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Optimal Design of Solvent Blend and Its Application in Coking Wastewater Treatment Process

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S Supporting Information

ABSTRACT: One of the key steps of coking wastewater treatment is phenolic and tar removal via extraction. However, the high loss of the extractant, i.e., methyl isobutyl ketone (MIBK), leads to the high cost of the process. The adoption of a novel solvent or solvent blend is considered as an efficient way to address this problem. In this paper, seven solvents (benzene, toluene, m-xylene, ethylbenzene, 1, 3, 5-trimethylbenzene, cyclohexane, and octanol), selected as candidate diluters for MIBK according to operating requirements, are studied with a nonlinear programming (NLP) model based on ideal counter-current extraction. The results, verified with experiments, suggest toluene is the most promising candidate. Further investigation of this solvent blend reveals that both D_{blend} (the distribution coefficient of phenol between solvent blend and water) and m_{MIBK} (the MIBK concentration in raffinate) increase with x_{MIBK} (the molar fraction of MIBK in blend). The trade-off between the extraction performance and MIBK loss recommends the blend with $x_{\text{MIBK}} = 0.05$ as extractant for coking wastewater treatment. An industrial process consisting of extraction, back stripping, distillation, and mixer is presented. A corresponding NLP model is established for its operating optimization. To improve the accuracy, the representatives of typical phenolics and tar in wastewater (2,4 dimethyl phenol, m-xylene, and quinolone) are also considered in addition to phenol. The case study indicates that the blend exhibits economic advantage over pure MIBK with a makeup cost of 11.15 ¥/t, much less than the 185.15 ¥/t in the case of MIBK.

1. INTRODUCTION

Coking wastewater, mainly discharged from coking plants and oil refining plants, comprises complex inorganic and organic contaminants such as phenolic compounds, polynuclear aromatic hydrocarbons (PAHs), polycyclic nitrogen-containing aromatics, ammonia- and sulfur-containing heterocyclics, and acyclic compounds.^{1–3} As most of these compounds are highly concentrated and hazardous to the environment, discharging with improper treatment might bring about severe environmental impacts.⁴ Its treatment is still considered to be one of the most challenging pollution control tasks. Because coal is one of the main energy sources in China, which witnessed the rapid development of coal-related chemical industry and steel production in the contemporary era, a sustainable and economic treatment process is of great significance.⁵

Liquid–liquid extraction (LLE) for phenolic and tar removal is one of the key units pervasively applied in the conventional coking wastewater treatment process. In the last decades, numerous solvents (octanol,⁶ diisopropyl ether (DIPE),⁷ methyl isobutyl ketone (MIBK),⁸ tributyl phosphate (TBP),⁹ methyl *tert*-pentyl ether (TAME),¹⁰ etc.) were investigated and assessed as potential extractants for the removal of phenolics from wastewater, and corresponding LLE processes were proposed, simulated, and optimized.^{6,7,11} Among these solvents, MIBK was comprehensively studied and proved effective and efficient in the extraction of both monophenolics and polyphenolics from water, especially at high concentration of phenolics.¹² It was also reported that MIBK had been inclusively employed in industrial practice, with the accomplish-

ment of the simulation and optimization of the extraction process.^{7,11}

However, the major drawback of MIBK is its high solubility in water (19 g/L at 25 °C) as well as its high price, implying the requirement of an extra energy-intensive stripping column, which discouraged its application.¹³ Regarding this problem, there are generally two solution approaches: (i) complete replacement of MIBK with a novel solvent or solvent blend and (ii) introducing additional solvent as diluter for MIBK to reduce its loss with the guarantee of extraction performance. For the first option, one of the systematic approaches of developing novel solvent is computer-aided molecular design (CAMD),¹⁴ a reverse engineering procedure which generates molecules that conform to various physical property requirements with specified structures.¹⁵ Although a plethora of algorithms has been proposed recently, there is still no particular algorithm that could tackle all the possible sophisticated molecules both effectively and efficiently.^{16,17} Nevertheless, CAMD merits further study in discovering an algorithm in high accuracy with minimum expenditure of time and effort. The other is the blending of the existing compounds based on primary structure theory, which proves much more effective and efficient, though a bit heuristic.^{18–20} Various achievements have been published, for instance: ABK, QH-1,

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developed by Qinghua University,²¹ and octanol with DIPE.¹⁸ Though some investigations have been carried out to analyze the extracting performance of MIBK with different solvents, systematic study for the selection of diluter and the performance of solvent blends are still absent.²² Thus, a study is carried out to find out a novel solvent blend for coking wastewater treatment in this paper via the second option.

To evaluate the performance of the designed solvent blend, the modeling and optimization of the corresponding LLE process is required. However, the complicated species contained in coking wastewater and the computational complexity make it impossible to take all the constituents into account.²³ Much of the work just choose phenol to represent all the contaminants in wastewater, which accounts for more than 70% (by wt.) of the organics in wastewater.³ This simplification works well for most of the studies with experimentations. However, the industrial coking wastewater contains many other species such as naphthalene, quinoline, pyridine, and indole, which are the main constituents of tar.^{3,7,24} These species behave differently against phenolics in the extraction and solvent recovery unit of the process. This issue presents a challenge for the current modeling of coking wastewater treatment process. The octanol–water partition coefficient (KOW) value was widely used for the estimation of the solubility of a compound in water and ground in the environmental industry.²⁵ Some researchers discovered that there is correlation between KOW and the distribution coefficient of phenolics between water and extractant.^{26,27} Therefore, the contaminants in coking wastewater could be grouped according to their KOW values and other properties. This compromising approach might improve the accuracy of modeling and calculation of industrial process with minimum component consideration.

In the current work, the design of the solvent blend is carried out via a nonlinear model (NLP) model, followed by experimental verification and discussion of corresponding results. In addition, a general treatment process of industrial coking wastewater containing phenolic and tar via extraction is presented and a corresponding model is proposed for its operating optimization. With the representative components determined by KOW values, a case study is conducted to compare the performance between the designed solvent blend and pure MIBK. In the last section, discussions and conclusions are presented.

2. OPTIMAL DESIGN OF THE SOLVENT BLEND

In this section, a NLP model based on the ideal extraction column assumption will be established for the evaluation as well as the composition optimization of potential solvent blends. Several solvents meeting the criteria will be assessed with the model to find out the most promising candidate, and simultaneously its composition will be determined.

2.1. NLP Model for Solvent Evaluation. As noted in the Introduction, a third solvent will be added to MIBK to reduce its loss with the assurance of extracting performance. Thus, the concentration of the solvent blend, including MIBK and solvent candidates, in the raffinate is set as the objective function. Outlet-discharging requirement for the specific components must be met, which is defined as constraints. Moreover, an ideal counter-current extraction column is assumed, wherein components in two phases achieve equilibrium at each theoretical stage, as depicted in Figure 1, which mainly consist

of material, equilibrium, and summation (MES) equation and are also considered as the constraints for the NLP model.

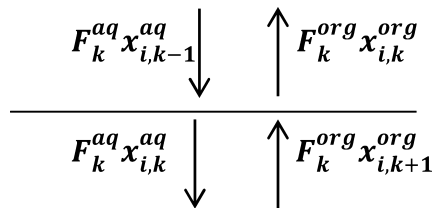


Figure 1. LLE at stage k of the column.

Hence, the NLP model for potential solvent evaluation can be expressed as

$$\begin{aligned} \min Z &= m_{\text{MIBK,out}}^{\text{aq}} + \sum_s m_{(i,\text{out})}^{\text{aq}} \\ \text{s.t. } m_{(i,\text{out})}^{\text{aq}} &\leq m_{(i,\text{out,require})}^{\text{aq}} \\ F_k^{\text{org}} + F_k^{\text{aq}} &= F_{k+1}^{\text{org}} + F_{k-1}^{\text{aq}} \\ F_k^{\text{org}} x_{i,k}^{\text{org}} + F_k^{\text{aq}} x_{i,k}^{\text{aq}} &= F_{k+1}^{\text{org}} x_{i,k+1}^{\text{org}} + F_{k-1}^{\text{aq}} x_{i,k-1}^{\text{aq}} \\ \gamma_{i,k}^{\text{org}} x_{i,k}^{\text{org}} &= \gamma_{i,k}^{\text{aq}} x_{i,k}^{\text{aq}} \\ \sum_i x_{i,k}^{\text{org}} &= \sum_i x_{i,k}^{\text{aq}} = 1 \end{aligned} \quad (1)$$

A non-random two liquid (NRTL) model is employed to calculate the activity coefficients of all the components involved in LLE model, and the missing binary interactive parameters are estimated using Aspen Plus with the UNIFAC method.^{28,29}

2.2. Selection of Candidate Solvents. Because numerous potential compounds are available, rules that could preclude irrelevant solvents before calculation are of great consequence. As extraction column is employed, the following rules should be obeyed:

- Compound should be no more than liquid and be completely miscible with MIBK in its fraction range to avoid a third phase;
- Specific gravity (ρ) should satisfy $\rho < 0.9$ or $\rho > 1.1$ for a good separation of raffinate and extractant;
- Boiling point of the solvent should satisfy $T_{\text{bp}} > 70$ °C at ambient atmosphere to avoid large volatile loss;
- The solubility should be not more than 2000 mg/L at any case for the consideration of less solvent loss in raffinate;
- A solvent reported for extraction in the literature is preferred;
- Only one of the isomers will be taken into account considering the limitation of UNIFAC.^{28,29}

Generally there are two alternative approaches available for solvent recovery: distillation and back stripping with alkali. Either of the following two criteria should be met for smooth operation:

- $T_{\text{bp}} < 170$ °C to separate it from phenols if distillation column is adopted for the stripping process;
- No ester is allowed if back-extraction with alkali is applied in the recovering process.

Considering the small boiling temperature differences between phenols and tar, back stripping with alkali is always applied in practice because of economic concern. Thus, rule (h)

should also be met. According to these rules, the following seven solvents are selected as the candidates: benzene (Benz), toluene (Tol), m-xylene (Xyl), ethylbenzene (Eth), 1,3,5-trimethylbenzene (Tri), cyclohexane (CyH), and octanol (Oct).

2.3. Comparison of Candidate Solvents with Experimental Verification. **2.3.1. Optimal Solutions of Evaluation Model.** To compare the performance of all the candidates, the developed NLP model is programmed and solved with CONOPT in GAMS for each of the alternatives with the same operating parameters (listed in Table 1). The comparison

Table 1. Operating Parameters of Extraction Column

$m_{in} \text{ PhOH (mg/L)}$	$m_{out} \text{ PhOH (mg/L)}$	$F^{NW} \text{ (m}^3/\text{h)}$	N	$T_{\text{extraction}} \text{ (}^\circ\text{C)}$
2000	100	35	4	25

of the concentrations of extractants in raffinate and the molar fraction of MIBK (x_{MIBK}) in seven blends are depicted in Figure 2. Note that only phenol is considered here to reduce the computation complexity, as well as to facilitate the experimental verification.

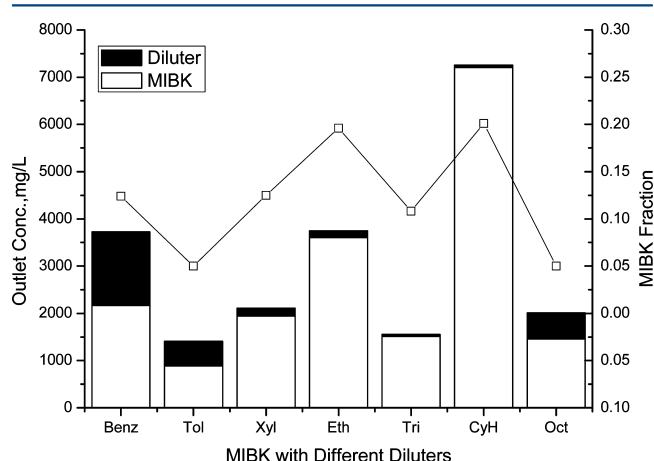


Figure 2. Comparison of raffinate concentration and MIBK fraction in blends.

On the basis of Figure 2, it can be found that under the same operating conditions, the blend of MIBK/toluene performs best with minimum outlet concentration ($m_{\text{MIBK}} = 884 \text{ mg/L}$ and $m_{\text{tot}} = 1408 \text{ mg/L}$). In this scenario, $x_{\text{MIBK}} = 0.05$, which is also rather small compared with others, implying less consumption of expensive MIBK. On the other side, the MIBK outlet concentration in MIBK/1,3,5-trimethylbenzene and MIBK/octanol are just a little greater than that in MIBK/toluene. Therefore, toluene might be highly preferred as the diluter of MIBK for phenol removal via extraction, while 1,3,5-trimethylbenzene and octanol also requires close attention.

2.3.2. Empirical Procedure. To verify the results obtained by the evaluation model, as depicted in Figure 2, the following experiment is carried out under conditions that are the same as

those adopted in the model calculation: The volumes of MIBK and candidate solvents are specified based on the calculation, as listed in Table 2. MIBK is blended with each of the alternatives to form solvent blends. Then, the same volume (10 mL) of solvent blend and phenol solution (1000 mg/L) are mixed. The mixtures, kept in conical flasks, are vibrated in a shaker for 2 h at a speed of 350 rpm and then settled in the separating funnels for another 3 h. The concentrations of phenol (m_{raf}) and MIBK (m_{MIBK}) in raffinate are measured by a gas chromatography (GC) instrument (7890A, Agilent) with a flame ionization detector.

The comparison of m_{MIBK} between calculation and experiments is demonstrated in Figure 3, suggesting the same result

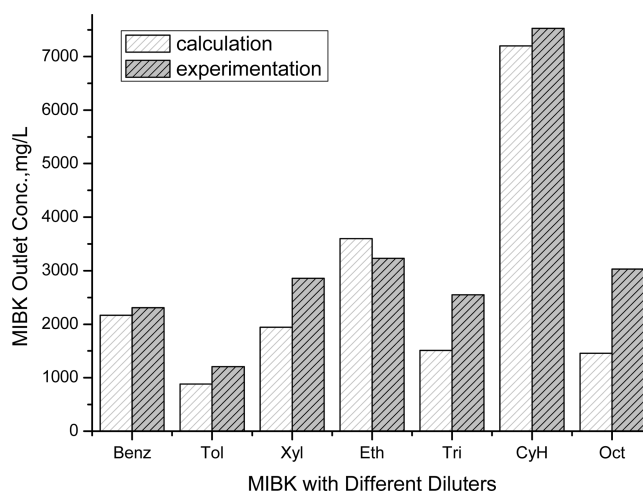


Figure 3. MIBK outlet concentration in different solvent blends (calculation versus experiment).

as shown in Figure 2. MIBK outlet concentration in the toluene case is the lowest in both calculation and experiments. Whereas in the 1,3,5-trimethylbenzene and octanol case, the MIBK outlet concentration in experiment is much higher than that in calculation; thus, these two solvents are excluded. Hence, MIBK/toluene is selected as the blend for phenol extraction.

It is also worth pointing out that Figure 3 depicts little difference between calculation and experiment for the hybrid systems of MIBK/benzene, MIBK/toluene, MIBK/ethylbenzene, and MIBK/cyclohexane. The deviation might stem from the ideality of extraction column assumption. However, this assumption cannot explain the large differences of the systems of MIBK/xylene, MIBK/trimethylbenzene, and MIBK/octanol. The possible reason might be the missing binary interactive parameters estimated with the UNIFAC method. Because UNIFAC cannot distinguish most of the isomers, especially the aromatic isomers, this method might lead to the degradation of the calculation accuracy to some extent and compromise the optimal solutions.

Table 2. Volume of MIBK and Candidate Solvent

serial	Benz	Tol	Xyl	Eth	Tri	CyH	Oct
MIBK molar fraction (%)	12.34	5.00	12.22	19.53	10.91	20.12	5.12
MIBK (mL)	4	1.25	3	5	2	5	1.2
solvent (mL)	20	20	21	20	18	17	18

Table 3. Volume of MIBK and toluene

label	T5	T10	T15	T20	T30	T40	T50
MIBK fraction (%)	5.00	10.01	15.03	20.17	29.64	40.26	50.27
toluene (mL)	20	20	20	20	20	10	10
MIBK (mL)	1.25	2.64	4.2	6	10	8	12

2.4. Further Study of MIBK/Toluene System with Experimental Verification. To study how MIBK fraction in the MIBK/toluene system affects the MIBK outlet concentration and the extracting performance of the blend, model calculation and experimental verification are carried out. The empirical procedure is the same as that in described section 2.3.2, except for the volume of the solvents, as listed in Table 3.

The distribution coefficient (D) of phenol between extractant and water reflects the extracting performance of the extractant, which could be determined in experiment by the following procedures.

The material conservation of phenol and the phase equilibria are expressed below.

$$V_{\text{raf}}m_{\text{raf}} + V_{\text{ext}}m_{\text{ext}} = V_{\text{ini}}m_{\text{ini}} \quad (2)$$

$$m_{\text{ext}} = Dm_{\text{raf}} \quad (3)$$

The volumes of the phenol solution and solvent blend are the same, and the two phases are also assumed to be immiscible under experimental conditions. When eqs 2 and 3 are combined, D can be determined.

$$D = \frac{m_{\text{ini}}}{m_{\text{raf}}} - 1 \quad (4)$$

Figure 4 shows a great consistency of calculation and experiments: m_{MIBK} grows almost linearly with a concomitant

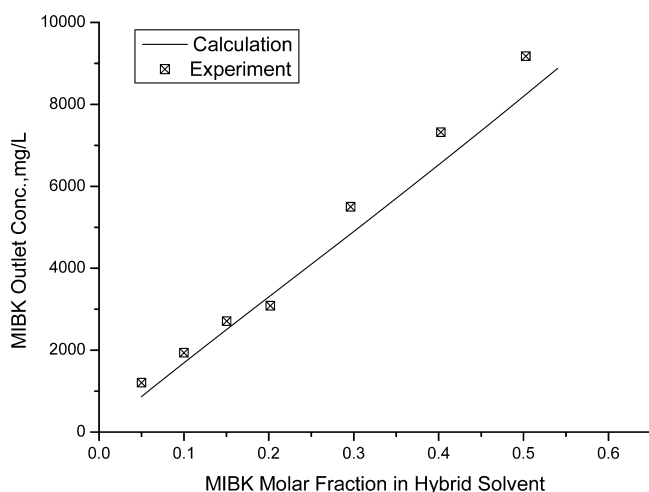


Figure 4. MIBK outlet concentration in different MIBK fractions (calculation versus experiment).

increase of x_{MIBK} in hybrid solvent, especially at low MIBK fraction. Therefore, small x_{MIBK} in hybrid solvent is preferred for the consideration of less loss of MIBK. What should be noted is that the deviation becomes a bit larger at high MIBK fraction. A possible reason might be the assumption of the highly diluted solution in two phases in the UNIFAC estimation.

Figure 5 indicates that the distribution coefficient increases with MIBK fraction in solvent blend, in both calculation and

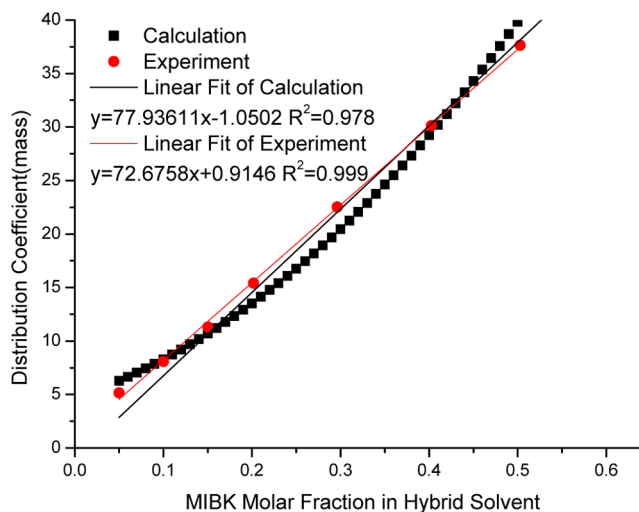


Figure 5. Distribution coefficient by mixture (experiment versus calculation).

experiment. It also suggests that the deviation between calculation and experiments is acceptable. The slight difference might derive from the ideality of calculation, the random error of measurement, and other uncontrolled empiric conditions.

Additionally, if the distribution coefficients of phenol between MIBK and water (D_{MIBK}) and the distribution coefficients of phenol between toluene and water (D_{Tol}) are assumed to be invariable in MIBK fraction range during the extraction process, which is the ideal case, the distribution coefficient of phenol between the hybrid solvent and water (D_{blend}) can be expressed as

$$\begin{aligned} D_{\text{blend}} &= D_{\text{MIBK}}x_{\text{MIBK}} + D_{\text{Tol}}x_{\text{Tol}} \\ &= (D_{\text{MIBK}} - D_{\text{Tol}})x_{\text{MIBK}} + D_{\text{Tol}} \\ &= aX + b \end{aligned} \quad (5)$$

Thus, D_{MIBK} and D_{Tol} could be determined according to the slope (a) and intercept (b) of the fitting line in Figure 5. These values are compared with literature values in Table 4. It is obvious that D_{MIBK} calculated in the model is almost the same as the published value,³⁰ while D_{Tol} shows a much greater difference.²²

Table 4. D of Phenol between MIBK, Toluene, and Water

parameters	D_{MIBK}	D_{Tol}
literature	77.20	1.90
calculation	76.89	-1.05
experiment	73.59	0.91

$$F_{in}^{strip,org} x_{i,in}^{strip,org} + F_{in}^{strip,aq} x_{i,in}^{strip,aq} = F_{out}^{strip,aq} x_{i,out}^{strip,aq} + F_{out}^{strip,org} x_{i,out}^{strip,org} \quad (13)$$

$$F_{in}^{strip,org} + F_{in}^{strip,aq} = F_{out}^{strip,aq} + F_{out}^{strip,org} \quad (14)$$

$$x_{i,out}^{strip,org} = K_i x_{i,out}^{strip,aq} \quad (15)$$

where K_i is the algebraic average of $\gamma_{i,k}^{aq}/\gamma_{i,k}^{org}$ in the extraction column, considering the low concentration of components in two phases.

3.3.3. Distillation for Tar Removal. For a given distillation column, the flow rate of the feed determines its operating cost at the same specifications. Because only part of the extractant is fed to the distillation column, a splitter factor sf reflecting the feed flow rate is introduced here to be optimized. As this unit is not the core of the overall process and generally less than 20% of the extractant is distilled in practice, a short-cut model is accurate enough. A sharp split is also assumed because of the large boiling point difference between tar and solvent. When the recovery of light key component (LK) and heavy key component (HK) are specified, the composition and flow rate can be determined by mass balance.

$$sf F_{out}^{strip,org} x_{i,out}^{strip,org} = F_D^{dist} x_{i,D}^{dist} \quad (16)$$

$$sf(1 - r_i) F_{out}^{strip,org} x_{i,out}^{strip,org} = F_B^{dist} x_{i,B}^{dist} \quad (17)$$

$$sf F_{out}^{strip,org} = F_B^{dist} + F_D^{dist} \quad (18)$$

Note that all water is in the distillate according to sharp split, implying the requirement of an oil–water separator. Thus, the following constraints are also considered:

$$F_D^{dist} x_{i,D}^{dist} = F_{out}^{dist,aq} x_{i,out}^{dist,aq} + F_{out}^{dist,org} x_{i,out}^{dist,org} \quad (19)$$

$$F_D^{dist} = F_{out}^{dist,aq} + F_{out}^{dist,org} \quad (20)$$

$$x_{i,out}^{dist,org} = K_i x_{i,out}^{dist,aq} \quad (21)$$

When the shortcut model is employed, the cost of the column could be determined by

$$C^{dist} = (P_{CW} + P_{LP}) \sum_i \Delta H_i^{vap} (R + 1) F_{out}^{dist,org} x_{i,out}^{dist,org} \quad (22)$$

where P_{CW} and P_{LP} are the price of cooling water and low-pressure steam, respectively (¥/kJ); ΔH_i^{vap} is the heat of evaporation of i at normal boiling point (kJ/mol); and R is the reflux ratio of the column, determined by the Underwood equation.³²

3.3.4. Makeup of Solvent. The last unit is a mixer where fresh solvent, making up the sink, mix with the remaining extractants. There might be two phases in the mixer because of the blending of the streams, and consequently phase equilibrium calculation is required to avoid operating problems in pumping and piping.

$$F_{mkp} + F_{out}^{dist,org} + (1 - sf) F_{out}^{strip,org} = F_{out}^{mix,aq} + F_{out}^{mix,org} \quad (23)$$

$$F_{mkp} x_{i,mkp} + F_{out}^{dist,org} x_{i,out}^{dist,org} + (1 - sf) F_{out}^{strip,org} x_{i,out}^{strip,org} = F_{out}^{mix,aq} x_{i,out}^{mix,aq} + F_{out}^{mix,org} x_{i,out}^{mix,org} \quad (24)$$

$$x_{i,out}^{mix,org} = K_i x_{i,out}^{mix,aq} \quad (25)$$

Note that the effect of pH is ignored in the whole process to reduce the model complexity and computation time.

3.4. Optimization Problem Presentation. For the extraction process illustrated in Figure 6, the operating cost is of great concern, which consists of the transportation consumption (pumping and piping, neglected), the chemical agent (alkali and solvent) consumption, and the income of phenolics and tar recovered. Thus, the objective function can be described as

$$Z = C_{NaOH} - C_{phenol} - C_{tar} + C_{mkp} + C^{dist} \quad (26)$$

where C_{NaOH} is the expense of alkali; C_{phenol} and C_{tar} are the cost of phenolate and tar (– implies income), respectively; C_{mkp} is the makeup of solvent; and C^{dist} is the cost of the distillation column for tar removal.

Each C_j above can be determined by its flow rate and price

$$C_j = F_j P_j \quad (27)$$

where F_j is the flow rate of stream j (kmol/h) and P_j is the price of stream j (¥/kmol).

Thus, the mathematical model of the operating optimization process could be established.

$$\min Z = F_j P_j + C^{dist}$$

$$\text{s.t. } \sum_i m_{i,out}^{aq} \leq m_{i,out,require}^{aq}$$

$$\gamma_{i,k}^{org} x_{i,k}^{org} = \gamma_{i,k}^{aq} x_{i,k}^{aq}$$

$$\sum_p F_k^p = F_{k+1}^{org} + F_{k-1}^{aq}$$

$$\sum_p F_k^p x_{i,k}^p = F_{k+1}^{org} x_{i,k+1}^{org} + F_{k-1}^{aq} x_{i,k-1}^{aq}$$

$$\sum_i x_{i,k}^{aq} = \sum_i x_{i,k}^{org} = 1$$

$$r^{lo} F_{in}^{aq} \leq F_{in}^{org} \leq r^{up} F_{in}^{aq}$$

$$(1 - \eta_i^{react}) F_{out}^{ext,org} x_{i,out}^{ext,org} = F_{in}^{strip,org} x_{i,in}^{strip,org}$$

$$\sum_p F_{in}^{strip,p} x_{i,in}^{strip,p} = \sum_p F_{out}^{strip,p} x_{i,out}^{strip,p}$$

$$\sum_p F_{in}^{strip,p} = \sum_p F_{out}^{strip,p}$$

$$sf F_{out}^{strip,org} x_{i,out}^{strip,org} = F_D^{dist} x_{i,D}^{dist}$$

$$sf(1 - r_i) F_{out}^{strip,org} x_{i,out}^{strip,org} = F_B^{dist} x_{i,B}^{dist}$$

$$sf F_{out}^{strip,org} = F_B^{dist} + F_D^{dist}$$

$$F_D^{dist} x_{i,D}^{dist} = \sum_p F_{out}^{dist,p} x_{i,out}^{dist,p}$$

$$F_D^{dist} = \sum_p F_{out}^{dist,p}$$

$$C^{\text{dist}} = (P_{\text{CW}} + P_{\text{LP}}) \sum_i \Delta H_i^{\text{vap}} (R + 1) F_{\text{D}}^{\text{dist}} x_{i,\text{D}}^{\text{dist}}$$

$$F_{\text{mkp}} + F_{\text{out}}^{\text{dist,org}} + (1 - \text{sf}) F_{\text{out}}^{\text{strip,org}} = \sum_p F_{\text{out}}^{\text{mix},p}$$

$$F_{\text{mkp}} x_{i,\text{mkp}} + F_{\text{out}}^{\text{dist,org}} x_{i,\text{out}}^{\text{dist,org}} + (1 - \text{sf}) F_{\text{out}}^{\text{strip,org}} x_{i,\text{out}}^{\text{strip,org}} = \sum_p F_{\text{out}}^{\text{mix},p} x_{i,\text{out}}^{\text{mix},p}$$

$$x_{i,\text{out}}^{\text{u,org}} = K_i x_{i,\text{out}}^{\text{u,aq}}$$

Note that other reasonable and necessary boundaries are also set to save computation time and to ensure global optimization. The overall NLP optimization model elaborated above is programmed in GAMS.

4. RESULTS AND DISCUSSION

To demonstrate the advantage of the designed solvent blend over pure MIBK, the same operating conditions are set in two cases, as listed in Tables 1 and 5. Other conditions are the

Table 5. Specification of Extraction Column

substituents	abbr.	inlet (mg/L)	outlet (mg/L)
phenolics		2500	100
phenol	PhOH	2000	
2,4-dimethyl-phenol	DiOH	500	
tar		800	100
m-xylene	Xyl	300	
quinoline	Qn	500	

reaction ratio of phenolics in the back-stripping column is assumed to be 0.99, and the recovery of the LK and HK of the tar removal column is set to 0.95, according to industrial practice. The comparison of outlet concentration and consumption in two cases is listed in Figures 8 and 9, respectively.

The large concentration differences of phenolics between two cases, as depicted in Figure 8, indicates that pure MIBK out-performs solvent blend in phenol removal, which is the

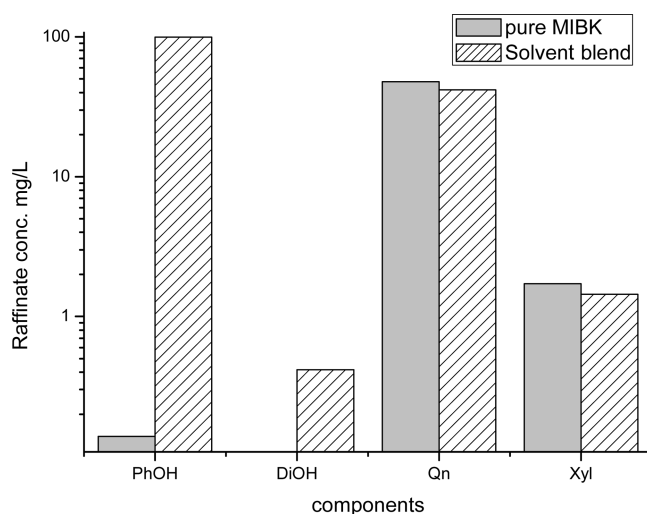


Figure 8. Concentration comparison of components in raffinate.

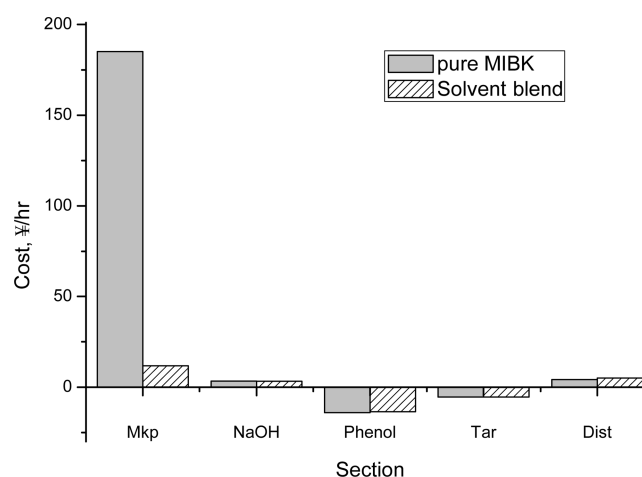


Figure 9. Unit cost comparison (pure MIBK versus solvent blend).

same as the trends in Figure 5. The outlet concentrations of tar in the two cases are almost the same, suggesting little difference in the performance of tar removal via extraction. The concentration of tar in raffinate almost meets the discharge limit, indicating the extraction of tar as the bottleneck of this process. Pure MIBK proves to be no advantage, and its large sink leading to huge makeup cost makes the case worse.

Results of the unit cost comparison demonstrated in Figure 9 reveal that the difference of the same unit in two cases is almost the same except in the case of the solvent makeup. The significant difference of makeup consumption mainly derives from the large difference of MIBK concentration in raffinate (17380.31 mg/L in the pure MIBK case versus 850.62 mg/L in the solvent blend case). The large makeup cost (185.15 ¥/t) in the pure MIBK case highly recommends a stripping column for its recover, which is the real case in industry.^{7,11,13} Note that the cost of makeup is only 11.15 ¥/t in the solvent blend case, which seems less than the operating cost of the MIBK stripping column (about 15–30 ¥/t⁷). The volume ratios (extractant/wastewater) of the two cases are 0.91 for pure MIBK and 0.85 for solvent blend, indicating almost the same transportation consumption (which is not considered in the objective function). Thus, the designed solvent blend shows great economic advantage in this scenario when compared to pure MIBK coupling with stripping column for MIBK recover.

5. CONCLUSIONS

This paper deals with the problem of the high loss of MIBK in coking wastewater treatment processes by introducing additional solvent as diluter of MIBK. To accomplish this goal, a NLP model based on the assumption of an ideal extraction column is put forward for evaluation; in addition, the composition optimization of the potential solvent blends is discussed. Seven candidate solvents (benzene, toluene, m-xylene, ethylbenzene, 1,3,5-trimethylbenze, cyclohexane, and octanol) are studied with the model. The results, which are in good agreement with experimental outcomes, suggest toluene as the most promising candidate solvent. Further investigation indicates that both D_{blend} and m_{MIBK} in raffinate increase with x_{MIBK} in solvent blend. The trade-off between the extraction performance and MIBK loss recommends that the blend with $x_{\text{MIBK}} = 0.05$ should be applied to the extraction of phenolic wastewater.

Furthermore, the designed solvent is applied to a general coking WW treatment process. It includes extraction column, back-stripping column for phenol recover, distillation column for tar removal, and the mixer for solvent makeup. A NLP model is proposed to obtain optimal operating parameters of the process. In order to improve model accuracy, more contaminants (2,4-dimethyl-phenol, m-xylene, and quinolone) in addition to phenol are considered according to their KOW values and concentrations. The results of the case study indicate that the solvent blend has economic advantage: the cost of makeup is only 11.15 ¥/t in the case of the solvent blend, which is rather small compared to that of the case of pure MIBK (185.15 ¥/t). The small loss of MIBK in raffinate also suggests that an extra stripping column for solvent recovery is unnecessary, which will greatly reduce both investment and operating cost.

■ ASSOCIATED CONTENT

● Supporting Information

The basic properties of candidate solvents, KOW value of the constituents in wastewater, NRTL equation and binary interactive parameters, model statistics, and further explanation of ABK and QH-1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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■ NOMENCLATURE

Variables

- C = cost, ¥/t
- F = flow rate, kmol/h
- K = distribution factor, by molar fraction
- sf = split factor
- V = volume of streams, m³/h
- x = molar fraction of components
- Z = objective function

Parameters

- m = mass concentration, mg/L
- D = distribution coefficient, by mass
- N = number of stages
- r = recovery of component in distillation
- R = reflux ratio in distillation
- T = temperature, °C

Sets

- i = components
- k = stages in extraction column
- j = streams
- s = candidate solvents
- p = phase
- u = unit

Greek Symbol

- γ = activity coefficient
- η = reaction ratio

Superscript

- aq = aqueous phase
- dist = distillation column
- ex = extraction column
- mix = mixer
- org = organic phase
- strip = back stripping
- WW = wastewater

Subscript

- B = bottom product of distillation column
- CW = cooling water
- D = distillate
- ext = extractant
- in = inlet
- ini = initial value
- LP = low-pressure steam
- mkp = makeup of the solvent
- out = outlet
- raf = raffinate

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