

Research on phenol wastewater treatment by low-temperature multi-effect distillation combining with super-critical water oxidation

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Abstract. Based on the mechanism of low-temperature multi-effect distillation combining with super-critical water oxidation (LT-MED&SCWO), a system that disposes phenol wastewater is introduced. Establishing a process of four-effect forward feed LT-MED concentrated phenol waste-water and a SCWO degradation of phenol by Aspen Plus software is essential to compare the effects of in-feed phenol mass concentration, system concentration ratio on phenol concentration ratio and mixing temperature of reaction required for degradation. The study shows that with the increase of in-feed phenol mass concentration, phenol concentration ratio keeps almost constant, 97.7%, but, preheating temperature of the concentrated water decreases when the final product mass phenol concentration is less than 0.5ppm; when system concentration ratio increases, phenol concentration ratio decreases from 99.5% to 96.7% and preheating temperature of the concentrated water also decreases when the final product mass phenol concentration is less than 0.5ppm.

1. Introduction

Phenol-containing wastewater is a common and harmful wastewater, which has the characteristics of refractory degradation, wide source and high damage. Phenolic substances in phenol-containing wastewater have the potential toxicity of carcinogenic, teratogenic and mutagenic, and it will cause great harm to human body, aquatic organisms and agriculture. Traditional phenol-containing wastewater treatment methods, such as physicochemical, biological, incineration, have many disadvantages like high cost, low degradation rate, and easy secondary derivation [1].

LT-MED which the heat sources of every evaporator are the secondary steam(SS) produced by the front evaporator except first-effect evaporator requiring external heat source, uses vacuum technology to reduce the boiling point of wastewater. Wastewater is separated into the concentrated water(CW) of



high-salt, high-concentration organics and the evaporated water(EW) of low-concentration organics as much as possible by regulating the working conditions of LT-MED. The EW containing a trace of organics is treated by appropriate measures to achieve discharge [1]. SCWO, a method for oxidatively degrading organics by using oxygen under the conditions of high temperature and high pressure ($P_c=22.1\text{MPa}$, $T_c=374^\circ\text{C}$), degrades the organics of the CW. The higher in-feed phenol mass concentration, the lower mixing temperature of reactor which the organics is completely degraded [2]. In this paper, phenolic wastewater is treated by LT-MED & SCWO to concentrate and degrade. At the same time, the high-temperature flow produced by the SCWO part is used as heat source which preheats the CW and the transpiring water 1, and reheats external heat source water required by first-effect evaporator for reducing system energy consumption and achieving energy self-sufficiency.

2. Process description

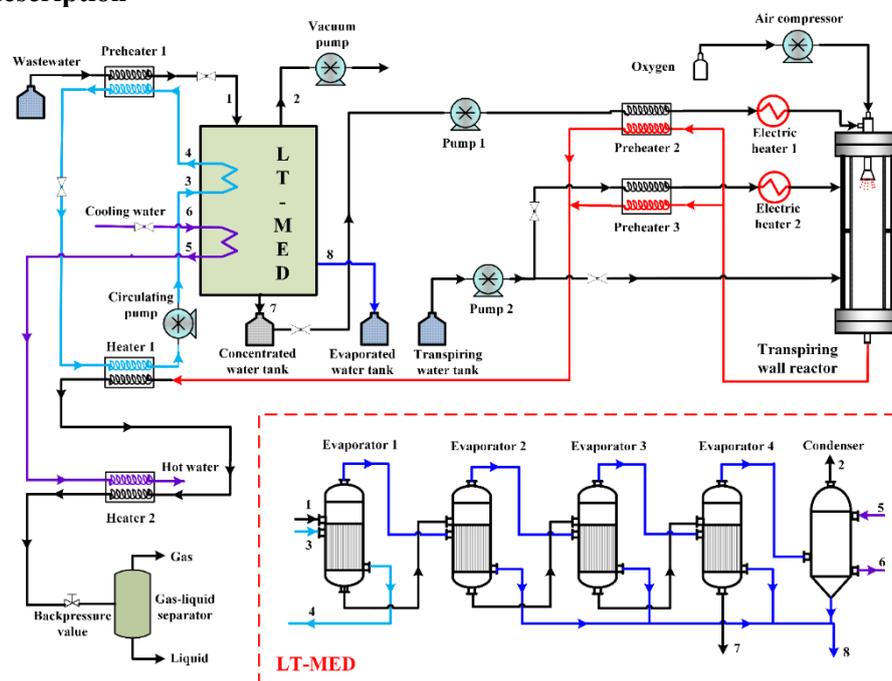


Figure 1. The diagram of the LT-MED&SCWO pilot plant

The diagram of LT-MED&SCWO system to treat phenol wastewater is shown in Figure 1. It mainly consists of 6 parts: the concentrated and oxidized wastewater system, the secondary steam system, the transpiring water system, the heat recovery system.

The concentrated and oxidized wastewater system: wastewater is firstly preheated by Preheat 1, then depressurized by Vacuum pump, and flows into Evaporator 1 to be heated and evaporated, generating the SS and the CW of first-effect under the condition of four-effect forward feed LT-MED. The SS1 enters Evaporator 2 as heat source, and then condenses to liquid, finally flows into the EW tank. The CW1 enters Evaporator 2 to be heated and evaporated. Three-effect process are similar to second-effect. Final-effect is carried out in Evaporator 4 and the SS4 is condensed by Condenser. Last, the CW in the CW tank is pressurized to 23 MPa by Pump 1, then flows into Preheater 2 and Heater 1 in succession, finally is oxidized in the transpiring wall reactor

The secondary steam system: the SS generated by the front effect is used as heat source required by next effect evaporator except Evaporator 1, and then condensed and collected into the EW tank.

The transpiring water system: the transpiring water(TW) is pressurized to 23 MPa by Pump 2, and then divided equally into two flows(TW1 and TW2). TW1 is preheated by Preheater 3, and heated by Heater 2, then flows into the transpiring wall reactor. TW2 directly flows into the subcritical section of the transpiring wall reactor.

The heat recovery system: it comprises two parts. The first one is reheating the heat source water required by LT-MED. After high-temperature fluid produced by the SCWO part preheats the CW and the TW, and then flows into Heater 1 to reheat external heat source. The second one is heating the cooling water by Heater 4 as hot water gain.

3. Process simulation

3.1. Kinetics of the transpiring wall reactor

The reaction kinetics adopts Thomas D. Thornton and Phillip E.Savage's [4]. The preheating temperature range of the cw is 300-420°C, and the pressure range is 18.8-27.8 MPa. The power exponential equation for the phenol's degradation reaction rate is shown:

$$r_{C_6H_5OH} = -\frac{d[C_6H_5OH]}{dt} = 303 \cdot \exp\left(\frac{-51.8816 \text{ kJ/mol}}{RT}\right) [C_6H_5OH]^1 [O_2]^{0.5} [H_2O]^{0.7} \quad (1)$$

3.2. Establish simulation process

The physical method of LT-MED selects NRTL according to the water-phenol gas-liquid equilibrium data [3]. The physical method of SCWO selects PRMHV2 [5]. The simulation process is presented in figure 2. Various process flow modules are shown in Table 1. The model parameters are consistent with the reference parameter settings in order to verify the accuracy and reliability of the model [6].

Table 1. Model units of simulation process

Aspen Plus	System
Heater	Electric heater 1, Electric heater 2
HeatX	Preheater 1, Preheater 2, Preheater 3, Heater 1, Heater 2, Condenser
HeatX+Flash2	Evaporator 1, Evaporator 2, Evaporator 3, Evaporator 4 [10]
Pump	Pump 1, Pump 2, Circulating Pump
Value	Vacuum pump [11]
Mixer+ RPlug Reactor+ Mixer	The transpiring wall reactor[12]

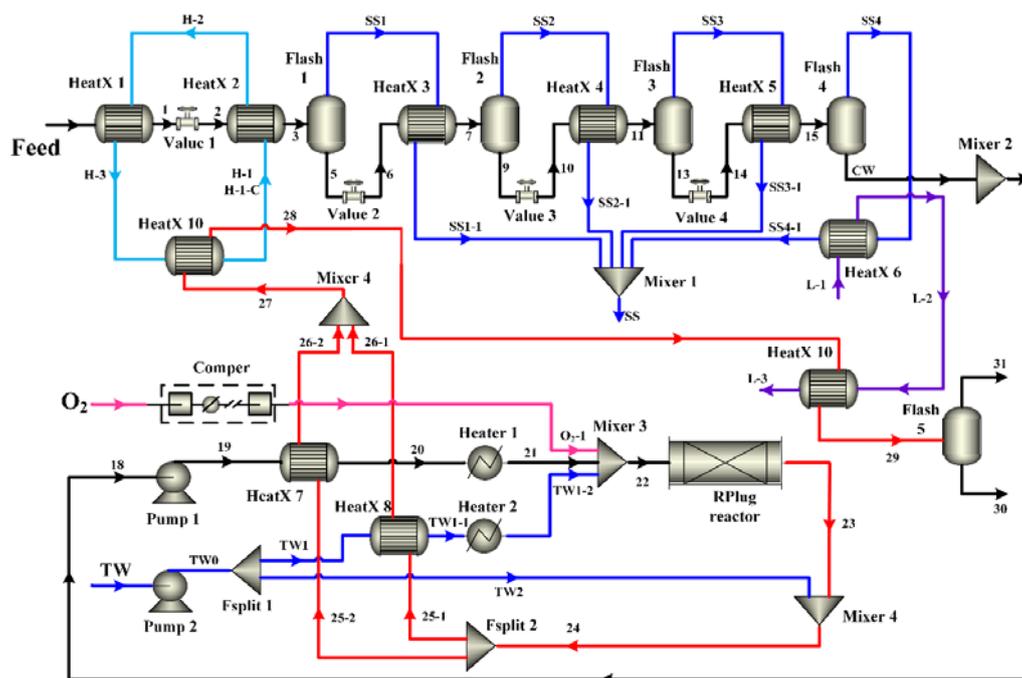


Figure 2. Aspen Plus model for LT-MED&SCWO process

3.3. Model verification

The model process for the SCWO treatment of phenol wastewater system is mature and has high accuracy and reliability. The LT-MED system is mostly used for desalination of seawater, and there are few processes for treating wastewater. Therefore, the model of LT-MED needs to be verified. A comparison between simulation results and reference data is summarized in Table 2. The reference has fresh water accumulation of 2848.54kg/h, Aspen plus simulated the EW of 2815.5kg/h, and the deviation is less than 2%. It can be considered that the LT-MED wastewater treatment model established by Aspen Plus software is credible.

Table 2. Parameters and results for reference and simulation.

Parameters		HeatX 1	HeatX 2	HeatX 3	HeatX 4	HeatX 5	HeatX 6
Heat duty (kw)	Simulation	195.38	404.62	404.62	453.488	502.341	551.179
	Reference	193.728	404.62	404.563	448.729	488.151	522.491
Exchanger area (m ²)	Simulation	/	21.7551	30.9984	36.0139	41.6525	26.8598
	Reference	19.4987	21.8388	31.1276	35.7938	40.6185	25.2042
Mass flow of the SS (kg/h)	Simulation	/	617.858	681.663	744.026	804.994	/
	Reference	/	616.871	680.188	735.626	782.815	/

4. Operational parameters analysis

In this paper, the effect of in-feed phenol mass concentration and system concentration ratio on preheating temperature was studied, which provided a theoretical basis for the optimization of the subsequent system.

4.1. In-feed phenol mass concentration

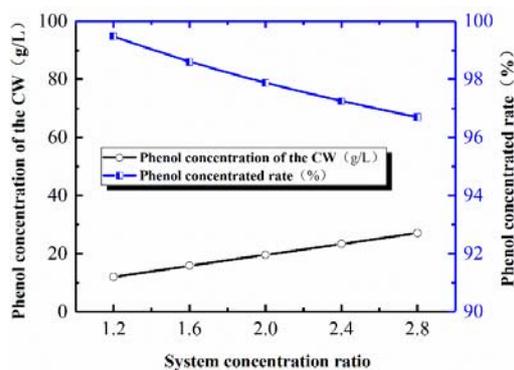


Figure 3. The effect of in-feed phenol mass concentration on phenol concentration of the CW, phenol concentration rate.

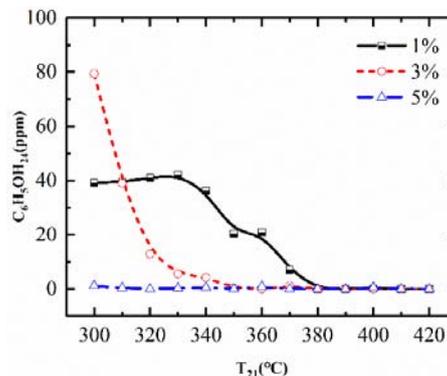


Figure 4. The effect of T21 on C6H5OH24 when in-feed phenol mass concentration is 1%, 3%, 5%.

As shown in Figure 3, the phenol concentrated rate was basically unchanged at 97.7%, and the phenol concentration of the CW was increased from 19.57 g/L to 97.72 g/L with in-feed phenol mass concentration increasing. Under the condition of certain concentration ratio, in other words, the flow of the EW is unchanged, the amount of phenol volatilization is increased owing to the phenol content in the EW is increased, resulting in a decrease in the phenol concentrated rate. As shown in Figure 4, when phenol concentration of feed is 1%, preheating temperature of the CW should be higher than 380°C to completely degrade the phenol in the CW; when the phenol concentration of feed is 3%, preheating temperature of the CW should be higher than 350°C; when the phenol concentration of feed is 5%, preheating temperature of the CW should be higher than 310°C.

4.2. The system concentration ratio

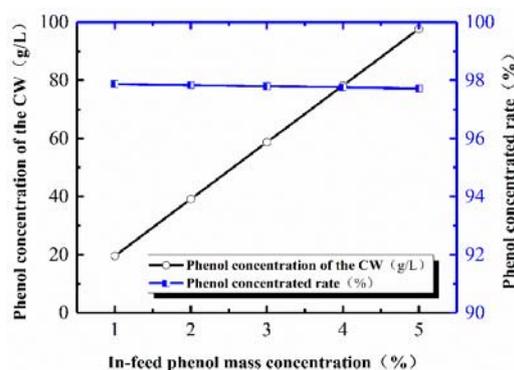


Figure 5. The effect of system concentration ratio on phenol concentration of the CW, phenol concentration rate.

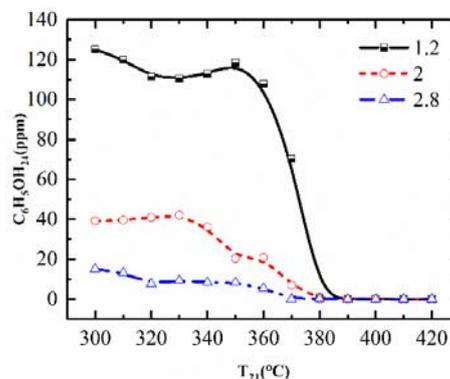


Figure 6. The effect of T21 on C₆H₅OH₂₄ when system concentration ratio is 1%, 3%, 5%.

As shown in Figure 5, with system concentration ratio increasing, phenol concentration of the CW is increased from 11.94 g/L to 27.08 g/L, and phenol concentrated rate is decreased from 99.5% to 96.7%. Increasing concentration ratio causes more wastewater to evaporate into the SS so that phenol concentration of the CW is increased, more phenol is volatilized to the SS to reduce the phenol concentration ratio. As shown in Figure 6, when system concentration ratio is 1.2, preheating temperature of the CW needs to be higher than 390°C to completely degrade phenol; when system concentration ratio is 2, preheating temperature of the CW needs to be higher than 380°C; when system concentration ratio is 2.8, preheating temperature of the CW should be higher than 370°C.

5. Conclusion

(1) Increasing the phenol concentration of feed, the phenol concentration rate was basically unchanged at 97.7%, the preheating temperature of the CW required to completely oxidize the phenol was reduced from 380°C to 310°C.

(2) Increasing the concentration ratio, the phenol concentration ratio decreases from 99.5% to 96.7%, the preheating temperature of the CW required to completely oxidize the phenol decreases from 390°C to 370°C.

(3) The higher the phenol concentration of the CW, the lower the reactor mixing temperature required for complete oxidative degradation of phenol.

Acknowledgments

This work is supported by National Natural Science Foundation of China (Grant No. 51506014), the Fundamental Research Funds for the Central Universities(Grant No. 2018CDQYDL0052, 106112016CDJXY145501), the Chongqing Research Program of Basic Research and Frontier Technology (Grant No. cstc2016jcyjA0486), the China Postdoctoral Science Foundation (Grant No. 2016M592638, 2017T100677), the National Key Basic Research Program of China (Grant No. 2014CB239200) and the Chongqing Postdoctoral Research Program(Grant No. 2016073).

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