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Rapid separation of organic compounds using continuous supercritical CO_2/liquid extraction process using micromixer

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Abstract

Apparatus for continuous supercritical CO_2/liquid extraction was developed. Aqueous solution which contains a target material is continuously mixed with supercritical CO_2 using a micromixer. The mixed solution is continuously separated in a developed separator; the level of liquid is controlled at a fixed height by differential pressure between top of the separator (CO_2 phase) and the hydraulic head pressure. The target material in CO_2 is continuously mixed with a good solvent and recovered as solution.

As an example, vanillin extraction from black liquor discharged in a paper manufacturing plant was investigated using the apparatus at an extraction condition of 40 °C and 20 MPa. Vanillin was mainly extracted to supercritical CO_2 phase. More than 75% of vanillin was extracted to supercritical CO_2 phase when CO_2/black liquor ratio of 4 (mass base).

As another example, a biphenyl compound extraction from model liquid solution of a cross-coupling reaction, which contains salts at high concentration, was investigated using the apparatus at the extraction conditions of 40 °C and 20 MPa. The target biphenyl compound was successfully extracted to CO_2 phase (yield is over 85%) and almost salts were remained in liquid phase.

Introduction

Both in bulk and fine chemical manufacturing, an environmentally benign and continuous separation process is desired. Extraction using supercritical CO_2 as solvent (SFE; supercritical fluid extraction) is one of the candidates of such process. CO_2 is not toxic but has very similar physical properties to that of organic solvents, thus supercritical

CO_2 has been viable alternative of organic solvent. Although there have been various reports on SFE [1, 2], batch type process is majority. However, continuous SFE processes have been reported, recently. Dominguez et al. have used micro mixer for ethanol extraction from aqueous ethanol solution and succeeded in extracting ethanol in a few seconds [3]. In the process, however, separation process is batch type. On the other hand, Ota et al. have reported on continuous SFE system, where separation is also conducted continuously [4]. They use two backpressure regulators, which function alternately by temporal difference. In their system, extraction and separation are conducted continuously, but the throughput is limited and may be difficult to satisfy commercialization.

In this study, we have developed an apparatus for continuous supercritical CO_2/liquid extraction. This apparatus enabled rapid extraction and continuous separation with higher throughput. In the presentation, overview of the continuous extraction and separation system, and its applications will be shown.

Materials and methods

The schematic diagram for the continuous extraction and separation system is shown in **Figure 1**. A liquid solution and CO_2 are separately pumped and mixed in a low-dead-volume tee (SWAGELOK Co. Ltd., i.d. 0.3 mm). The mixed fluid enters a separation cell. In the cell it separates into a CO_2-rich phase and a liquid-rich phase. Since the fluid level is proportional to the differential pressure between the head pressure and the supercritical CO_2 phase, the fluid level can be controlled by the value of the differential pressure. The control bulb is regulated to maintain a constant value for the differential pressure, which enables controlled liquid level in the separation cell. The pressure is controlled by a backpressure regulator in the CO_2 line. Before depressurization, a solvent is introduced to avoid precipitation in the CO_2 depressurization process. Effluents were sampled three times for 10 min each.

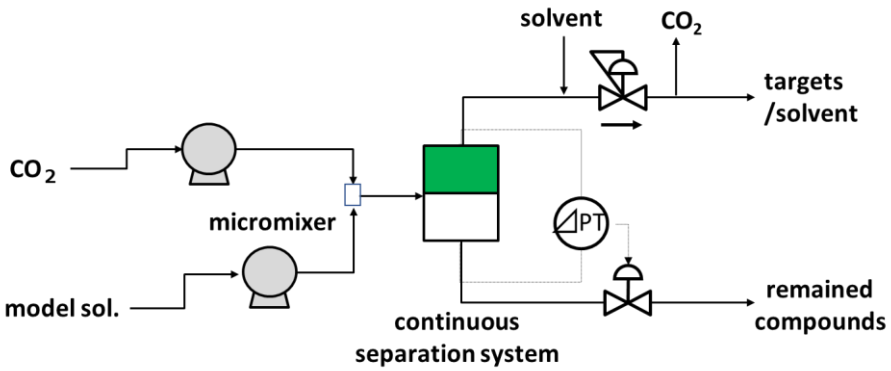

Figure 1. Schematic diagram for the continuous extraction and separation system

Results

First, 1 wt% vanillin aqueous solution was processed at 40 °C and 20 MPa. The vanillin solution and CO_2 flow rate were set at 10 and 40 g/min, respectively. Yield in CO_2 phase was 0.742, which was over 97% equilibrium value calculated based on a previous research on vanillin-CO_2-H_2O system [5], where equilibrium value was obtained in about 2 h. In this study the residence time from mixing point to separation cell is about 10 s, which indicates that our system realized much faster extraction.

Black liquor filtrate was also processed. Black liquor filtrate is produced as a byproduct of paper manufacturing process, and it contains vanillin and its related compounds, which are valuable materials for fine chemicals. The black liquor filtrate used in this study was given by a paper manufacturing company, and it contained about 0.1 wt% of vanillin, its related compounds, and more than 5 wt% salts. The SFE/separation was done for the black liquor filtrate at 40 °C and 20 MPa. The flow rate of black liquor filtrate and that of CO_2 were set at 10 and 40 g/min, respectively. Yield of vanillin in CO_2 phase was 0.754; the value is similar to that of vanillin extraction from 1 wt% vanillin aqueous solution shown above, which suggests that the SFE/separation system can work properly for the black liquor filtrate as an example of real waste solutions.

As another example, a model solution obtained after an organic reaction, cross-coupling reaction, was processed by our SFE/separation apparatus. The model solution was the mixed solution of ethanol and water (50vol/50vol) and it contains 0.38 wt% 4-cyanobiphenyl, 0.32 wt% K_2CO_3, 0.22 wt% $KHCO_3$, 0.28 wt% KBr and 0.14 wt% $B(OH)_3$. The SFE/separation was conducted for the model solution at 40 °C and 20 MPa. The flow rate of the model solution and that of CO_2 were set at 10 and 20 g/min, respectively. Yield of 4-cyanobiphenyl in CO_2 phase was 0.898 and almost salts were recovered in liquid phase, which indicates that the target material, 4-cyanobiphenyl, was successfully separated from salts with over 85% recovery rate.

Conclusion

An experimental apparatus was developed for rapid and continuous supercritical CO_2 extraction and separation of hydrophobic organic compounds from liquid solutions. Almost equilibrium yield of vanillin can be achieved within 10 s. The apparatus is applicable to black liquor filtrate which is aqueous solution that contains vanillin, its related compounds and salts, and over 75% vanillin was extracted to CO_2 phase. Further, the apparatus is applicable to ethanol and water mixed solution which contains biphenyl

and salts, and over 85% biphenyl was extracted to CO_2 phase and separated from salts.

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