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Preparation of calcium carbonate and hydrogen chloride from distiller waste based on reactive extraction–crystallization process

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HIGHLIGHTS

- A novel route was proposed based on a reactive extraction–crystallization process.
- Calcite and HCl gas were produced with CO_2 fixed in this process integration.
- The atom utilization is 100% and the transformation efficiency of DW is high.
- The multiphase process was studied and optimal reaction conditions and the mechanism were given.

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ABSTRACT

The distiller waste containing mainly calcium chloride ($CaCl_2$) is being discharged in the Solvay process, and it has not been recycled comprehensively. In this study, a novel route for the treatment of the distiller waste was developed, in which $CaCl_2$ solution was transformed into calcium carbonate and hydrogen chloride based on a reactive extraction–crystallization process using N235–isoamyl alcohol as the extraction system. Experimental results showed that the optimum conditions were 240 min as reaction time, 20 °C as the best temperature, 1.0 mol L^{-1} as initial concentration of $CaCl_2$, 50% volume fraction of N235, 2:1 as the best phase ratio, and one-time feeding pattern. The conversion rate of $CaCl_2$ was up to 75% under the optimized conditions; moreover, the concentration of H^+ in organic phase was 0.70 mol L^{-1} and rhomibic calcite of high purity could be obtained. The products were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and thermogravimetry/differential scanning calorimetry. The extraction mechanism involved the ion-pair formation and the extraction complex $R_3N{\cdot}HCl$ was determined by saturation method. The enthalpy change of the overall reaction ΔH was -36.47 kJ mol^{-1}, indicating that it was an exothermic reaction with the possibility of getting hindered at high temperature.

1. Introduction

The past five years have seen significant increase in the global needs for soda from 44 to 53 Mt [1]. In China, the total output of soda was 22.36 Mt in 2011 [2], half of which was produced by ammonia–soda process [3]. About 10 m^3 of distiller waste is discharged while 1 ton of soda is produced in the ammonia–soda process [4]. Nowadays, waste liquids in most cases are directly discharged as sewage to the nearest river, lake, or sea and the residue is usually stacked. Therefore, it leads to environmental pollution posing serious health hazards and serious waste of resources. It has become a potential problem to the soda industry [5,6] and has created a number of practical issues.

The main components of the distiller waste are calcium chloride ($CaCl_2$, 90–120 g L^{-1}) and unreacted sodium chloride (NaCl, 40–50 g L^{-1}). Scholars around the world have made significant contributions in the treatment of the distiller waste. Kasikowski et al. [7] in Poland presented five methods in details to reduce the negative influence of soda ash factories on the natural environment. The production of calcium–magnesium phosphates [8] and gypsum for building [9,10] proved to have a positive financial effect on the soda plants in Poland as well as being well justified economically. The application of neutralization of combustion gases [11] was still investigated in the laboratory. Some researches were focused on the reactive crystallization processes, in which calcium sulfate dehydrate [12] and calcium carbonate with various morphologies were obtained, respectively [13,14]. Although there are numerous processes dealing with distiller waste, the industrial application nowadays is mainly focused on the recycling of $CaCl_2$ which is

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low value-added and its market is depressing [15]. Therefore, significant amount of distiller waste is still not used comprehensively.

The coupled process has been a hotspot in the field of chemical engineering. Liquid–liquid extraction, combined with chemical reaction, can improve the overall yields of the product [16,17]. In this study, a novel coupled process route for the comprehensive utilization of distiller waste was proposed to mollify the above-mentioned contradiction. When the extractant N235-a mixture of tertiary amines and the diluent-isoamyl alcohol were added to the $CaCl_2$ solution with carbon dioxide (CO_2) passing through at the same time, the reaction generating calcium carbonate ($CaCO_3$) and hydrogen chloride (HCl) could be carried forward because the organic tertiary amine could remove HCl out of the aqueous solution. Moreover, the extractant could be recycled and reused after the extract complex was heated, which will be reported later. This similar idea of coupled process was first proposed by Kosswig and Praun [18] exactly in the soda industry. They presented a new process to produce soda using organic amines which could be recycled through distillation instead of inorganic ammonia. Later, Xu et al. [19] developed this method based on the study of Kosswig and examined the most suitable technological conditions for the coupled process in a series of laboratory experiments. Moreover, this coupled process using organic amine as a solvent extractant was frequently applied for the production of formic acid [20] and strontium carbonate [21]. However, utilization of distiller waste by the coupled process has rarely been studied and documented and the extraction mechanism was investigated not combing with the coupled process but just in the conventional way. Besides, the crystallization process was, in general, ignored in the previous reports.

In this study, a reactive extraction–crystallization coupled process was investigated systematically and optimal conditions were determined. The products were analyzed by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetry/differential scanning calorimetry (TG/DSC) and the mechanism was illustrated. The coupled process is expected to offer a reference for the industrial application. Moreover, CO_2 was exploited and fixed in this process integration, which is a type of CO_2 sequestration [22] by mineral carbonation for the reduction of CO_2 emissions into the atmosphere. This study provides a new perspective to the understanding of utilization of distiller waste by the coupled process.

2. Experimental

2.1. Materials and apparatus

Anhydrous $CaCl_2$ (purity ⩾96.0%, Shanghai Ling Feng Chemical Reagent Co., Ltd.) was employed in this study, isoamyl alcohol (purity ⩾98.5%, Shanghai Ling Feng Chemical Reagent Co., Ltd.) was used as the diluent, and a commercial tertiary amine, namely, N235 (Shanghai Rare-earth Chemical Co., Ltd.) was used as the extractant. Anhydrous ethanol (purity ⩾99.5, Shanghai Titan Scientific Co., Ltd.) and sodium hydroxide (NaOH, purity ⩾96.0%, Shanghai Ling Feng Chemical Reagent Co., Ltd.) were employed in the titration of organic samples.

The primary experimental devices are a homemade-jacked reactor, a high precision low temperature thermostat (Ningbo Tianheng Instrument Factory), and a precision power electric blender (RW20, IKA), as shown in Fig. 1.

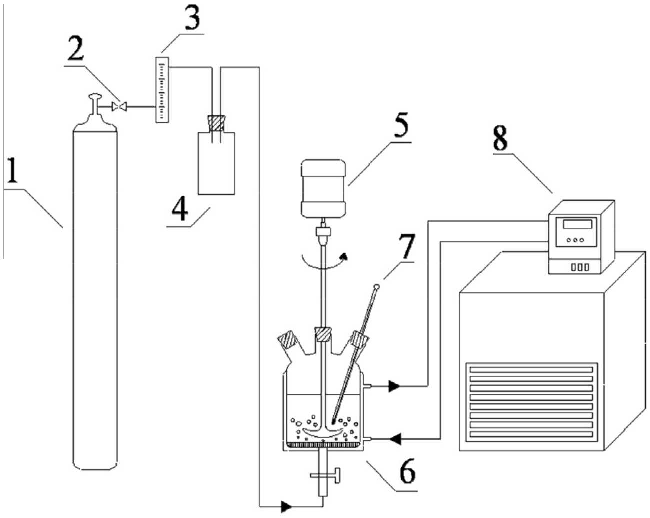

Fig. 1. Schematic illustration of the device employed in the coupled process 1-CO_2 gas; 2-reducing valve; 3-gas flowmeter; 4-buffer; 5-stirring motor; 6-jacked reactor; 7-thermometer; and 8-thermostatic bath.

2.2. Experimental method

$CaCl_2$ solution, N235, and isoamyl alcohol were added into a homemade-jacked reactor with the sparging of pure CO_2. The suspension was filtered and the solid was washed with anhydrous ethanol and deionized water and then dried at 60 °C in a dryer. The leachate was separated in a separating funnel after 12 h. A few experiments were performed in duplicate, and consistency was within 5%. The concentration of acid in organic phase was determined by titration dissolving in ethanol with a calibrated NaOH solution. The conversion rate of $CaCl_2$ can be calculated by using the following expression:

$$\varepsilon(\mathrm{CaCl_2}) = \frac{V_{(o)} \cdot c(\mathrm{H^+})_{(o)}}{2V_{(aq)} \cdot c(\mathrm{CaCl_2})_{(init)}} \tag{1}$$

where $\varepsilon(\mathrm{CaCl_2})$ is the conversion rate of $CaCl_2$, $V_{(o)}$ is the volume of organic phase, $c(\mathrm{H^+})_{(o)}$ is the equilibrium concentration of acid in organic phase, $V_{(aq)}$ is the initial volume of aqueous phase, and $c(\mathrm{CaCl_2})_{(init)}$ is the initial concentration of $CaCl_2$.

2.3. Characterization

The crystal structure of the product was examined by XRD (D/MAX-B, Rigaku Co., Japan). Morphology of $CaCO_3$ microspheres was characterized by SEM (Quanta 250, FEI Co., US). The extracted organic phase was analyzed by FTIR (Spectrum 1, PerkinElmer Co., US). The thermal analysis of $CaCO_3$ was performed by TG/DSC (STA 449, NETZSCH Co., GER). Particle size distribution of $CaCO_3$ was determined by a Malvern particle size analyzer (Mastersizer 2000, Malvern Co., UK).

3. Results and discussion

3.1. Optimization of the conditions for the reactive extraction–crystallization process

The effects on the reactive extraction–crystallization process were quantified by single-factor experiments in order to determine the optimal conditions for the coupled process.

3.1.1. Effect of reaction time

The reaction equilibrium was achieved after a long contact time due to the complicated gas–liquid–liquid–solid phase system. The relationship between the concentration of hydrogen ions (H^+) in organic phase and reaction time is shown in Fig. 2 at different initial concentrations of $CaCl_2$.