Extraction selection and process optimization of phenol-containing wastewater from coal chemical industry

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Abstract—In order to efficiently remove phenolics from coal chemical wastewater, this study utilizes molecular simulation to determine the most effective extractant. And the extraction effect is verified through simulation results. The energy of hydrogen bonding dominates the extractant's extraction ability. The interaction between phenols the and solvent was examined using molecular simulation calculations, and it was discovered that the strong H-bond interaction between the CYC/1-PA synergistic extractant and phenols produces outstanding extraction effects. The results of the full process simulation validation showed that the CYC/1-PA synergistic extractant could properly treat the wastewater.

1. Introduction

In the past years, China's coal supply has grown rapidly yearly, accounting for more than 65% of primary energy consumption [1]. At the same time, the wastewater produced by the coal chemical industry has also increased, which aggravated environmental pollution and water shortage. The environmental pressure has forced us to improve waste recycling, separate and recoup valuable resources, and reduce pollution generation and emissions [2]. Currently, ammonia, nitrogen, and phenolics are among the main contaminations in coal chemical wastewater, which seriously impair the growth of surface flora and fauna and even threaten adrinking water safety [3]. In view of the continuous production of the coal-chemical industry, strict water quality targets must be established. So as to pursue the goal of zero discharge of wastewater and realizing clean production.

Physical, chemical, and biological treatments are the most prevalently used technologies for managing phenol-containing wastewater. Yet, solvent extraction is the most cost-effective means of removing phenols since coal chemical effluent contains phenolics in huge amounts and at elevated levels. To improve the extraction rate, the development of new phenolic extractants is a more cost-effective approach. While methyl isobutyl ketone (MIBK) [4] is the current industrial extractant, newly developed extractants such as methylene oxide (MO) [5], methyl propyl ketone (MPK) [6], and cyclohexanone (CYC) [7] also have better extraction effects. In particular, the extractant of CYC has shown excellent performance on phenols, with less toxicity and lower cost compared to commonly used organic solvents. However, the effectiveness of these single solvents for dihydrophenols can still be improved. Synergetic extractants have thus been developed in recent years, greatly enhancing extraction efficiency. This paper utilizes molecular simulation to compare the interactions between CYC, MIBK, CYC/l-pentanol(1-PA), and MIBK/1-PA with phenol and hydroquinone, screening for the CYC/1-PA synergistic extractant with superior extraction effects. The selected extractants were validated through full process simulation with Aspen Plus software, optimizing for the lowest TAC while meeting design specifications.

2. Solvent selection

In order to analyze the interaction between the extractant and phenols, hydroquinone, Gaussian 09 software [8] was used to calculate the structure and energy. Taking into account variables like computation precision, calculation volume, and laboratory resources, the optimized structure were implemented at the B3LYP/6-311g(d,p) level. The interaction energy of the optimized configuration was calculated at the B3LYP/6-311++g(d,p) level, and the basis set superposition error (BSSE) was corrected by the equilibrium process technique [9]. And the chromatic dispersion need to be taken into account to enhance the exactitude of the density functional calculations.

The interaction between extractants with phenols in the molecular can affect the effect of removing phenols in wastewater. Interaction energy simulations were done to examine the interaction between extractants and phenols. Following the E_{BSSE} corrections, the system's interaction energy is determined, as shown in Eq. (1),(2):

$$\Delta E_{\text{int}}^{2} = E_{AB} - E_{A} - E_{B} + E_{BSSE} \quad (1)$$

$$\Delta E_{\text{int}}^{3} = E_{ABC} - E_{A} - E_{B} - E_{C} + E_{BSSE} \quad (2)$$

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According to Eq. (3), the following is the formula for generating the EBSSE corrective energy:

$$E_{BSSE} = (E_A - E_{AE}) + (E_B - E_{BE}) + (E_C - E_{CE}) \quad (3)$$

E^2_{int} and E^3_{int} represent the interaction energy between single extractant, synergistic extractant and phenols molecules.The E_{BSSE} formula eliminates the energy generated by monomer overlap, which reduces the energy between the extractant and the phenolic compound. So as to accurately and reasonably acquire intermolecular interaction. The interaction energies of MIBK, CYC, MIBK/1-PA and CYC/1-PA with phenols and hydroquinone are given in Table 1. The results indicates that CYC is an effective solvent for dephenolization, while the synergistic extractant comprising CYC and 1-PA exhibits optimized extraction efficiency due to their synergistic interaction.

Table 1. Interaction energy between extraction solvents and phenolics.

System	BSSE Corrected energy (kJ·mol^{-1})	Uncorrected interaction energy (kJ·mol^{-1})	Corrected interaction energy (kJ·mol^{-1})
MIBK/phenol	2.94	-30.07	-27.13
CYC/phenol	3.18	-68.68	-65.50
MIBK/1-PA/phenol	4.84	-78.08	-73.24
CYC/1-PA/phenol	3.55	-127.68	-124.13
MIBK/hydroquinone	4.66	-24.09	-19.43
CYC/hydroquinone	2.94	-58.24	-55.30
MIBK/1-PA/hydroquinone	4.82	-74.66	-69.84
CYC/1-PA/hydroquinone	4.05	-119.34	-115.29

3. Simulation and optimization of coal chemical wastewater dephenolization process

3.1 Process Simulation

The interaction energy calculation of extractant and phenols was used to screen the CYC/1-PA synergistic extractant with superior extraction effects. Aspen Plus software was used to simulate the entire process of the synergetic extractant for phenols removal in order to further investigate the extractant's performance. The wastewater dephenolization process is shown in Fig.1, involves treatment through a extraction tower (T01), solvent recovery tower (T02), and stripping tower (T03). The phenol-containing wastewater is pre-separated through T01, the synergetic extractant CYC/1-PA is introduced from the bottom of the tower in counter-current contact with the phenol-containing wastewater entering from the top. The extraction phase flows out from the top of the tower into T02 to further separate the phenols in the extraction phase, where the crude phenols product is extracted from the T02's base up and the synergetic extractant is separated from the phenols. The extractant is then extracted from the top of the T02 and returned to T01. The residual phase from T01 enters T03 to vaporize the residual extractant and water mixture. The extractant and water pass through the oil and water phase separator to separate the extractant as the oil phase, which is then recycled to T01.

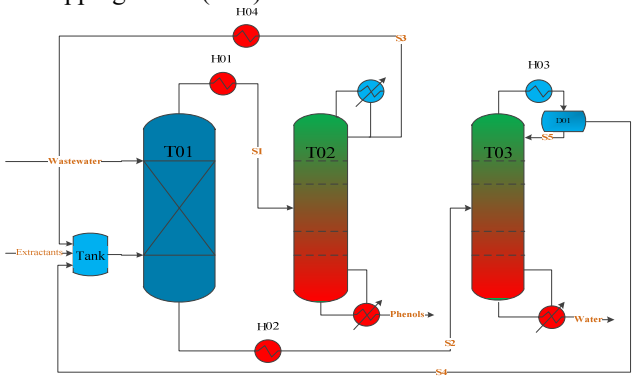
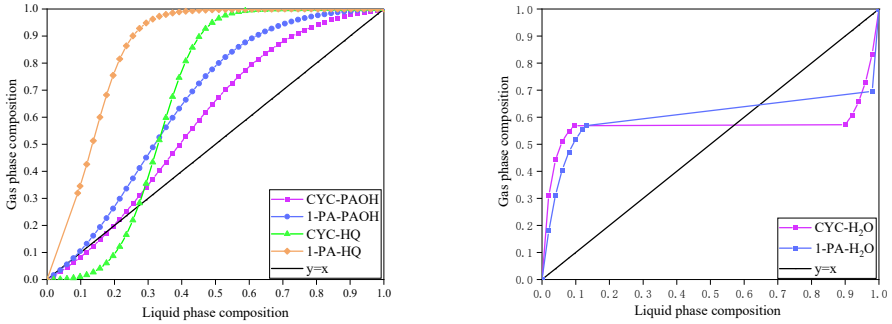


Fig. 1 Process flow chart of synergistic extraction dephenolization

3.2 Selection of thermodynamic model

The selection of an accurate and trustworthy thermodynamic model is crucial when conducting chemical process simulation. In this study, the thermodynamic model employed was the UNIQUAC model. Some thermodynamic parameters were obtained through data regression of CYC/phenol/water by Wang

[10] and Cai [11]et al. , while other unmeasured parameters were sourced from the Aspen Plus user manual. Fig.2 illustrates the vapor-liquid phase equilibrium curves of the synergetic extractant/phenols. In the solvent recovery tower, the vapor-liquid equilibrium curves of the synergetic extractant and phenols reveal that the relative volatilities between extractants and phenols are all greater than 1. Hence, the synergetic extractant and crude phenols can be effectively separated in the solvent recovery tower. The vapor-liquid equilibrium curves of the vapor extraction tower synergistic extractant and water demonstrate that CYC/water and 1-PA/water form binary azeotropes in the vapor extraction tower, allowing for easy separation of extractant and water through simple distillation. With the relative volatility curves established, the design of the solvent vapor extraction tower can be determined based on the separation requirements.

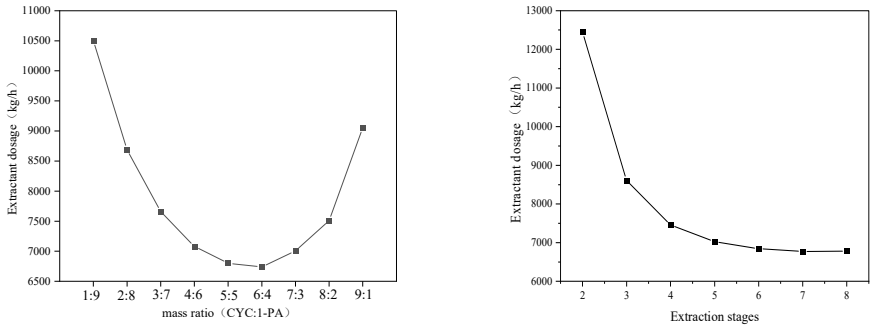


(a) Solvent recovery tower (b) Stripping tower

Fig.2 Vapor-liquid equilibrium curve of the synergistic extractant and phenols

3.3 Result and discussion

When the total phenols concentration of the raffinate phase was lowered to 50 ppm in order to maximize the amount of extractant, the relationship between the mass ratio of the synergistic extractants in the extraction tower, the extraction stage, and the quantity of extractant was investigated, as shown in Fig. 3. The optimization results in Fig.3(a) showed that the amount of extractant reached the minimum when the mass ratio of synergistic extractant (CYC:1-PA) was 6:4. As depicted in Fig.3(b), increasing the number of extraction stages and the amount of extractant can reduce the concentration of phenolics. However, this comes at a higher energy consumption and cost. Notably, when the number of extraction stages n=4, the amount of extractant is significantly reduced.



(a) Mass ratio of synergistic extractant (b) Extraction stages

Fig.3 Relationship between mass ratio of synergistic extractant, extraction stages and amount of extractant

After determining the mass ratio between synergetic extractants and the number of extraction stages, the ratio of extractant to phenol-containing wastewater was further determined. The mass fraction of different compared phenolic substances at different extraction stages in Fig.4 indicates that the number of extraction stages and the amount of extractant is relatively suitable when compared to 1:13. This approach can reduce energy consumption while ensuring that the amount of extractant will not grow too much.

The effects of the number of towers and feed position of T02 and T03 on TAC were investigated under constant feed conditions, and the analysis and optimization of parameters were carried out; The impacts of the T02 and T03 tower parameters on TAC are shown in Figs. 5 and 6, separately. According to Fig. 5, the TAC of T02 exhibits a tendency of first falling and then increasing as the number of plates rises., and the TAC results are optimal when plate number N_{T02}=28. This is because the required heat load is too large when the number of plates is small, and the same heat load cannot meet the separation requirements, and the heat load is too large to cause the TAC to increase.And the TAC tends to increase continuously with the increase of the feed plate of the T02, and the optimal result of TAC is obtained at feed plate NF_{T02}=4. As shown in the Fig.6,

with the increase of the number of stripper plates, TAC shows a decreasing trend, because the equipment's input cost will rise as the number of plates rises, so the TAC results are optimal when N_{T03}=14. And the TAC is the smallest,when NF_{T03}=1.

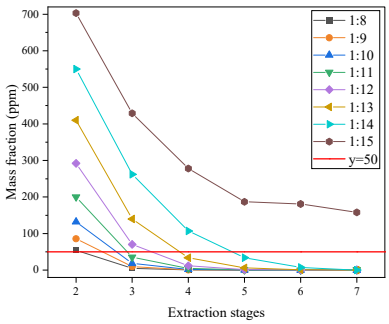


Fig.4 The mass fraction of phenols at different phase ratios under different extraction stages

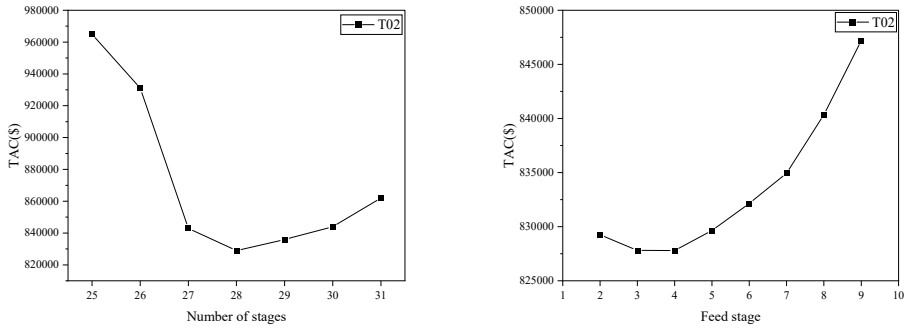


Fig.5 The relationship between the number of stages , the feed stage and TAC of the solvent recovery tower (T02)

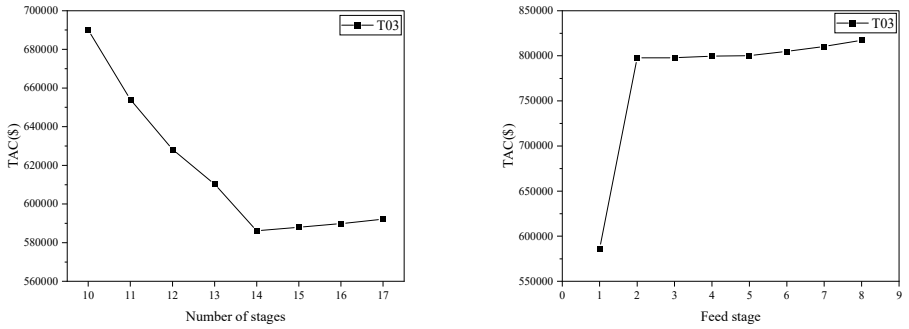


Fig.6 The relationship between the number of stages , the feed stage and TAC of the solvent recovery tower (T03)

4. Conclusion

The CYC/1-PA synergistic extractant with strong interaction was screened by molecular simulation and used as the best extractant for the extraction and dephenolization process to perform full process simulation and optimization to verify the extraction effect. The simulation and optimization of the dephenolization process determined that the number of extraction stages was 4, and the ratio of CYC to 1-PA was 6:4, compared with 1:13; When N_{T02}=28, NF_{T02}=4, N_{T03}=14, NF_{T03}=1, TAC is optimal. The removal rate of phenol reached 99.98%, and the polyphenol had a 96.94% removal rate, which reached the extraction standard. The results show that CYC/1-PA synergistic extractant has a good treatment effect. Not only the extractant dosage is less, and the extraction rate of phenols is high, but also the TAC is reduced, which has a good economy.

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