, and then the tear streams are converged one by one. In order to avoid the influence of the flow rate change of tear stream during convergence iteration, a design specification was set in column T02 when converging stream B02R. The design specification adjusts the distillate rate to limit the content of phenol and acetophenone in the bottom discharge of T02, or the else the flowrate of feed of T02, i.e. stream 012, will vary with the flowrate of tear streams B02R which varies during the convergence iteration, so some phenol and acetophenone will be lost in the bottom discharge of T02 with the increment of flowrate of 012, then the flowrate of stream HEAVY will increase. If the distillate of all the columns and flowrate of stream FEED were fixed, then the calculated flowrate of tear stream B02R must be increased to satisfy the mass balance of the process during the iteration, so the process will not be converged, and vice versa with the decrease of flowrate of stream 012.

4. Results and discussions

With the mentioned strategy the process converged quickly, and the simulation results were shown in Table 4. To show the benefit of heat integrated PSD, the total annual cost (TAC) of PSD and heat-integrated PSD need to be calculated and compared in the Table 5. According to the literature (Wang et al., 2016), the price of condensate water and steam are set as $0.354·GJ^{-1} and $13.28·GJ^{-1} to calculate the operation cost of process, and the formulas for calculating investment cost of heat exchanger are $7,296*$(heat exchange area, m^2)$^{0.65}$ and $17,640*$(column diameter, m)$^{1.066}*$(column height, m)$^{0.802}$. The height of the column is calculated by the height equivalent of theoretical plate of the Mellapack 250Y structured packing used in the column, which is set as 0.5 m when designing. The TAC of the PSD and heat integrated PSD is calculated and shown in Table 6.

Table 4: Simulation results of the heat integrated PSD process

Material stream	Temperature (K)	Total flow rate (kg/h)	W (C6H6O)%	W (C8H8O)%	W (C12H1-01)%	W (C15H16O)%
FEED	402.934	462	0.491	0.148	0.188	0.173
V01	424.599	475.797	1	0	0	0
V011	424.599	2.871	1	0	0	0
V012	424.599	280.76	1	0	0	0
V013	424.599	192.166	1	0	0	0
V011-	424.599	2.871	1	0	0	0
012	457.492	301.89	0.064	0.383	0.288	0.265
021	350.143	135	0.142	0.858	0	0
022	396.515	166.89	0	0	0.521	0.479
031	381.34	68.54	0.004	0.996	0	0
RT01	424.599	249.227	1	0	0	0
R012	424.599	280.76	1	0	0	0
R013	424.599	192.166	1	0	0	0
R02	424.599	475.797	1	0	0	0
B02R	396.515	363.534	0.001	0.006	0.969	0.024
B03R	385.211	202.915	0.285	0.715	0	0
B02L	387.749	530.424	0.001	0.004	0.828	0.167
B03L	385.211	269.375	0.285	0.715	0	0
B02LV	396.515	530.424	0.001	0.004	0.828	0.167
B03LV	385.211	269.375	0.285	0.715	0	0
F03-OUT	385.211	66.460	0.285	0.715	0	0
PHENOL	424.599	226.57	1	0	0	0
RECYCLE	385.286	66.46	0.285	0.715	0	0

Table 5: Objective functions and necessary parameters for economical evaluation

Parameters	Data
Heat transfer coefficient	Condenser :0.852 kW/(m^2 *K)
Heat exchanger cost	Reboiler: 0.568 kW/(m^2*K) C = 7,296*(A, m^2)$^{0.65}$
Column vessel cost	C = 17,640*(D, m)$^{1.066}$*(H, m)$^{0.802}$
TAC	TAC = total capital cost/ payback period + annual energy cost
Payback period	3 y

Table 6: TAC comparison of PSD and heat-integrated PSD

	Conventional PSD			Heat integrated PSD		
	T01	T02	T03	T01	T02	T03
Condensate consumption (t/y)	78,711	62,835	28,906	475	62,835	28,906
Steam consumption (t/y)	6,568	3,185	2,212	6,568	0	0
Heat transfer area (m^2)	3.09	2.88	0.80	2.03	2.32	0.62
TAC ($.y^{-1})		269,248			243,947	

The advantages of heat integration can be seen from Table 5, where the consumption of condensate for high pressure column, i.e. T01, has saved 78,236 t/y, because its overhead vapor is mostly condensed by the bottom liquid of T02 and T03; the steam for low pressure columns, i.e. T02 and T03, has saved 5,397 t/y. The area of heat exchange has been saved with 1.06 m^2, because most of the heat exchange area for column

T01's condenser has shift to the reboiler of T02 and T03, this result shows that the equipment cost can also be reduced via heat integration. At last TAC has been reduced with 9.4 % for the entire process because of the saving of energy and equipment cost.

5. Conclusion

In this paper, the separation of pyrolysis products of phenol tar with heat integrated PSD is proposed, which avoids the salty waste water produced by sodium salt method and the high energy consumption of conventional PSD, while the purity of phenol and acetophenone products are not less than 99 %. The convergence strategy for PSD with strong coupling effect in is given, and the columns' parameters can be optimized with sensitivity analysis independently based on the strategy. When simulating the heat integrated PSD, a design specification was set to satisfy the mass balance requirement of the process. Compared with the conventional PSD process, due to heat integration of high pressure column and low-pressure columns, heat integrated PSD is more energy efficient and economical and the total TAC is reduced by 9.4 %.

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