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Recovery of Lactic Acid from Corn Stover Hemicellulose-Derived Liquor

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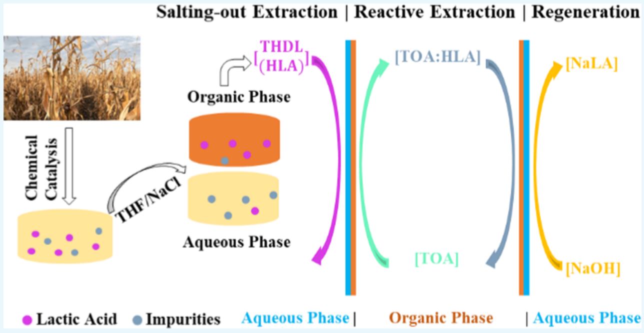
ABSTRACT: Lactic acid is an attractive target platform chemical obtained from biorefinery processes based on renewable resources. This study focuses on the recovery of lactic acid from corn stover hemicellulose-derived liquor. Two processes were investigated comparatively. In process I, under the optimized conditions of 10 wt % trioctylamine/octanol, the extraction efficiency and distribution coefficient of lactic acid were 50.8% and 1.03, respectively. In process II, a salting-out extraction step was introduced, which had significant impacts on the following reactive extraction process. The extraction efficiency and distribution coefficient of lactic acid were about 32.2% and 3.85 times higher than that of process I, respectively. All residual sugars and most of the salts (82.8%) could be removed by the salting-out extraction system used. Additionally, five extraction cycles with back-extraction and solvent regeneration were performed, and the results showed that the extraction system still exhibited stable performance. Effective extraction of lactic acid from crude reaction liquor of corn stover was realized by first salting-out and consecutive reactive extraction, which provided a potential method for recovery of lactic acid from actual biomass-derived liquor.



1. INTRODUCTION

Due to the depletion of resources and increasing environmental impacts, the traditional methods of obtaining chemicals from fossil resources have been facing more and more challenges, and there is a growing emphasis on converting renewable resources to chemicals.[1] Biomass, especially lignocellulosic biomass, is considered to be a promising substrate due to its widespread existence and its current low utilization rate.[2] Various technologies are used to convert lignocellulosic biomass into chemicals, among which the chemical catalytic conversion of lignocellulose to lactic acid is a promising and versatile technique.[3−7] Lactic acid is an important industrial chemical product and is considered to be one of the top 10 chemicals obtained from biorefineries as declared by the United States Department of Energy.[8] The largest application of lactic acid is being used as a food additive, followed by being used to produce poly(lactic acid). The latter is one kind of environment-friendly and biodegradable plastic, and its potential wide application has been attracting more and more attention.[9,10] At present, lactic acid is mainly produced by bacterial fermentation of carbohydrates (e.g., glucose). However, owing to high costs of carbon sources, the economic feasibility of industrial production of the rather inexpensive product, lactic acid, is challenging.[11] Recently, many scholars have used lignocellulosic biomass as a cheap carbon source to develop a highly cost-efficient chemical catalytic conversion process for the production of lactic acid. Although the production of lactic acid from lignocellulosic biomass has multiple advantages, the downstream processing of reaction liquor has met with some difficulties. The crude reaction liquor is a complex mixture system, and the concentration of lactic acid is very low.[4] Thus, it is imperative to explore an efficient process for the recovery of lactic acid, especially the recovery of lactic acid from the reaction liquor obtained directly from the catalytic conversion of lignocellulose, which is crucial for the comprehensive utilization of lignocellulosic biomass.

A classical way of recovering lactic acid from fermentation broth is the precipitation of lactic acid by adding $Ca(OH)_2$ to the broth forming calcium lactate. Some of the disadvantages include the tedious multistep process, which could lead to the loss of lactate, and the gypsum ($CaSO_4$) residue formed must be discarded.[10] Therefore, some new and economically effective downstream routes, which could avoid the inherent drawbacks of the conventional route, have been developed to recover lactic acid from different industrial waste streams or fermentation broths, including adsorption,[12−14] membrane separation,[15,16] electrodialysis,[17] solvent extraction,[18] esterification hydrolysis,[19] molecular distillation,[20] etc. However, the wide application of these techniques is limited due to some

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drawbacks, such as small processing capacity, high energy consumption, and the use of expensive equipment. In view of these limitations, the reactive liquid–liquid extraction process—with the advantages of low temperature, low cost, high efficiency, high yield, and simple operation—has been considered as a promising recovery technology.[21] High-molecular-weight alkylamine[22−25] and organophosphorus compounds[10,26] dissolved in diluents such as oleyl alcohol have a higher extraction efficiency for lactic acid. Due to the existence of high hydrogen-bonding acceptor basicity in the extractant, lactic acid is extracted to the organic phase by strong interaction with the extractant forming acid–amine complexes, and finally the lactic acid is stripped from the load phase by vacuum evaporation or back-extraction.[27,28] In addition, different diluents influence the extraction degree, of which polar diluents are more effective than nonpolar ones.[29,30] Many new attempts have been made to obtain higher extraction efficiency of lactic acid, such as using quaternary ammonium salts[31,32] and mixed extractants[33] and the development of new extractants.[34] It was found that the mixtures of alkylamine and tri-*n*-butylphosphate had a synergistic effect on the extraction of lactic acid.[35]

In recent years, although the conversion of lignocellulosic biomass to lactic acid has been extensively studied, only limited research on the recovery of lactic acid from actual lignocellulose derived liquor has been reported.[36−38] Reactive extraction is considered a promising recovery technology and has been reported in the recovery of high-value chemicals from hydrolysates of lignocellulose.[39−41] However, for lactic acid, most investigations on the extraction are based on simulated solutions, whereas only a few exploratory studies have focused on recovery of lactic acid from actual fermentation broth, and the yield was much lower than that in the aqueous solution.[10,42] In this work, through preliminary exploration, it was found that the direct reactive extraction of lactic acid in corn stover hemicellulose-derived liquor was not effective enough.

Salting-out extraction—which is based on the different distribution behavior of chemicals in the two phases composed of H_2O, low-molecular-weight organic solvent as the extractant, and inorganic salt as the salting-out reagent[43]—as a promising strategy for the preliminary purification and recovery of bio-based molecules, exhibits excellent recovery performance for lactic acid in fermentation broths.[44−46] For example, the extraction efficiency and distribution coefficient of 90.6% and 3.23, respectively, were obtained by using a salting-out system of K_2HPO_4/ethanol to recover lactic acid from fermentation broths.[46] However, for the mixture directly derived from the conversion of corn stover by chemical catalysis, after preliminary exploration, the selectivity of salting-out extraction to lactic acid was not satisfied due to its complexity.

In this work, a salting-out extraction system was introduced into the recovery process to treat the corn stover hemicellulose-derived liquor for reducing its complexity so that the high selectivity of the reactive extraction could perform better. Two parallel experiments between the hemicellulose-derived liquor (HDL) and treated hemicellulose-derived liquor ((THDL), by salting-out extraction) were conducted, and three key variables (extractant amount, pH, and phase ratio) were adopted to evaluate the lactic acid recovery performance of the extraction system. In addition, to obtain higher lactic acid extraction performance and a complete recovery process, multistage extraction, stripping, and recycle of the extraction system were also investigated.

2. RESULTS AND DISCUSSION

2.1. Characteristics of the Initial and Treated Corn Stover Hemicellulose-Derived Liquor. The hemicellulose in the corn stover was converted to lactic acid by a two-step process, where MgO was used as the catalyst for lactic acid production in the second step. The pH of the initial reaction liquor was 6.9 ± 0.1. According to the high performance liquid chromatography (HPLC) and inductively coupled plasma atomic emission spectrometry (ICP-AES) results, the concentrations of the components in the initial reaction liquor, HDL, and THDL are listed in Table 1. The principal component in the initial reaction liquor was lactic acid, and limited glucose, xylose, and furfural were obtained. The K^+ and Mg^{2+} contents reached approximately 122 and 460 ppm, respectively, for the initial reaction liquor. Activated carbon could adsorb colored substances (e.g., furfural, humins) from the initial reaction liquor, and there was a slight removal of K^+ and Mg^{2+}, whereas sugars and lactic acid remained almost unchanged. After the salting-out treatment, the concentration of sodium ions increased due to the use of sodium chloride, but the total ion concentration of THDL decreased significantly, and no residual sugars were detected.

Table 1. Compositions of Initial Reaction Liquor, HDL, and THDL

	organic component (g L^{-1})				cations (ppm)			
	glucose	xylose	furfural	LA[b]	K^+	Ca^{2+}	Na^+	Mg^{2+}
IRL[a]	0.1	0.05	0.04	1.8	122	11	8	460
HDL	0.1	0.05		1.78	117	11	11	427
THDL				1.73	4	2	90	1

[a] IRL = initial reaction liquor. [b] LA = lactic acid.

2.2. Effect of Extractant Concentration. The organic phases with different trioctylamine (TOA) concentrations were configured to extract lactic acid from HDL and THDL. Figure 1A,B shows the relationship between the initial TOA concentration with extraction efficiency and the distribution coefficient, respectively. As can be seen in Figure 1, when TOA was mixed with active diluent octanol, the extraction efficiency and equilibrium distribution coefficient (K_D) of lactic acid significantly improved. When pure octanol was used, only 13% lactic acid was extracted from THDL. However, at TOA concentration of 2%, the extraction efficiency reached 49.8%. At low TOA concentration, both the extraction efficiency and the distribution coefficient increased with the TOA concentration. It could be seen that increasing TOA concentration had a positive effect on the recovery of lactic acid. The influencing trend for HDL was the same as that for THDL, but the extraction performance of THDL was significantly higher than that of HDL. For instance, at TOA concentration of 10 wt %, the extraction efficiency and distribution coefficient of lactic acid in HDL were up to 50.8% and 1.03, respectively. Under the same condition, the extraction efficiency and distribution coefficient of lactic acid from THDL reached 83% and 4.88, respectively, which were 32.2% and 3.85 higher than that with HDL.

In the process of reactive extraction, lactic acid and amines form ion pairs and then enter the organic phase.[21] The degree

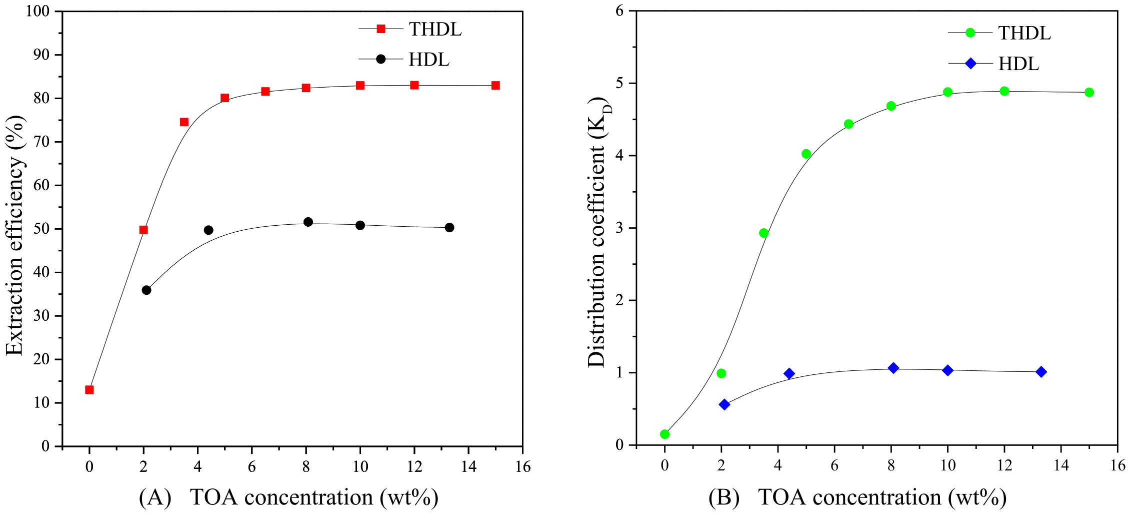

Figure 1. Effect of extractant concentration in octanol on lactic acid extraction efficiency (A) and distribution coefficient (B) (conditions: 10 min, 25 °C, pH = 1.6, O/A = 1).

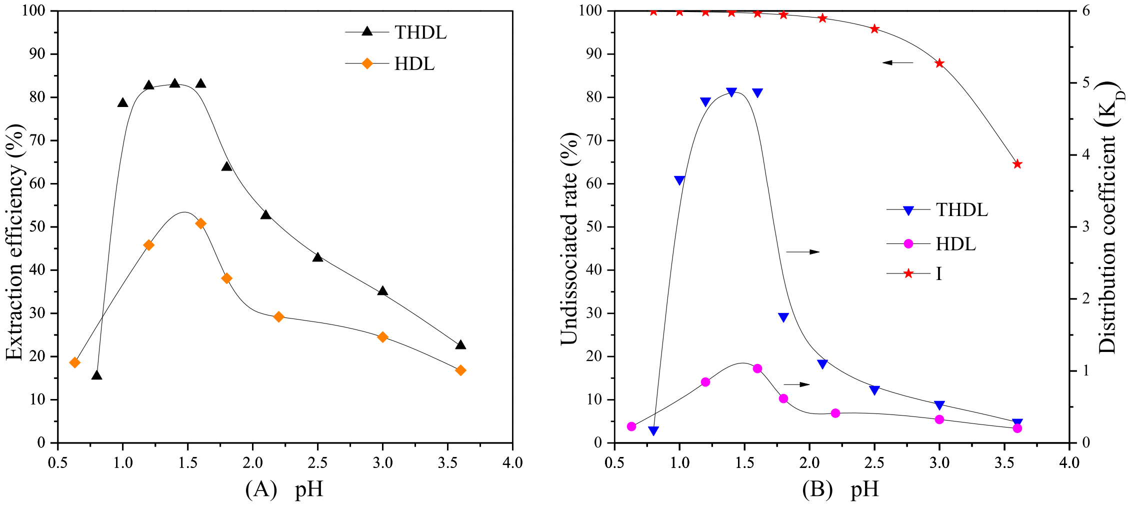

Figure 2. Effect of pH on lactic acid extraction efficiency (A), and on distribution coefficient and undissociated rate (B) (conditions: 10 min, 25 °C, O/A = 1, 10 wt %).

of TOA dilution plays a key role, which could affect the basicity of the amine and the stability and solvation of the formed ion pair. The polar active diluent octanol might dissolve the acid−amine complex through specific hydrogen bonds between the octanol and the acid−amine complex.[23] At lower extractant concentration, the polarity of the solvent system was still high. With the increase of TOA concentration, this synergistic effect increased the interaction of TOA with lactic acid and promoted the transfer of lactic acid to the organic phase. However, at 10 wt % or even higher TOA concentration, the distribution coefficient of lactic acid remained constant since equilibrium was reached. Although excessive TOA was conducive for the formation of the acid−amine complex, poor solvation ability and high viscosity of TOA might inhibit the accumulation of the complex. Moreover, the price of TOA is higher than that of octanol, which can inhibit the economic applicability of this process at a high amine loading rate. According to the above considerations, the optimal extraction process using 10 wt % concentration was chosen in this work.

2.3. Effect of pH. To evaluate the effect of pH on lactic acid extraction, the extraction of lactic acid was carried out with different pH values. The results are shown in Figure 2. It can be seen that the pH value had a significant influence on both the extraction efficiency and distribution coefficient of lactic acid. As the pH increased, the extraction efficiency and distribution coefficient of lactic acid both increased sharply first and then decreased, whereas the undissociated rate of lactic acid continuously decreased. It might be caused by the fact that TOA could only form ion pairs with the lactic acid molecule, whereas the deprotonated lactic acid still remained in the aqueous phase.[47] According to the ionization of lactic acid, the existence form of lactic acid was determined by the pH values. Therefore, the extraction efficiency and distribution coefficient were sensitive to pH condition, and more lactic acid was extracted at lower pH. However, poor extraction efficiency of lactic acid was obtained at very low pH condition, which might be caused by the stripping effect of sulfuric acid. Kyuchoukov et al.[28] found that lactic acid could be stripped from the loaded organic phase using acid, alkali, or salt. Additionally, competition extraction was found between the

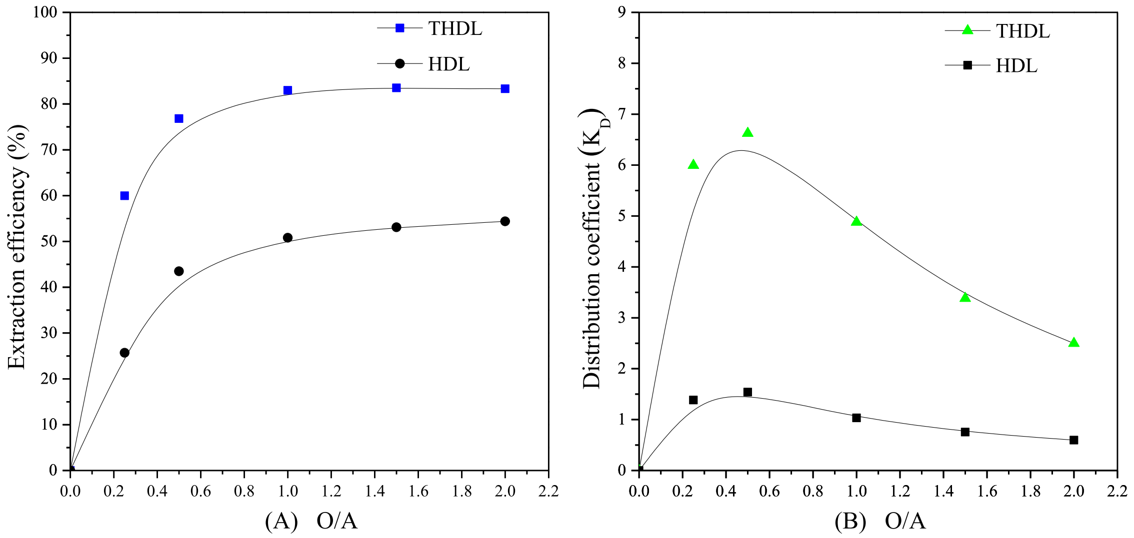

Figure 3. Effect of phase ratio on lactic acid extraction efficiency (A) and distribution coefficient (B) (conditions: 10 min, 25 °C, pH = 1.6, 10 wt %).

hydrochloric acid and lactic acid.[21] In other words, sulfuric acid used to regulate pH might be substituted for lactic acid to be extracted into the organic phase.

As shown in Figure 2, the experimental data of HDL and THDL showed a similar trend, but the extraction efficiency of lactic acid in THDL increased by 3.6−32.2% compared with that of HDL. The maximum value was reached with the pH value of about 1.6, and the extraction efficiencies of lactic acid were 83 and 50.8% from THDL and HDL, respectively. At this point, the existence of lactic acid was mainly undissociated molecules (>99%) (lactic acid $pK_a = 3.86$). However, when the pH was close to the pK_a of lactic acid, about half of the lactic acid was dissociated, and only 16.8 and 22.4% lactic acid were extracted from HDL and THDL at pH 3.6, respectively. Therefore, a relatively low pH of around 1.6 was considered the optimum extraction condition.

2.4. Effect of Phase Ratio. The effect of phase ratio (O/A) on liquid−liquid extraction of lactic acid was evaluated. The organic phase and HDL or THDL were mixed to different volume ratios, and the equilibrium data of extraction efficiency and distribution coefficient of lactic acid are shown in Figure 3. It could be seen that with increasing value of O/A, the extraction efficiency initially increased, reached the maximum value at about O/A of 1, and then basically remained stable. However, the distribution coefficient increased first and then decreased. This might be because the amount of organic solvent increased with the increase of O/A, which might have increased the interaction of lactic acid and the extractant, but at the same time, the decrease in the concentration of the acid−amine complex led to the reduction of the distribution coefficient. Compared with the HDL, the increase of extraction efficiency and distribution coefficient of lactic acid from THDL was significant. Operating at an O/A of 1:2, the maximum distribution coefficient was reached, and 76.8 and 43.5% lactic acid were extracted from THDL and HDL, respectively. For the best extraction performance, it was favorable and feasible to choose the O/A of 1:1, where the maximum extraction efficiency was reached and had a relatively high distribution coefficient of lactic acid. Further increase of O/A was useless for improving the extraction efficiency, and the distribution coefficient was sharply diminished. This meant that a large amount of organic solvent had been consumed when the phase ratio was further increased, but no further positive effect was achieved, which also led to a huge waste of organic solvent.

2.5. Effect of the Salting-Out Extraction Step. The reaction liquor is a complex mixture system. In the extraction process, the competition extraction or interaction of other substances in the solution occurred frequently, which might have further influenced the distribution coefficient and extraction efficiency of lactic acid. By extracting lactic acid from simulated fermentation broth, Yankov et al.[48] found that acetate in the solution could affect the extraction process. San-Martín et al.[49] found that when ions were present, less lactic acid was extracted using Alamine 336 as the extractant.

In this work, a salting-out extraction step was introduced into the recovery process to treat the corn stover hemicellulose-derived liquor for reducing the influence of impurities in the feedstock. Due to the presence of inorganic salt in the salting-out extraction system, water molecules were attracted by the salt ions and then departed from organic solvent molecules. Therefore, a two-phase system was obtained, which led to selective extraction of the substrate from the bottom phase to the top phase.[36] It reduced the complexity of the corn stover hemicellulose-derived liquor. As we can see in Table 1, 82.8% ions were removed compared with that in HDL, and no residual sugars were detected in THDL. From the results of the above three sets of parallel experiments, it could be found that the reactive extraction performance significantly increased by introducing the salting-out extraction step in the recovery process. This was because the salting-out extraction step effectively removed hydrophilic impurities, thus reducing the mass transfer resistance of the reactive extraction process and promoting the transfer of lactic acid to the organic phase. It was concluded that the complexity of the product usually restricted the mass transfer, which made the extraction inefficient. If the salting-out and reactive extraction processes are combined, the recovery of lactic acid would be simpler and more effective. Therefore, process II was chosen for further investigation.

2.6. Effect of Contact Time and Extraction Temperature. It is well known that the extraction time and temperature can affect the heat transfer and mass transfer.

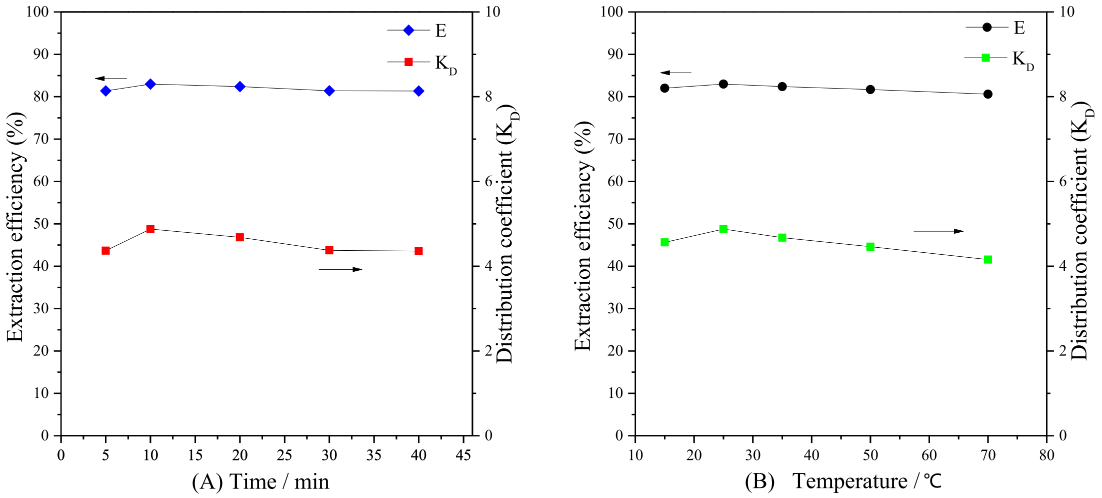

Figure 4. Effect of contact time (A) and extraction temperature (B) on recovery of lactic acid from THDL (conditions: pH = 1.6, O/A = 1, 10 wt %).

To investigate the effect of contact time and extraction temperature on the recovery of lactic acid from THDL, an equal volume of organic phase (containing 10 wt % TOA) and THDL was mixed in varying times and temperatures. As shown in Figure 4A, the extraction efficiency reached 83% within 10 min. However, with prolonged contact time, a slight decline could be seen for the distribution coefficient, which might be caused by the effect of emulsification in long-time agitation. The result showed that extraction equilibrium was reached quickly.

Figure 4B shows the effect of temperature on the extraction of lactic acid from THDL. The result shows that the temperature slightly affected the distribution coefficient and extraction efficiency in the range of 15−70 °C, which was consistent with the extraction of lactic acid from fermentation using Alamine 336 as the extractant.[47] As shown in Figure 4B, the increase of liquid viscosity at low temperature might be not conducive to mass transfer. On increasing the extraction temperature to 25 °C, the maximum distribution coefficient of lactic acid was obtained, which then decreased slowly with further increase in extraction temperature. It is obvious that the process of extracting lactic acid was exothermic using tertiary amine as the extractant, and rising temperature was not conducive to extraction. In addition, the lactic acid−amine complex might be unstable at elevated temperatures.[50] Furthermore, at high temperature, the solvent loss would increase because of increased solubility and volatility, and the process of regulation of temperature was energy consuming, which could increase the production costs. Therefore, 25 °C (room temperature) and contact time of 10 min seemed to be a good choice.

2.7. Multistage Extraction. To further improve the extraction efficiency, multistep extraction was performed to recover lactic acid from THDL. Sequential extraction steps (one, two, three, and four) were performed at O/A values of 1:1 and 1:2. Figure 5 shows the accumulated extraction efficiency of lactic acid with different extraction steps. Operating at O/A of 1:2, the extraction efficiency of one-step extraction was 76.8%. After performing a second extraction, 84.4% lactic acid was obtained. When the O/A was 1:1, the experimental results showed that the observed trend was consistent with that for O/A of 1:2, that is, 89.4% extraction efficiency of lactic acid could be obtained by two-step extraction, which was slightly higher than 83% of one-step extraction. However, as Figure 5 shows, the third- and fourth-step extraction could not significantly increase the recovery of lactic acid in comparison with two-step extraction. This might be because an equilibrium between the two phases was achieved after two-step extraction. According to the experimental results, two-step extraction at O/A of 1:2 achieved almost the same performance of lactic acid extraction as one-step extraction at O/A of 1:1, but these results were slightly lower than that of two-step extraction at O/A of 1:1. To obtain high extraction performance and solvent utilization at the same time with convenient operation, one-step extraction seemed to be a good choice when O/A was 1:1.

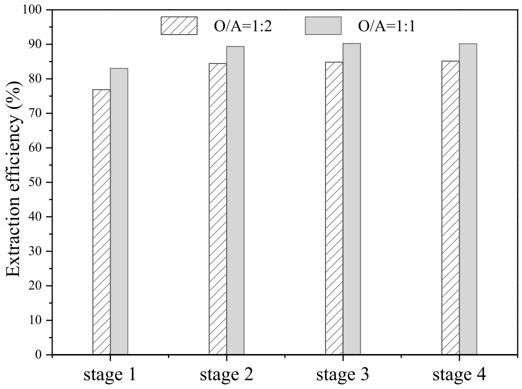

Figure 5. Effect of sequential extraction steps on recovery of lactic acid from THDL (conditions: 25 °C, 10 min, pH = 1.6, 10 wt %).

2.8. Stripping and Repeated Experiments. The stripping of carboxylic acid from the loaded organic phase and recycling of the extraction system are vital parts of the recovery process.[51] Since lactic acid is easily available in the market, distillation is an effective method used to strip lactic acid from the organic phase after extraction. However, in the present work, the boiling points of TOA and octanol were high, which made it difficult to be distilled at atmospheric pressure. The alternative method was back-extraction. It turned the extracted lactic acid into downstream chemical products, such as sodium lactate, which could be used in pharmaceuticals (e.g., dialysis) and could be further converted into lactic acid.

In the present work, the extracted lactic acid in the organic phase was stripped via back-extraction. After loading with lactic acid, the loaded organic phase was mixed with sodium hydroxide of different concentrations for 30 min at 25 °C and the phase ratio of 1. Sodium hydroxide reacted with lactic acid in the acid−amine complex to form sodium lactate, and subsequently the extraction phase was regenerated. The results in Table 2 show that the efficiency of stripping lactic acid using NaOH was very effective, which increased with the increase of NaOH concentration. Within 0.4 g L^{-1} of NaOH concentration, only 20% lactic acid could be stripped, and the degree of stripping could reach 99.5% when the concentration of NaOH was increased to 6 g L^{-1}. The lactic acid stripped from the load phase entered the aqueous phase, and the organic phase was collected for the next run through a simple phase separation.

Table 2. Effect of the Concentration of NaOH on Stripping Lactic Acid from the Loaded Organic Phase (Conditions: 25 °C, 30 min, O/A = 1)

no	C_{NaOH} (g L^{-1})	stripping degree (ε) (%)	distribution coefficient (K_D)
1	0.4	20	3.90
2	0.8	33	2.00
3	1.6	52	0.91
4	3	70	0.42
5	6	99.5	0.005

To verify the extraction performance of the regenerated organic solvent after back-extraction, the regenerated organic phase was reused for the next extraction operation. The results of five repeated experiments are shown in Figure 6. It can be seen that the extraction efficiency of lactic acid remained about 83% for the five cycling times in the condition of O/A of 1. This result showed that the extraction system could be recycled. Thus, the feasibility of using reactive liquid−liquid extraction for the recovery of lactic acid from THDL had been confirmed.

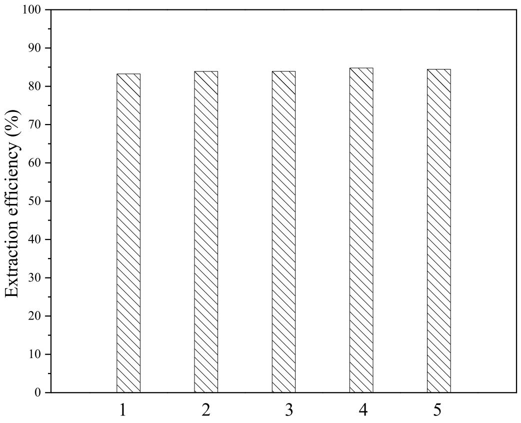

Figure 6. Effect of the reuse of extractant on recovery of lactic acid from THDL (conditions: 10 min, 25 °C, pH = 1.6, O/A = 1, 10 wt %).

3. CONCLUSIONS

In this study, we have demonstrated that the introduction of the salting-out extraction step had an excellent effect on the recovery of lactic acid from the mixture derived from corn stover by liquid−liquid reactive extraction. The extraction performance of the reactive extraction process could be significantly affected by the concentration of TOA, pH value, and the value of O/A. At the optimum extraction condition, the extraction efficiency and distribution coefficient of lactic acid in THDL were 83.0% and 4.88, respectively, which were 32.2% and 3.85 times higher than that of HDL, respectively. The marked increase in extraction performance was attributed to the salting-out extraction step in the novel process, which could remove most of the salts (82.8%) and almost all of the residual sugars in HDL. Moreover, multistage extraction could be more effective, and 89.3% lactic acid could be extracted from THDL by two-step extraction at the phase ratio of 1:1. The lactic acid in the load organic phase could be stripped using sodium hydroxide solution via one-step back-extraction, whereas the extraction system was regenerated and directly used for the next run by a simple phase separation. Five repeated experiments showed that the extraction system still exhibited stable performance. Thus, it is considered that the present work might provide a promising method for the recovery of lactic acid from hemicellulose-derived liquor of the actual biomass.

4. MATERIAL AND METHODS

4.1. Materials.

The chemical catalytic conversion of hemicellulose to lactic acid has been reported previously, and the chemical composition of the initial reaction liquor is shown in Table 1.[4] The activated carbon used was provided from Adamas (Shanghai, China), the Brunauer−Emmett−Teller surface area, pore volume, and pore size of which were 1732 m^2 g^{-1}, 1.16 cm^3 g^{-1}, and 26.7 Å, respectively. Lactic acid standard solution was derived from commercial lactic acid (95%, Enamine) and then diluted with deionized water. Trioctylamine (TOA, 98%) and octanol (99%) were purchased from TCI (Shanghai, China). Analytical-grade sulfuric acid, sodium hydroxide, sodium chloride, and tetrahydrofuran (THF) were obtained from Kelong Chemical Reagent (Chengdu, Sichuan, China). All of the reagents and solvents were used directly from commercial sources without further purification.

4.2. Activated Carbon Treatment.

The initial reaction liquor directly derived from corn stover was mixed with activated carbon at room temperature with stirring for 3 h. The dosage of activated carbon was 2%. Then, the HDL was collected after filtration with a Nylon 66 membrane with a pore size of 0.22 μm for removing large particles and impurities.

4.3. Studied Processes for Recovery of Lactic Acid.

The flow sketch of the processes of lactic acid recovery is shown in Figure 7. Two processes, that is, process I and process II, were studied comparatively. For process I, TOA was dissolved in octanol to obtain the organic phase extractant, and then the required amount of the organic phase extractant and HDL was added to centrifuge tubes. The two-phase system was stirred at constant temperature by a magnetic stirrer at 300 rpm to mix the two phases. The extraction time and temperature were varied from 5 to 40 min and 15 to 70 °C, respectively. Then, the stirrer was stopped, and the hybrid system was centrifuged at 6000 rpm for 5 min to assist in separation of organic and aqueous phases. After phase separation, the concentration of lactic acid in raffinate was analyzed immediately. For the stripping experiment, the loaded organic phase was allowed to come in contact with sodium

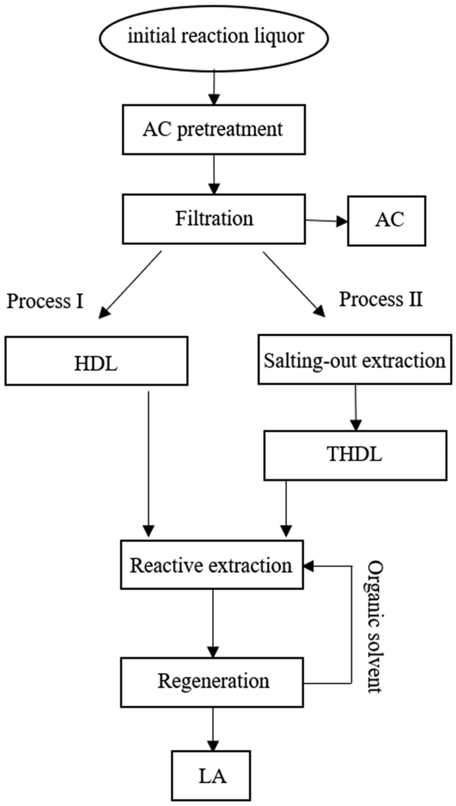

Figure 7. Schematic flowsheet of recovery processes.

hydroxide solution in a centrifuge tube. The extraction time and temperature were 30 min and 25 °C, respectively. The followed treatment and analysis processes were consistent with the above extraction experiment.

Process II was proposed by adding a salting-out extraction step between the simple activated carbon treatment and the reactive extraction. THF/NaCl, as the salting-out extraction system, was employed in this procedure. Compared to the conventional ethanol salting-out extraction system,[46] THF had a lower boiling point and stronger volatility, which could be removed more easily. The process was as follows: first, the pH of the filtrate was regulated to 1.4 by adding a diluted sulfuric acid, and then sodium chloride was added. The weight ratio of filtrate to sodium chloride was 3:1. Second, tetrahydrofuran was added, and the separatory funnel was shaken for 5 min; then, the top phase was collected, and this operation was repeated five times. Finally, the collected top phase was evaporated to remove THF and then diluted to the initially added HDL volume by deionized water to obtain THDL to make a little difference in the concentration of lactic acid between THDL and HDL. The followed processes of liquid−liquid reactive extraction of lactic acid from THDL were consistent with that from HDL described above.

4.4. Analysis. The quantitative analysis of lactic acid was performed by HPLC using Shimadzu liquid chromatography (column: MCIGEL CRS10W 50 × 4.6 mm) with a UV detector whose wavelength was set at 254 nm. The mobile phase was a 1 mM copper sulfate aqueous solution with flow rate of 0.3 mL min^{-1}. The detection temperatures of the column and the UV detector were 35 and 40 °C, respectively. In addition, the HPX-87 analytical column was used to analyze simultaneously the sugar and sugar degradation products in liquid samples, and the column was maintained at 50 °C with a 5 mM H_2SO_4 eluent at a flow rate of 0.6 mL min^{-1}. The external standard method was adopted to quantify the products using calibration curves from standard samples (e.g., lactic acid), which was based on the functional relationship between the response value of the standard sample and the concentration of the standard substance to calculate the concentration of the detected component in the unknown samples. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was applied to analyze the ion content of the samples. All experiments were performed three times, and the relative deviations were found to be within 1.5%. The graph showed the average of three experimental data.

The concentration of lactic acid transferred to the organic phase was calculated by a mass balance (eq 1). According to the concentration of lactic acid in the organic and aqueous phases, the distribution coefficient (K_D) can be defined as the ratio of lactic acid concentration in the organic phase to that in the aqueous phase, which could be calculated by eq 2.

$$([\mathrm{LA}]_{\mathrm{org}})_{\mathrm{eq}} = \frac{([\mathrm{LA}]_{\mathrm{aq}} V_{\mathrm{aq}})_{\mathrm{initial}} - ([\mathrm{LA}]_{\mathrm{aq}} V_{\mathrm{aq}})_{\mathrm{eq}}}{(V_{\mathrm{org}})_{\mathrm{eq}}} \tag{1}$$

$$K_D = \left(\frac{[\mathrm{LA}]_{\mathrm{org}}}{[\mathrm{LA}]_{\mathrm{aq}}}\right)_{\mathrm{eq}} \tag{2}$$

The phase ratio (O/A) can be defined as the ratio of volume of the organic phase to that of the aqueous phase.

$$\mathrm{O/A} = \left(\frac{[V]_{\mathrm{org}}}{[V]_{\mathrm{aq}}}\right)_{\mathrm{initial}} \tag{3}$$

The extraction efficiency (E) can be defined as the ratio of lactic acid mass in the organic phase to that in the aqueous phase, which could be calculated by eq 4.

$$E = \frac{([\mathrm{LA}]_{\mathrm{org}} V_{\mathrm{org}})_{\mathrm{eq}}}{([\mathrm{LA}]_{\mathrm{aq}} V_{\mathrm{aq}})_{\mathrm{initial}}} \times 100\% \tag{4}$$

The undissociated rate (I) of lactic acid can be calculated using eq 5.

$$I = \left(1 - \frac{1}{1 + 10^{\mathrm{p}K_a - \mathrm{pH}}}\right) \times 100\% \tag{5}$$

where $[\mathrm{LA}]_{\mathrm{aq}}$ and V_{aq} represent the concentration of lactic acid and the volume of the aqueous phase, respectively. $[\mathrm{LA}]_{\mathrm{org}}$ and V_{org} represent the concentrations of lactic acid and the volume of the organic phase, respectively. Subscripts "initial" and "eq" represent the initial and equilibrium states, respectively.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J., Jr; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; et al. The path forward for biofuels and biomaterials. *Science* **2006**, *311*, 484−489.

(2) Kumar, P.; Barrett, D. M.; Delwiche, M. J.; Stroeve, P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Ind. Eng. Chem. Res.* **2009**, *48*, 3713−3729.

(3) Yang, L.; Su, J.; Carl, S.; Lynam, J. G.; Yang, X.; Lin, H. Catalytic conversion of hemicellulosic biomass to lactic acid in pH neutral aqueous phase media. *Appl. Catal., B* **2015**, *162*, 149−157.

(4) He, T.; Jiang, Z.; Wu, P.; Yi, J.; Li, J.; Hu, C. Fractionation for further conversion: from raw corn stover to lactic acid. *Sci. Rep.* **2016**, *6*, No. 38623.

(5) Chambon, F.; Rataboul, F.; Pinel, C.; Cabiac, A.; Guillon, E.; Essayem, N. Cellulose hydrothermal conversion promoted by heterogeneous brønsted and lewis acids: Remarkable efficiency of solid lewis acids to produce lactic acid. *Appl. Catal., B* **2011**, *105*, 171−181.

(6) Wang, F.-F.; Liu, C.-L.; Dong, W.-S. Highly efficient production of lactic acid from cellulose using lanthanide triflate catalysts. *Green Chem.* **2013**, *15*, No. 2091.

(7) Mandegari, M. A.; Farzad, S.; van Rensburg, E.; Görgens, J. F. Multi-criteria analysis of a biorefinery for co-production of lactic acid and ethanol from sugarcane lignocellulose. *Biofuels, Bioprod. Biorefin.* **2017**, *11*, 971−990.

(8) Abdel-Rahman, M. A.; Sonomoto, K. Opportunities to overcome the current limitations and challenges for efficient microbial production of optically pure lactic acid. *J. Biotechnol.* **2016**, *236*, 176−192.

(9) Vijayakumar, J.; Aravindan, R.; Viruthagiri, T. Recent trends in the production, purification and application of lactic acid. *Chem. Biochem. Eng. Q.* **2008**, *22*, 245−264.

(10) Von Frieling, P.; Schügerl, K. Recovery of lactic acid from aqueous model solutions and fermentation broths. *Process Biochem.* **1999**, *34*, 685−696.

(11) Pleissner, D.; Qi, Q.; Gao, C.; Rivero, C. P.; Webb, C.; Lin, C. S. K.; Venus, J. Valorization of organic residues for the production of added value chemicals: A contribution to the bio-based economy. *Biochem. Eng. J.* **2016**, *116*, 3−16.

(12) Delgado, J. A.; Águeda, V. I.; Uguina, M. Á.; García, Á.; Matarredona, J.; Moral, R. Modeling of the separation of lactic acid from an aqueous mixture by adsorption on polyvinylpyridine resin and desorption with methanol. *Sep. Purif. Technol.* **2018**, *200*, 307−317.

(13) Pradhan, N.; Rene, E.; Lens, P.; Dipasquale, L.; D'Ippolito, G.; Fontana, A.; Panico, A.; Esposito, G. Adsorption behaviour of lactic acid on granular activated carbon and anionic resins: Thermodynamics, Isotherms and Kinetic Studies. *Energies* **2017**, *10*, No. 665.

(14) Stassin, T.; Reinsch, H.; Voorde, B. V.; Wuttke, S.; Medina, D. D.; Stock, N.; Bein, T.; Ameloot, R.; Vos, D. D. Adsorption and reactive desorption on metal-organic frameworks: A direct strategy for lactic acid recovery. *ChemSusChem* **2016**, *10*, 643−650.

(15) Roque, L.; Escudero, I.; Benito, J. M. Separation of sodium lactate from Span 80 and SDS surfactants by ultrafiltration. *Sep. Purif. Technol.* **2017**, *180*, 90−98.

(16) Geanta, R. M.; Olga Ruiz, M.; Escudero, I. Micellar-enhanced ultrafiltration for the recovery of lactic acid and citric acid from beet molasses with sodium dodecyl sulphate. *J. Membr. Sci.* **2013**, *430*, 11−23.

(17) Wang, Q.; Cheng, G.; Sun, X.; Jin, B. Recovery of lactic acid from kitchen garbage fermentation broth by four-compartment configuration electrodialyzer. *Process Biochem.* **2006**, *41*, 152−158.

(18) Hu, Y.; Kwan, T. H.; Daoud, W. A.; Lin, C. S. K. Continuous ultrasonic-mediated solvent extraction of lactic acid from fermentation broths. *J. Clean. Prod.* **2017**, *145*, 142−150.

(19) Kumar, R.; Mahajani, S. M. Esterification of lactic acid with n-butanol by reactive distillation. *Ind. Eng. Chem. Res.* **2007**, *46*, 6873−6882.

(20) Komesu, A.; Wolf Maciel, M. R.; Rocha de Oliveira, J. A.; da Silva Martins, L. H.; Maciel Filho, R. Purification of lactic acid produced by fermentation: Focus on non-traditional distillation processes. *Sep. Purif. Rev.* **2016**, *46*, 241−254.

(21) Wasewar, K. L.; Yawalkar, A. A.; Moulijn, J. A.; Pangarkar, V. G. Fermentation of glucose to lactic acid coupled with reactive extraction: A review. *Ind. Eng. Chem. Res.* **2004**, *43*, 5969−5982.

(22) Kahya, E.; Bayraktar, E.; Glu, U. M. Optimization of process parameters for reactive lactic acid extraction. *Turk. J. Chem.* **2001**, *25*, 223−230.

(23) Winkelman, J. G.; Schuur, B.; Heeres, H. J.; Yue, J. Lactic acid extraction and mass transfer characteristics in slug flow capillary microreactors. *Ind. Eng. Chem. Res.* **2016**, *55*, 4691−4702.

(24) Aimer, M.; Klemm, E.; Langanke, B.; Gehrke, H.; Stubenrauch, C. Reactive extraction of lactic acid by using tri-n-octylamine: structure of the ionic phase. *Chem. - Eur. J.* **2016**, *22*, 3268−3272.

(25) Udachan, I. S.; Sahoo, A. K. A study of parameters affecting the solvent extraction of lactic acid from fermentation broth. *Braz. J. Chem. Eng.* **2014**, *31*, 821−827.

(26) Labbaci, A.; Kyuchoukov, G.; Albet, J.; Molinier, J. Detailed investigation of lactic acid extraction with tributylphosphate dissolved in dodecane. *J. Chem. Eng. Data* **2010**, *55*, 228−233.

(27) Wasewar, K. L.; Heesink, A. B. M.; Versteeg, G. F.; Pangarkar, V. G. Intensification of conversion of glucose to lactic acid: equilibria and kinetics for back extraction of lactic acid using trimethylamine. *Chem. Eng. Sci.* **2004**, *59*, 2315−2320.

(28) Kyuchoukov, G.; Yankov, D. Theoretical and experimental study of lactic acid stripping from loaded organic phase. *Ind. Eng. Chem. Res.* **2010**, *49*, 8238−8243.

(29) Joglekar, H. G.; Rahman, I.; Babu, S.; Kulkarni, B. D.; Joshi, A. Comparative assessment of downstream processing options for lactic acid. *Sep. Purif. Technol.* **2006**, *52*, 1−17.

(30) Yang, G.; Jahan, M. S.; Ahsan, L.; Ni, Y. Influence of the diluent on the extraction of acetic acid from the prehydrolysis liquor of kraft based dissolving pulp production process by tertiary amine. *Sep. Purif. Technol.* **2013**, *120*, 341−345.

(31) Fleitlikh, I. Y.; Kuznetsov, B. N.; Nikiforova, L. K.; Grigorieva, N. A.; Beregovtsova, N. G. Lactic acid extraction in systems containing organic amines. *Ind. Eng. Chem. Res.* **2018**, *57*, 1331−1336.

(32) Kyuchoukov, G.; Yankov, D.; Albet, J.; Molinier, J. Mechanism of lactic acid extraction with quaternary ammonium chloride (Aliquat 336). *Ind. Eng. Chem. Res.* **2005**, *44*, 5733−5739.

(33) Hossain, M. M.; Maisuria, J. L. Effects of organic phase, fermentation media, and operating conditions on lactic Acid extraction. *Biotechnol. Prog.* **2008**, *24*, 757−765.

(34) Krzyżaniak, A.; Leeman, M.; Vossebeld, F.; Visser, T. J.; Schuur, B.; de Haan, A. B. Novel extractants for the recovery of fermentation derived lactic acid. *Sep. Purif. Technol.* **2013**, *111*, 82−89.

(35) Matsumoto, M.; Takahashi, T.; Fukushima, K. Synergistic extraction of lactic acid with alkylamine and tri-n-butylphosphate: effects of amines, diluents and temperature. *Sep. Purif. Technol.* **2003**, *33*, 89−93.

(36) Xu, S.; Lan, K.; Li, J.; He, T.; Hu, C. Separation of lactic acid from synthetic solutions and the mixture directly derived from corn stover by aqueous two phase extraction. *Sep. Purif. Technol.* **2018**, *204*, 281−289.

(37) Kim, G. H.; Park, S. J.; Um, B. H. Response surface methodology for optimization of solvent extraction to recovery of acetic acid from black liquor derived from Typha latifolia pulping process. *Ind. Crops Prod.* **2016**, *89*, 34−44.

(38) Yousuf, A.; Bonk, F.; Bastidas-Oyanedel, J. R.; Schmidt, J. E. Recovery of carboxylic acids produced during dark fermentation of

food waste by adsorption on Amberlite IRA-67 and activated carbon. *Bioresour. Technol.* **2016**, *217*, 137−140.

(39) Cebreiros, F.; Guigou, M. D.; Cabrera, M. N. Integrated forest biorefineries: Recovery of acetic acid as a by-product from eucalyptus wood hemicellulosic hydrolysates by solvent extraction. *Ind. Crops Prod.* **2017**, *109*, 101−108.

(40) Kim, S. J.; Kwon, H. S.; Kim, G. H.; Um, B. H. Green liquor extraction of hemicellulosic fractions and subsequent organic acid recovery from the extracts using liquid−liquid extraction. *Ind. Crops Prod.* **2015**, *67*, 395−402.

(41) Um, B.-H.; Friedman, B.; van Walsum, G. P. Conditioning hardwood-derived pre-pulping extracts for use in fermentation through removal and recovery of acetic acid using trioctylphosphine oxide (TOPO). *Holzforschung* **2011**, *65*, 51−58.

(42) Tik, N.; Bayraktar, E.; Mehmetoglu, Ü. In situ reactive extraction of lactic acid from fermentation media. *J. Chem. Technol. Biotechnol.* **2001**, *76*, 764−768.

(43) Fu, H.; Sun, Y.; Hu, T.; Zhang, D.; Xiu, Z. Salting-out extraction of carboxylic acids. *Sep. Purif. Technol.* **2015**, *139*, 36−42.

(44) Aydoğan, Ö.; Bayraktar, E.; Mehmetoğlu, Ü. Aqueous two-phase extraction of lactic acid: optimization by response surface methodology. *Sep. Sci. Technol.* **2011**, *46*, 1164−1171.

(45) Song, Z. Y.; Sun, Y. Q.; Wei, B. C.; Xiu, Z. L. Two-step salting-out extraction of 1,3-propanediol and lactic acid from the fermentation broth of Klebsiella pneumoniae on biodiesel-derived crude glycerol. *Eng. Life Sci.* **2013**, *13*, 487−495.

(46) Wei, B. C.; Song, Z. Y.; Sun, Y. Q.; Xiu, Z. L. Salting-out extraction of lactic acid from fermentation broth. *Chin. J. Process Eng.* **2012**, *12*, 44−48.

(47) Wasewar, K. L.; Pangarkar, V. G.; Heesink, A. B. M.; Versteeg, G. F. Intensification of enzymatic conversion of glucose to lactic acid by reactive extraction. *Chem. Eng. Sci.* **2003**, *58*, 3385−3393.

(48) Yankov, D.; Molinier, J.; Kyuchoukov, G.; Albet, J.; Malmary, G. Improvement of the lactic acid extraction. Extraction from aqueous solutions and simulated fermentation broth by means of mixed extractant and TOA, partially loaded with HCl. *Chem. Biochem. Eng. Q.* **2005**, *19*, 17−24.

(49) San-Martín, M.; Pazos, C.; Coca, J. Reactive extraction of lactic acid with Alamine 336 in the presence of salts and lactose. *J. Chem. Technol. Biotechnol.* **1992**, *54*, 1−6.

(50) Tamada, J. A.; King, C. J. Extraction of carboxylic acids with amine extractants. Effect of temperature, water coextraction, and process considerations. *Ind. Eng. Chem. Res.* **1990**, *29*, 1333−1338.

(51) Ahsan, L.; Jahan, M. S.; Ni, Y. Recovery of acetic acid from the prehydrolysis liquor of kraft based dissolving pulp production process: sodium hydroxide back extraction from the Trioctylamine/Octanol system. *Ind. Eng. Chem. Res.* **2013**, *52*, 9270−9275.

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