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The Study of Fluid Dynamics in Countercurrent Multi-Stage Micro-Extraction System

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Abstract

Compare to the conventional extraction systems, the microextractoin systems are more efficient. However, difficulty in achieving countercurrent two-phase flow is a barrier to its application. The human cardiovascular system gives us inspiration to solve the problem in the micro-fluidic system. In our previous work, a bionic system simulating the cardiovascular system was built to realize a countercurrent multi-stage micro-extraction. We mainly studied the fluid dynamics of the two phase flow in the system in the present work.

TBP-kerosene/water two phase system was used as the test system. The pressure on several key points of the system was measured by pressure sensors and the pressure-flow relationship was investigated under different flow ratio, pulse frequency and stroke. The pressure at all points changed continuously and periodically. When the pulse frequency was increased, the amplitude of the pressure change gets bigger. The reason was that the flow velocity in the system get higher and flow resistance caused the increasing of the pressure amplitude.

Keywords: fluid dynamics; micro-extraction; countercurrent; multi-stage; pressure

1. Introduction

Liquid-liquid extraction is a key process in the spent fuel reprocessing (SFR) and is also the only separation technology which has been used in the industrial SFR. Even so, conventional extraction systems, such as mixer-settlers, pulse columns, and centrifugal contactors, suffer from low efficiency, high energy consumption, large equipment dimensions, and high critical danger. Comparably, the micro-

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extraction systems are more efficient. In the past decade, microfluidic devices have been the focus of numerous studies because of their high efficiency, safety, repeatability and facile controllability. [1] At present significant advances have been made in the use of microfluidic devices for controlling multiphase flow. Numerous studies on microfluidic flow patterns such as drop flow, slug flow and co-laminar flow [2-6] have been done. Because of the precise shape controlling, large interfacial area, and high mass transfer performance, these flow patterns have been widely used for chemical reaction, [7, 8] crystallization, [9] nanoparticle synthesis, [10-13] structural material preparation [14-19], biological analysis, [20] and liquid-liquid extraction. [21-27] Especially for liquid-liquid extraction, high speed and high performance can be achieved by the microextraction system, benefiting from the large specific interface area, the large interface-to-volume ratio, and the short diffusion distance which results in a short diffusion time. Comparing to the conventional extraction systems, such as mixer-settlers, pulse columns, and centrifugal contactors, the microextractoin systems are more efficient: they can reach high extraction performance without any mechanical stirring, mixing, or shaking and can be integrated with other operation units in a small space to realize a plant on table. Owing to these advantages, microextraction has been used in the separation of metal ions [21, 22], the detection of pesticide [23], the optical resolution of amino acids [24], the separation of steroids [25], the clean-up of alkaloids [26], and the separation of proteins [27].

The feasibility of microextraction in chemical processes, however, is still limited by some other factors. The existing microextraction systems are mostly cocurrent-flow operated. Though the mass transfer speed is much faster than that of the conventional extractors, the recovery efficiency of the cocurrent solvent extraction on microscale can reach no higher than that of a conventional device with a single theoretical separation stage. To increase recovery efficiency, countercurrent flow of two immiscible liquids to achieve multi-stage extraction is often used. In fact, the conventional macroscale extraction systems, which are widely used in the industry, are generally countercurrent-flow operated. However, it is difficult to realize countercurrent flow at the micro-scale because viscosity and surface wetting dominate over gravity and inertial effects. Difficulty in achieving countercurrent two-phase flow has been a barrier to the application of micro-extraction in chemical processes. Some efforts to overcome this problem have been reported. Hibara et al. [28] reported a countercurrent microextraction by two-phase confluence and separation in glass microchips. However, the contact area is small and the flow rate is sufficiently low to achieve relatively high extraction efficiency. To increase the contact area, a countercurrent laminar microflow extraction method was developed by the same group [29]. The countercurrent microflow was realized in a glass microchip which was selectively modified on the lower half of the microchannel. High recovery efficiency was reached when the flow rate was not very high. However, the physical properties of the fluid and the operation conditions are limited in a narrow range in order to keep the laminar interface steady [30-32].

To extend the application field of microextraction, countercurrent flow approach feasible for a wide range of materials and operation conditions is required. Comparing to laminar flow, segmented flow is much easier to control and the operation scope is much larger. Moreover, segmented flow microextraction is more efficient because it facilitates convective mass-transfer between the two phases [2, 7, 33]. If we can combine several segmented flow microextractors into a countercurrent multi-stage extraction system just like the combination of several mixer-settlers which is widely applied in chemical industry (as shown in Fig.1), the high throughput countercurrent microextraction can be realized. The problem within such a system is that a pump is needed for each stage to draw the streams R_{i-1} and E_{i+1} into the ith stage extractor. So many pumps will compose a huge system which is not applicative. The mixer-settler system solves this problem by a specifically designed stirrer in the mixer which provides a pump effect when rotating. But this method is not feasible for the micro-fluidic system because there is no stirrer in the micro-fluidic system. The human cardiovascular system which transports blood to every part of the body gives us inspiration to solve the problem in the micro-fluidic system. In our previous work [34], a bionic system

simulating the cardiovascular system was built to realize a countercurrent multi-stage microextraction. Similar to the cardiovascular system, pulse driving and check-valve controlling were two main factors of the system. In this work, The fluid dynamics of this system was studied by the two phase flow of water-TBP/ kerosene. The operation condition in which a steady countercurrent flow could be maintained was concluded.

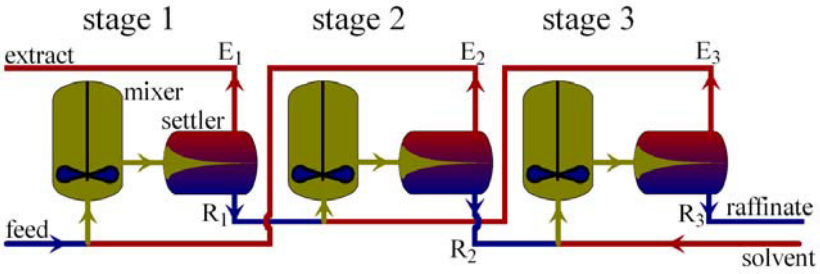

Fig. 1 Multi-stage mixer-settler for countercurrent extraction

2. Experiment

Fig.2 shows the experimental setup of the countercurrent multi-stage micro-extraction system. The system is mainly composed of two parts, the driving part and the function part. The driving part contains six check valves and two pairs of airtight syringes, pair A-B and pair C-D. The two pairs of syringes move in the opposite direction, but the reciprocation frequencies of the two pairs are the same. The strokes and radii of syringes A and C (or B and D) are identical, to ensure equal inlet and outlet flow rates of the aqueous (or organic) phases. Reciprocation of the syringes drives the flow of the two phases while the check valves control the flow direction. Fluid circulates in the system when the syringe pistons move back and forth. The function part is composed of four stages of micro-extractors. Each micro-extractor is composed of two check valves, a micro-contactor and a phase separator. Two check valves are placed at the organic and aqueous inlets to each stage of micro-extractor, preventing back flow of the organic and aqueous liquids.

When the syringe pistons of pair A-B move forward and that of pair C-D move backward, the solvent in syringe B is pushed into the micro-extractor. In the micro-extractor, the solvent passes through check valve at the organic inlet but is stopped by check valve at the aqueous inlet. Thus, all of the solvent flows into the micro-contactor, without backflow to the aqueous phase inlet, and is finally injected into syringe D. Simultaneously, the raffinate in syringe A is pushed into the raffinate collection tank. The syringe pistons then reverse direction and the solvent is drawn from its tank into syringe B. Simultaneously, the aqueous feed in syringe C is pushed into the micro-extractor and finally into syringe A. The extract in syringe D is pushed into the extract collection tank. The total flow rate is determined by the stroke length and frequency. The flow ratio between the two phases can be regulated by changing the stroke lengths or the radii of the syringes (ensure the strokes and radii of syringes A and C (or B and D) be identical).

The experimental setup was arranged on a 20×50 cm panel. The multi-channel contactor was fabricated on a 60×80 mm polymethyl methacrylate (PMMA) sample plate using an end mill and was sealed using another PMMA thin plate (1 mm in thickness) by high-pressure thermal sealing techniques. The upper part of the phase separator was fabricated from Teflon tube and the lower part from stainless steel tube.

On-line Pressure sensors were used to measure the pressure at the inlets and the outlets of the two phases, marked as P_1, P_2, P_3, and P_4. The pressure difference between the inlets and the outlets was calculated from the data. Then, the relation between the average pressure difference and the flow rate of the two phases was studied.

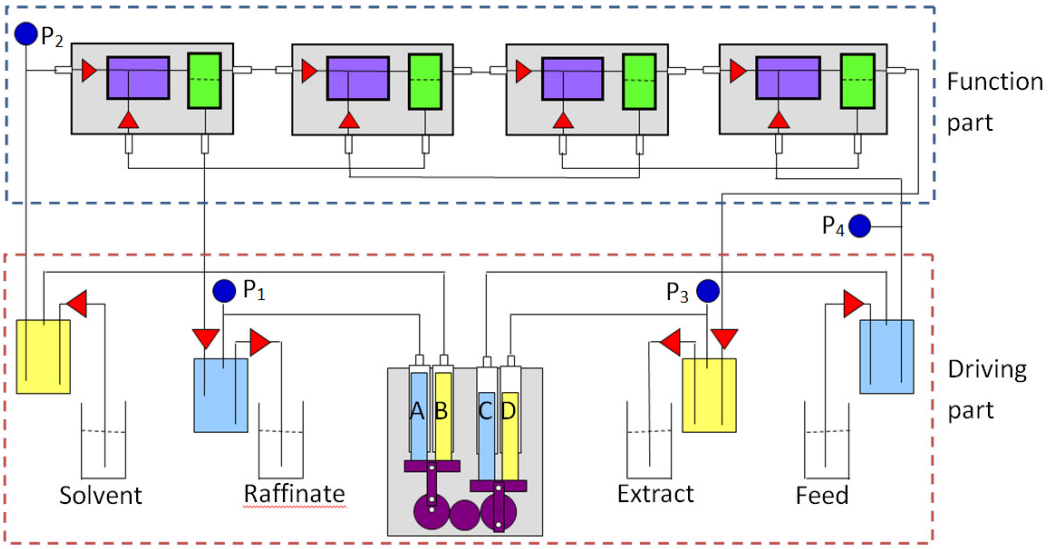

Fig.2 Sketch of the experimental setup

3. Result and discussion

3.1. Pressure curves

The pressure curves was meassured when the system become steady. Fig. 3 showed the pressure curves in different flow ratio when the pulse frequency was at 0.043 s^{-1}, and the stroke of the aqueous phase was 80 μL. The relation between the pressure curves must obey two rules to maintain the countercurrent flow steady:

(1) The relation $P_1 > P_2$ and $P_3 > P_4$ must be ensured throughout the process. This situation can be achieved by adjusting the heights of the four reservoirs. If $P_2 > P_1$, there will be an undesirable flow from the solvent tank to the raffinate tank through the first stage of the extractor, and the same applies to P_3 and P_4.

(2) The curves of P_2 and P_3 must be intersectant and the same applies to P_1 and P_4. The flow of the organic phase is driven by the pressure difference between P_2 and P_3, i.e., $\Delta P_o = P_2 - P_3$ so that the organic phase flows from syringe B to syringe C through the extractors only under the condition $\Delta P_o > 0$. When $\Delta P_o < 0$, the check valves prevent reverse flow of the organic phase. Similarly, the flow of the aqueous phase is driven by the pressure difference $\Delta P_a = P_4 - P_1$. The organic and aqueous phases flow alternately in each period.

We can see that all figures in Fig. 3 obey the two rules. That is to say, the countercurrent micro-flow was steady and the period-average interface location in each phase separator did not visibly change.

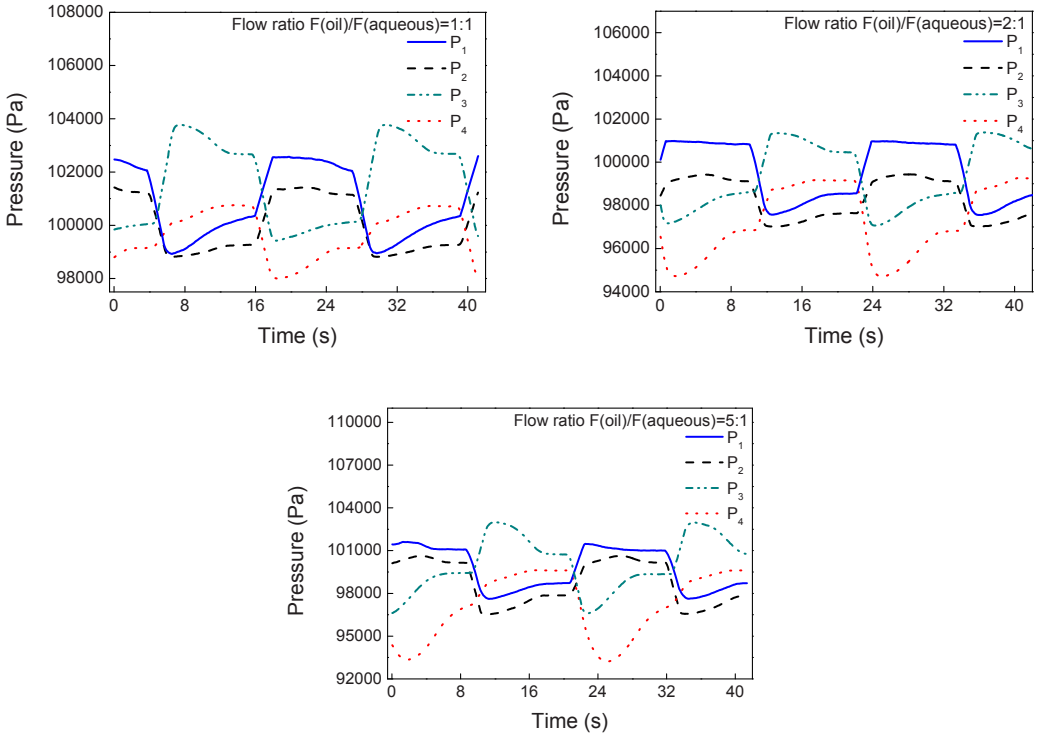

Fig.3 Pressure curves at different flow ratio

3.2. Relation between the pressure difference and the flow rate

The average value of ΔP_o (orΔP_a) at its positive period could be used to characterize the driving force of the organic flow (or the aqueous flow). We can see from Fig. 3 that, the driving forces of the organic flow and the aqueous flow are almost the same for the flow ratio of 1:1. In contrast, the driving force of the organic flow is larger than that of the aqueous flow when the flow ratio is 2:1 and 5:1. There is a monotonic relationship between the flow rate and the driving force. The driving force and the flow rate could be changed by adjusting the stroke or the frequency. Fig. 4 shows the relation between the driving force and the flow rate of the two phases when changing the frequency. We can see that the slope of the aqueous phase curve is larger than that of the organic phase at phase ratio 1:1. The reason is that the total tube length of the aqueous phase is smaller than that of the organic phase and the flow resistance of the aqueous phase is smaller. The slopes of the curves for the organic phase are almost the same due to the constant flow resistance of the organic phase. The curves for the aqueous phase move rightwards when the phase ratio increased. The reason is that the pressure increasing of the organic phase has a resistant effect on the aqueous phase flow.

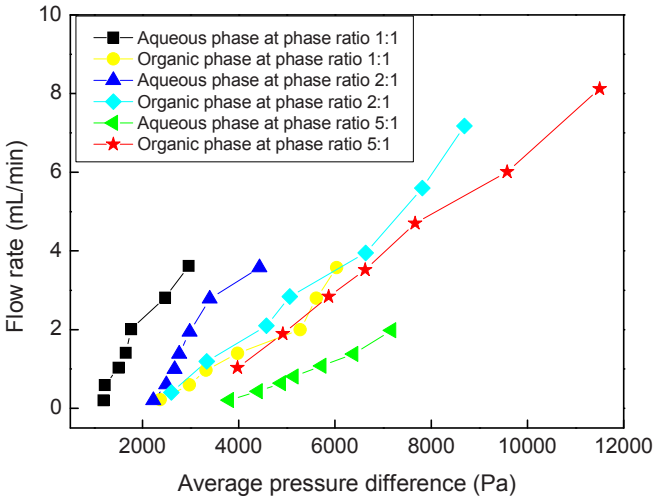

Fig. 4 Relation between the pressure difference and the flow rate

4. Conclusions

A bionic system simulating the cardiovascular system was built to realize a countercurrent multi-stage micro-extraction. The fluid dynamics of the two phase flow in the system was studied. TBP-kerosene/water two phase system was used as the test system. The pressure in the four syringes, which are set at the inlets and outlets of the two phases, were measured by on-line pressure sensors and the pressure-flow relationship was investigated under different flow ratio, pulse frequency and stroke. The pressure at all points changed continuously and periodically. When the pulse frequency was increased, the amplitude of the pressure change gets bigger.

The relation $P_1 > P_2$ and $P_3 > P_4$ must be ensured to maintain a steady countercurrent flow. The curves of P_2 and P_3 (and P_4 and P_1) must be intersectant, so that a driving force is formed to keep the two phase flowing. When increasing the driving force at phase ratio 1:1, the flow rate of the aqueous phase increase faster than that of the organic phase because of the lower flow resistance. The pressure increasing of the organic phase has a resistant effect on the aqueous phase flow.

Acknowledgements

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