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# Simulated moving bed separation of agarose-hydrolyzate components for biofuel production from marine biomass

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ABSTRACT

The economically-efficient separation of galactose, levulinic acid (LA), and 5-hydroxymethylfurfural (5-HMF) in acid hydrolyzate of agarose has been a key issue in the area of biofuel production from marine biomass. To address this issue, an optimal simulated moving bed (SMB) process for continuous separation of the three agarose-hydrolyzate components with high purities, high yields, and high throughput was developed in this study. As a first step for this task, the adsorption isotherm and mass-transfer parameters of each component on the qualified adsorbent were determined through a series of multiple frontal experiments. The determined parameters were then used in optimizing the SMB process for the considered separation. Finally, the optimized SMB process was tested experimentally using a self-assembled SMB unit with four zones. The SMB experimental results and the relevant computer simulations verified that the developed process in this study was quite successful in the economically-efficient separation of galactose, LA, and 5-HMF in a continuous mode with high purities and high yields. It is thus expected that the developed SMB process in this study will be able to serve as one of the trustworthy ways of improving the economic feasibility of biofuel production from marine biomass.



## 1. Introduction

The energy crisis and the environmental pollution due to the depletion of petroleum resources and the combustion of fossil fuels have been a growing worldwide concern [1,2]. This issue has ignited a considerable interest in developing the upcoming alternative energy sources with definite merits in sustainability, environmental friendliness, and economic feasibility [1,2]. One of such energy sources is the biomass-derived biofuel, which has been in the limelight of renewable chemical industries [1–4].

In the initial stages, most of the sources for biofuel production came from land biomasses such as sugar-based, starch-based, and wood-based biomasses [1,5,6]. It is, however, known that such land biomasses can compete with agricultural crops for land or fresh water, which has the potential to raise food costs [1,2]. To overcome such problems, the current interest in the source for biofuel production has been moved to marine biomasses, which had a clear advantage over the land biomasses in terms of growth rate, cultivation area, and the level of dependency on expensive resources [2,7].

There are several types of marine biomasses, including red, green, and brown algae. Among them, it was reported that the content of the carbohydrate convertible into biofuel was the highest in red algae, which has thus been at the center of attention in the field of biofuel production from marine biomasses [1,2,8]. The main carbohydrate component in red algae is agarose, which can easily be hydrolyzed by a solid acid catalyst such as Amberlyst 36 [1,8–10]. According to the literature, the solid acid catalyst can easily be separated from the agarose-hydrolysis output by filtration [9,10]. The preferred product from such an agarose-hydrolysis output after the catalyst removal is galactose, because it can readily be converted into bioethanol through fermentation. However, such acid hydrolysis of agarose generates not only galactose (target product) but also two side-products, which include levulinic acid (LA) and 5-hydroxymethylfurfural (5-HMF) [1,2,8–10]. Since the two side-products (LA and 5-HMF) are toxic to the downstream fermentation [1,2,8–10], they need to be removed from the agarose-hydrolyzate components in order to ensure high level of conversion of galactose

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into bioethanol. Besides such a top priority of the separation task, it is additionally known that the two side-products can be of value as platform and building-block chemicals, if they are further separated into LA and 5-HMF with high purities [9,10].

For the aforementioned separation tasks, only a few batch-mode processes have been tested in previous publications [9,10], one of which clarified that a Dowex-50WX8 resin could function as a proper adsorbent for the relevant separation [10]. However, it is widely accepted that a batch-mode separation process has some limitations in its separation performance and economical efficiency, which were reported to be significantly lower than those of a continuous-mode separation process [11–14]. For this reason, an essential perquisite for guaranteeing the economic feasibility of the biofuel production from red algae is to develop a highly efficient continuous-mode separation process for the agarose-hydrolyzate components (galactose, LA, and 5-HMF), in which the continuous loading of a feed mixture and the continuous collection of a product can be implemented while maintaining high purities and high yields. In regard to such pattern of continuous operation, it is quite worth considering the adoption of the process structure and the operation principle of a simulated moving bed (SMB) technology, which has proved to be highly suitable for separating bioproducts in a continuous mode [15–19].

Fig. 1 illustrates the structure and operation pattern of a four-zone SMB process for binary separation [11,12,19,20]. It consists of multiple columns and multiple ports. The multiple columns are packed with an effective adsorbent for a target separation, and they are connected in series. The connected columns are partitioned into four zones by inlet and outlet ports as depicted in Fig. 1. The four partitioned zones can be configured to form one of the following three configurations (Fig. 1a–c); a closed loop, an open loop based on the cut-off between zones I and IV (open loop (I:IV)), or an open loop based on the cut-off between zones I and II (open loop (I:II)). Under such configuration, a counter-current flow between liquid and solid phases is created by moving the ports in the direction of the liquid-phase flow at a predetermined time interval (or switching time). If the flow rates and port switching time are properly determined under such circumstances, both a continuous feed-loading and a continuous product-collection can be realized while guaranteeing high purities and high yields. This enables an SMB

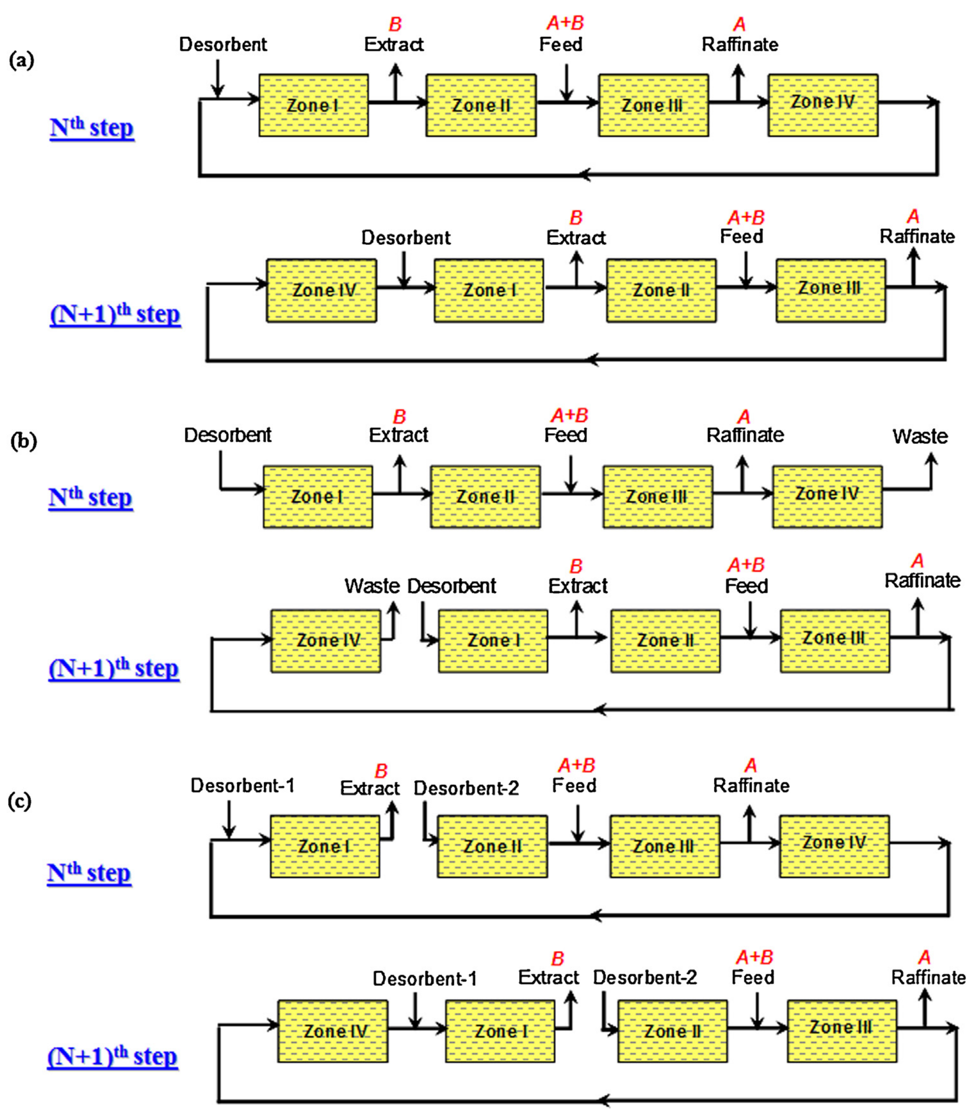


**Fig. 1.** Schematic diagram of a four-zone SMB process with one column per zone for continuous separation of a binary mixture. (a) Closed-loop configuration, (b) open-loop configuration based on the cut-off between zones I and IV (open loop (I:IV)), and (c) open-loop configuration based on the cut-off between zones I and II (open loop (I:II)). A: The less retained component, B: The more retained component. *N*th step: $N \cdot t_{sw} \le t < (N+1) \cdot t_{sw}$, $(N+1)$th step: $(N+1) \cdot t_{sw} \le t < (N+2) \cdot t_{sw}$, $t$: SMB operation time, $t_{sw}$: port switching time, $N$: positive integer.