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Title

Process design for green and selective production of bio-based surfactant with heterogeneous resin catalyst

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Abstract

The aim of this study was to construct an environmentally and eco-friendly production process of a bio-based surfactant, namely a sugar fatty acid ester (SE), using a heterogeneous catalyst. A strongly basic resin was found to show a fairly high catalytic activity in the transesterification of sucrose and a fatty acid methyl ester to produce an SE under mild conditions, i.e., 60°C and atmospheric pressure, especially when sufficient sucrose was adsorbed on the resin active sites. In a continuous process using a flow reactor packed with the resin, an appropriate combination of sucrose adsorption and sucrose supply during the reaction enabled to maintain the sucrose concentration at high levels. As a result, continuous SE production succeeded in a short residence time of 1.5 h without saponification to form soap for the first time. In this process, the downstream operations to separate the soap and the catalyst from the product were unnecessary. This heterogeneous resin catalyst enables simple, efficient, and environmentally friendly SE production and this process has potential commercial applications.

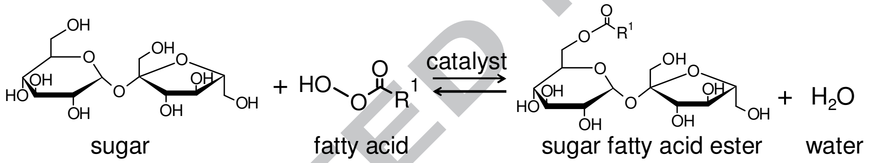
Keywords

bio-based surfactant; flow reactor; heterogeneous catalysis; ion-exchange resin; transesterification

1. Introduction

A sugar fatty acid ester (SE) has a structure in which a sugar and some fatty acids are linked by ester bonds. SEs have received much attention for use as bio-based, biodegradable, and renewable surfactants [1–12]. In addition to good emulsification properties [2–4], SEs have a wide range of hydrophilic–lipophilic balance values, depending on the number and type of fatty acid chains [5–8]. They have antimicrobial activities against microorganisms that cause foodborne illnesses [2,9–12]. However, both reactants are immiscible and sugars have multiple binding sites, therefore the efficient production of SEs with desired structures is difficult [13–16].

There are two routes for synthesizing SEs; one is esterification of a sugar and a fatty acid (Eq. 1) and the other is transesterification of a sugar and a fatty acid methyl ester (FAME; Eq. 2) [17,18].



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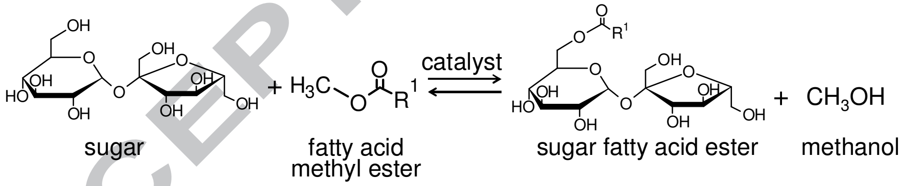

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The use of homogeneous acid catalysts such as hydrochloric acid and sulfuric acid in the first esterification route has been explored. However, acid catalysts cause sugar hydrolysis [19,20], therefore only small amounts of SEs were formed. Recently, many researchers have studied enzymatic esterification using lipases [2,3,11,14–18,21]. In this system, an SE can be synthesized by selecting an appropriate solvent, i.e., one that can dissolve both reactants and does not inhibit the enzymatic activity. However, there are many problems to be solved to make this method suitable for commercial production of SEs, e.g., slow reaction rates and low catalytic stabilities.

In the second, transesterification route, homogeneous alkaline catalysts such as sodium carbonate and potassium carbonate are used. A few companies have achieved industrial-scale SE production using homogeneous alkaline catalysts [22–25]. In this system, amphiphilic solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide are used. Water, which inhibits the reaction, must be removed before the reaction to achieve high conversions. Vacuum conditions to shift the reaction equilibrium by removing the by-product, i.e., methanol, are required, therefore a multi-reflux system to condense the solvent is also necessary. In addition, homogeneous alkaline catalysts react with FAMEs to form soap, and this decreases the reaction rate and product purity. After the reaction, the homogeneous catalyst and impurities must be separated from the product. This process uses large amounts of energy for heating and evacuation, and complicated upstream and downstream operations are involved; these increase the production costs and environmental impact.

A strongly basic resin was reported to be a heterogeneous alkaline catalyst with high activity in the transesterification of triglycerides and alcohols [26–36]. A triglyceride was completely converted to a fatty acid ester at 50°C and atmospheric pressure without dehydration pretreatment and addition of excess alcohol [30]. Unlike homogeneous alkaline catalysts, the resin catalyst did not form a soap and was easily separated from the product. Although the catalytic activity of the resin was lowered by the ion-exchange reaction between fatty acid group and the active site of the resin, i.e., hydroxyl group, the activity was completely restored using a reported regeneration method [29,31,32]. Such resins can therefore potentially be used to catalyze transesterification of sugars and FAMEs and could provide a simple, efficient, and environmentally friendly method for SE production.

The purpose of this study was to explore the possibility of using a resin catalyst to develop a simple, efficient, and commercially viable SE production process. In this system, the desired transesterification of a sugar and a FAME to produce an SE and side ion-exchange reactions between the FAME fatty acid groups and active sites of the resin, which reduce the catalytic activity, occur simultaneously. It is therefore important to prevent side ion-exchange reactions to achieve efficient SE production. The resin has a high affinity for sugars [37], therefore we developed a new method in which the sugar is fully adsorbed on the resin active sites before the reaction to prevent direct contact between the active sites and the FAME. First, we used a batch system to investigate the effect of sugar adsorption on SE synthesis. The results obtained using the resin were compared with those achieved using a conventional homogeneous catalyst. Next, we used a flow reactor system with a column packed with the resin to determine the optimum conditions for maintaining a high sugar concentration in the resin. The SE yield and selectivity for the desired transesterification were explored.

2. Experimental Section

2.1 Materials

Sucrose (Wako Pure Chemical Industries, Ltd., Osaka, Japan, special grade) and methyl oleate (OAMe; Wako Pure Chemical Industries, Ltd.) were used as model reactants. The solvent was DMSO (Wako Pure Chemical Industries, Ltd., special grade), which is currently used in industrial SE production. A porous and strongly basic resin (Diaion PA306S, Mitsubishi Chemical Co., Ltd., Tokyo, Japan) was used as the heterogeneous alkaline catalyst. This resin with a smaller particle size and lower cross linking density, has been reported to show a higher activity in the transesterification of triglycerides and alcohols [26]. In addition, the maximum operating temperature is recommended to be 60°C by the supplier. Before the experiments, the resin was activated by displacing chloride ions with hydroxyl ions and swollen with the solvent, i.e., DMSO, based on a previously reported resin regeneration method [29].

2.2 Batch experiments

First, sucrose was adsorbed on the resin by adding the resin to a solution of sucrose in DMSO in a reaction bottle and shaking the mixture well at 150 spm in a reciprocating shaking water bath at 60°C. Next, to initiate transesterification, the other reactant, OAMe, was added to the bottle. The amount of resin added was kept constant at 20wt% of the reaction volume (sum of the reaction solution and resin). The initial sucrose concentration was regulated in the range 0.10–0.30 mol/dm^3. Under these conditions, the shaking condition was confirmed not to affect the reaction rate in the preliminary experiment.

Three additional experiments were performed for comparison. In the first experiment, OAMe was adsorbed on the resin and then sucrose was added to start the reaction. In the second experiment, the resin was added to a reaction solution containing both reactants. In the third experiment, a homogeneous alkaline catalyst, i.e., 3.75wt% sodium carbonate, instead of the resin catalyst, was added to a reaction solution containing both reactants. The dosage of sodium carbonate was determined based on the preferred amount of homogeneous alkaline catalyst in the current process [38]. The above resin dosage 20wt% was determined to keep the amount of hydroxyl ion in the resin system same as that of sodium carbonate. These experimental conditions are summarized in Table 1. The underlining indicates that the reactant was adsorbed on the resin before the reaction.

In each experiment, solution samples were withdrawn at specific time intervals. The concentrations of the reactants, i.e., sucrose and OAMe, and the product, sucrose oleate (OASuc), were determined as follows. The concentrations of sucrose and OASuc were measured using a high-performance liquid chromatography (HPLC) system (ACQUITY UPLC H-Class system, Waters Corp., Milford, MA, USA) equipped with an evaporative light-scattering detector and an ACQUITY UPLC BEH amide column (particle size 1.7 µm, i.d. 0.21 cm, length 5 cm, Waters Corp.). Acetonitrile (Wako Pure Chemical Industries, Ltd., HPLC grade) containing 0.2vol% triethylamine (Wako Pure Chemical Industries, Ltd., special grade) and ultrapure water were used as the mobile phase at a flow rate of 0.3 cm^3/min for gradient elution. The temperatures of the column oven and drift tube were kept constant at 35 and 50°C, respectively. Nitrogen at a pressure of 40 psi was used as a nebulizer gas. For OASuc determination, a sugar ester consisting mainly of sucrose stearate (DK ester SS, DKS Co. Ltd., Tokyo, Japan), which is used as a food additive, was used as a standard because OASuc is not commercially available. The concentration of OAMe was determined using an HPLC system (ACQUITY UPLC H-Class system, Waters Corp.) equipped with an ultraviolet detector and an ACQUITY UPLC BEH C18 column (particle size 1.7 µm, i.d. 0.21 cm, length 15 cm, Waters Corp.). Acetonitrile, 2-propanol (Wako Pure Chemical Industries, Ltd., HPLC grade), and ultrapure water were used as the mobile phase at a flow rate of 0.4 cm^3/min for gradient elution. The temperature of the column oven was 30°C and the detection wavelength was 210 nm.

2.3 Continuous experiments

A water-jacketed glass column (i.d. 1.1 cm, length 30 cm) was packed with 22 g-wet of the resin and kept at 60°C by circulating hot water. First, for sucrose adsorption, a solution of sucrose (0.30 mol/dm^3) in DMSO was fed to the bottom of the column at 0.76 cm^3/min using a pump. When the sucrose concentration in the effluent from the column became almost equal to that in the feed, the supply of sucrose solution was stopped. Next, for the reaction, a mixed solution of sucrose and OAMe in DMSO was supplied to the column at 0.15 cm^3/min (the residence time of 1.5 h). The sucrose concentration was regulated in the range 0–0.23 mol/dm^3, by keeping the OAMe concentration constant at 0.10 mol/dm^3. In each experiment, the concentrations of the reactants and the product in the effluent from the column were determined in the same way as described above.

3. Results and discussion

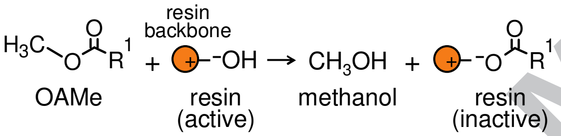
3.1 Effect of reactant adsorption on SE synthesis in batch system

Figure 1 shows the concentration profiles of the product, i.e., OASuc, during the batch experiments. The abscissa shows the reaction time after adsorption. When sucrose was adsorbed on the resin catalyst at 0.10 mol/dm^3 (run 1), OASuc was hardly produced. In run 2, with sucrose adsorption at 0.20 mol/dm^3, OASuc was formed immediately and after 0.50 h the concentration became almost constant. When the adsorbed sucrose concentration was increased to 0.30 mol/dm^3, the OASuc concentration increased up to 1.0 h and then gradually decreased. In the cases with OAMe adsorption (run 4) and without any adsorption (run 5), no OASuc was produced. When the homogeneous catalyst was used (run 6), the OASuc concentration slowly increased and after 24 h reached the same level as the maximum value achieved at 1.0 h with the resin catalyst. These results show that with the resin catalyst, OASuc synthesis proceeded rapidly when there was sufficient sucrose in the resin. In addition, decomposition of the formed OASuc proceeded as the sucrose was consumed by transesterification.

The reaction mechanism in the system was clarified as follows. The selectivity for transesterification to form OASuc was defined as

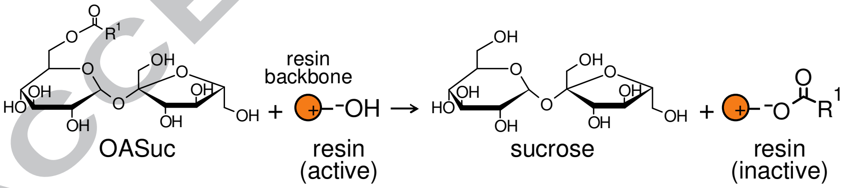
$$\mathbf{selectivity}\ [\%] = \frac{\textbf{produced amount of OASuc [mol]}}{\textbf{consumed amount of OAMe [mol]}} \times 100 \tag{3}$$

and calculated based on the experimental results under the conditions in which OASuc formation was observed (runs 2, 3, and 6). The changes in the selectivity with reaction time are shown in Fig. 2. When the resin catalyst was used, the maximum selectivity was reached at an early stage in the reaction and then gradually decreased. The selectivity in run 3, with sucrose adsorption at 0.30 mol/dm^3, was higher than that in run 2, with sucrose adsorption at 0.20 mol/dm^3. The OAMe decomposed via the ion-exchange reaction (Eq. 4) between the fatty acid group of OAMe (R^1 = $C_{17}H_{33}$), and the active sites of the resin, i.e., hydroxyl groups; this reaction occurs preferentially in this system.



(4)

However, the desired transesterification to form OASuc (Eq. 2) occurred easily at a higher sucrose concentration in the resin. In addition, the produced OASuc decomposed via the following ion-exchange reaction between the fatty acid groups of OASuc and the active sites of the resin as the sucrose concentration in the resin decreased.



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The by-products of Eqs. 4, 5, i.e., methanol and sucrose, were the same as the by-product and the reactant in the desired transesterification (Eq. 2), respectively. New substances and soaps were never formed in the system. Figure 2 shows that when a homogeneous alkaline catalyst was used, the selectivity gradually increased and became constant, at about 40%, after 12 h.

This shows that the alkaline catalyst preferentially reacted with OAMe to form soap [39]. The selectivity was low in the early stage of the reaction because the reaction rate of saponification was higher than that of transesterification.These results suggest that the resin catalyst preferentially produced OASuc when sufficient sucrose was adsorbed on the resin active sites to prevent direct contact between the resin and the FAME (Fig. 3). If the sucrose concentration in the system can be kept at high levels, OASuc can be produced with high selectivity. A continuous system using a column reactor packed with the resin can maintain steady-state conditions and keep the sucrose concentration at high levels.

3.2 Effect of sucrose concentration on SE synthesis in flow reactor system

Figure 4 shows the concentration profiles of each component in the effluent during a continuous experiment. The abscissa shows the total effluent volume, i.e., the volume collected from the beginning of sucrose adsorption to the end of the reaction. The horizontal lines represent the feed concentrations of sucrose and OAMe. The sucrose feed concentration during the reaction was regulated at (a) 0, (b) 0.12, and (c) 0.23 mol/dm^3. During sucrose adsorption, breakthrough occurred after the effluent volume reached around 0.050 dm^3, regardless of the conditions. During the reaction, in the case without a sucrose supply (Fig. 4a), the sucrose concentration in the effluent gradually decreased to zero. The OASuc concentration increased and reached a maximum at an effluent volume of 0.12 dm^3 and then decreased with decreasing sucrose concentration. When sucrose was supplied at 0.12 mol/dm^3 (Fig. 4b), the sucrose concentration in the effluent became constant at around 0.1 mol/dm^3 after the effluent volume reached 0.15 dm^3, the OASuc concentration also became constant. A steady state was therefore achieved. When sucrose was supplied at 0.23 mol/dm^3 (Fig. 4c), the steady-state concentration of sucrose in the effluent was higher than that achieved using 0.12

mol/dm^3, therefore the OASuc concentration was higher. The maximum or steady-state concentrations of OASuc (C_{OASuc}) and its yields, defined by the following equation, are listed in Table 2.

$$\textbf{yield [\%]} = \frac{C_{\mathbf{OASuc}}\ [\mathbf{mol/dm^3}]}{C_{\mathbf{OAMe,\ feed}}\ [\mathbf{mol/dm^3}]} \times \mathbf{100} \tag{6}$$

Here, $C_{\mathrm{OAMe,feed}}$ represents the feed concentration of OAMe. The higher the feed sucrose concentration during the reaction, the higher the OASuc yield was. In the continuous system, a combination of sucrose adsorption at 0.30 mol/dm^3 and sucrose supply at 0.23 mol/dm^3 during the reaction enabled the sucrose concentration to be maintained at high levels, and the OASuc yield therefore improved.

The selectivity for transesterification was calculated in the same way as for the batch experiments; the results are shown in Fig. 5. In the case without sucrose supply during the reaction, the maximum selectivity, around 40%, was obtained at an effluent volume of 0.14 dm^3. When sucrose was supplied at 0.12 mol/dm^3, the selectivity remained at around 60%. When the sucrose supply concentration was increased to 0.23 mol/dm^3, the selectivity increased to around 70% and remained almost constant during the reaction. In addition, 87wt% of the OASuc monoester was formed in this system.

Under the condition giving the maximum selectivity, which was the same as that in Fig.4c, the continuous experimt was performed until the catalytic activity of the resin completely disappeared. The result is shown in Fig.6. The steady state was maintained up to the total effluent volumne of around 0.50 dm^3. After then the product OASuc concentration graduary decreased and became almost zero at 0.90 dm^3, and the concentrations of reactants, sucrose and OAMe, increased and reached the same as those in the feed solution. After the experiment, the resin was regenerated by the proposed method [29] and was confirmed to be used in the next experiment similaly to the previous reports [29,31,32].

In Table 3, this method using the resin catalyst is compared with various previously reported methods. In the conventional method using a homogeneous alkaline catalyst and an amphiphilic solvent, reduced pressure is commonly used to shift the equilibrium in Eq. (2) toward the product by causing methanol evaporation. A FAME conversion of almost 100% was achieved at 90°C and 3.0 h [23]. However, saponification to form soap occurred as a side reaction in this system, therefore the actual SE yield was lower than the FAME conversion. In addition, the removal of the soap was difficult due to its similar separation characteristics to SE and the complicated downstream operation is indispensable.

In the microemulsion method using a homogeneous alkaline catalyst, the produced SE is used as an emulsifier to dissolve each reactant in the absence of a solvent [40]. This solvent-free method does not require a downstream solvent removal operation. The FAME conversion reached 98% at 120°C and 4.0 h under reduced pressure. However, the amount of sucrose was half that of the FAME, so that the actual SE yield was lower than 50%. In addition, the FAME was found to be consumed by the formation of di- and tri-esters and saponification and sucrose was decomposed because of a high temperature more than 100 °C.

In an ultrasound method using a homogeneous alkaline catalyst, ultrasound irradiation improved the reactant miscibility by disrupting the phase boundary [41]. An SE yield of 78% was obtained at 70°C and 2 h under reduced pressure, and selectivity for the monoester was high. However, the complicated downstream operation to remove the soap from SE is still required. In a microwave method combined with the ultrasound irradiation, SE produced without alkaline catalyst and hence saponification did not occur [42]. However, under atmospheric pressure, an SE yield reached only 33% after 10 h reaction time at 90°C.

In contrast, in our method using a heterogeneous resin catalyst, an SE yield of about 50%

was obtained in a short residence time of 1.5 h under milder condition, i.e., 60°C and atmospheric pressure than the microwave method. This reaction rate with mass transfer resistance within the resin is considered to be faster than that using a homogeneous catalyst without mass transfer resistance. In addition, high selectivity for the monoester was obtained. The SE yield seems to improve by conducting the reaction under reduced pressure. In this system, by-products such as soap were not formed, therefore downstream operations to separate the soap from the product were not needed. The flow reactor packed with the resin can be repeatedly used for SE production without loss of catalytic activity by using a previously reported resin regeneration method [29]. This heterogeneous resin catalyst therefore provides a simple, efficient, and environmentally friendly SE production method and has potential for commercial use.

4. Conclusions

Transesterification experiments using a sugar and a FAME to form an SE were performed using a strongly basic resin as a heterogeneous catalyst. First, batch experiments were performed to investigate the effect on SE synthesis of reactant adsorption. The results show that three reactions occurred: SE production (Eq. 2), FAME decomposition (Eq. 4), and SE decomposition (Eq. 5). When sugar adsorption on the resin active sites was sufficient to prevent direct contact between the resin and the FAME, the SE was quickly formed. Next, continuous experiments using a flow reactor packed with the resin were performed to identify the optimum condition for maintaining a high sugar concentration on the resin. An appropriate combination of sugar adsorption and sugar supply during the reaction enabled to keep the sugar concentration at high levels. As a result, a high selectivity, about 70%, was kept almost constant and an SE yield of about 50% was obtained at 1.5 h under mild conditions, i.e., 60°C and atmospheric pressure. High selectivity for the monoester was also obtained. This heterogeneous resin catalyst enables simple, efficient, and environmentally friendly production of SEs.

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Figure captions

Fig. 1. Concentration profiles of OASuc during batch transesterification

Fig. 2. Profiles of transesterification selectivity during batch experiments

Fig. 3. Schematic diagram of reaction mechanism of transesterification to form SE using resin catalyst

Fig. 4. Concentration profiles of each component in effluent during continuous experiments with supply of 0 (a), 0.12 (b), and 0.23 (c) mol/dm^3 sucrose during the reaction

Fig. 5. Profiles of transesterification selectivity during continuous experiments

Fig. 6. Concentration profiles of each component in effluent during long-term continuous experiment with supply of 0.23 mol/dm3 sucrose during the reaction

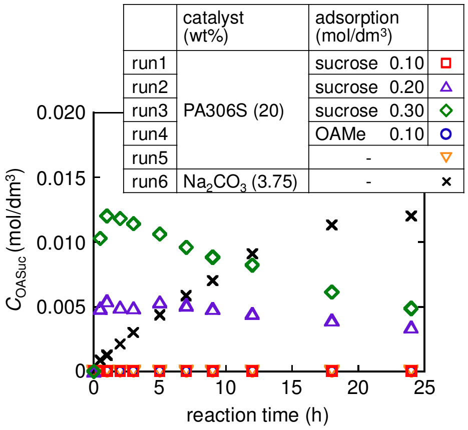


Fig. 1. Concentration profiles of OASuc during batch transesterification

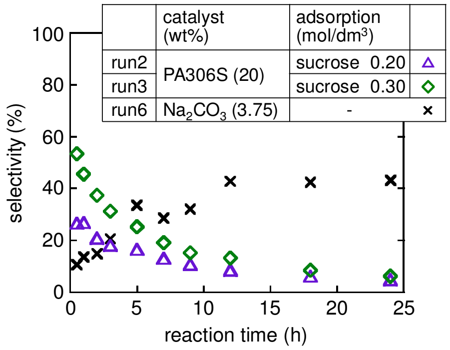


Fig. 2. Profiles of transesterification selectivity during batch experiments

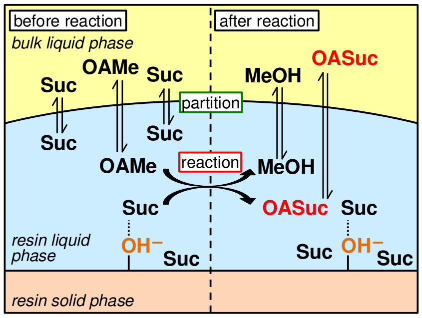


Fig. 3. Schematic diagram of reaction mechanism of transesterification to form SE using resin catalyst

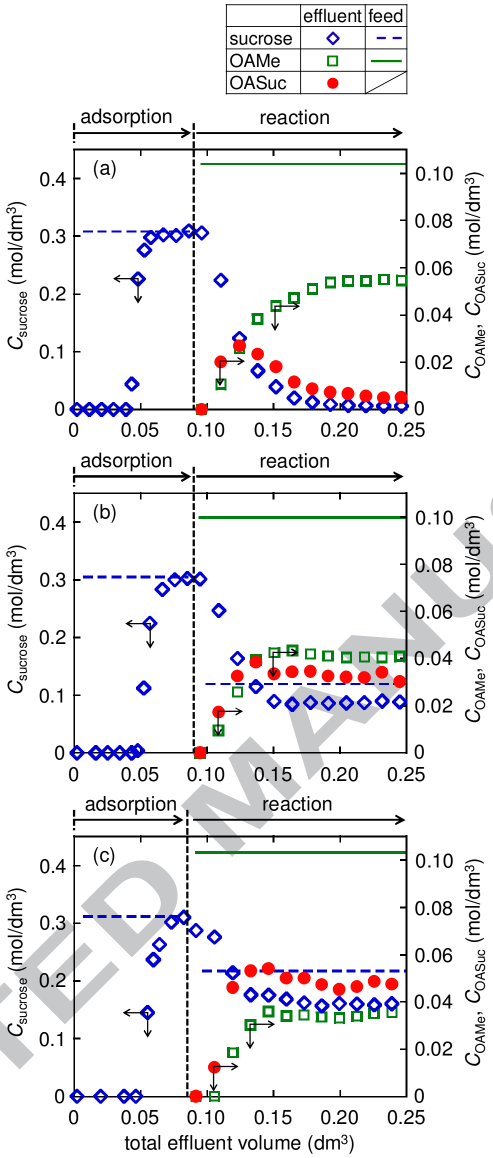
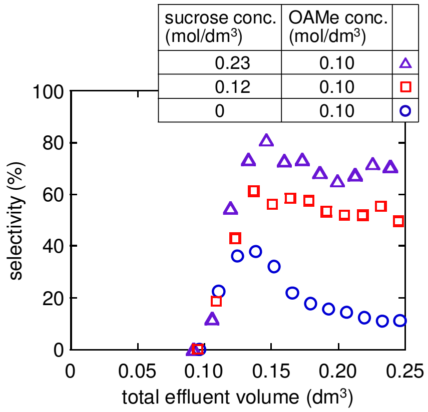


Fig. 4. Concentration profiles of each component in effluent during continuous experiments with supply of 0 (a), 0.12 (b), and 0.23 (c) mol/dm3 sucrose during the reaction



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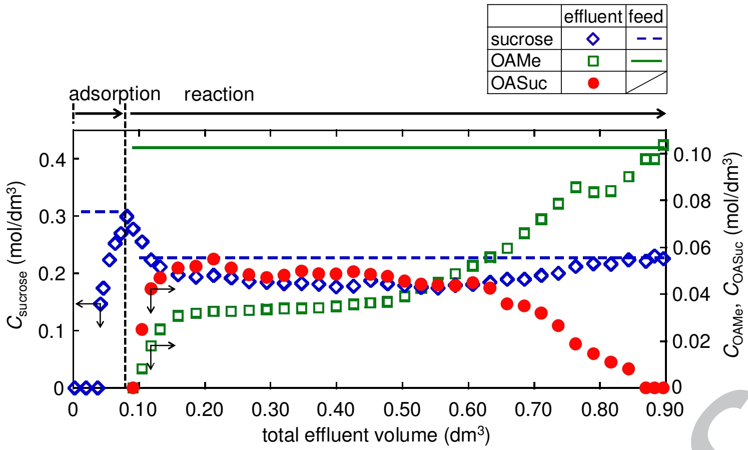
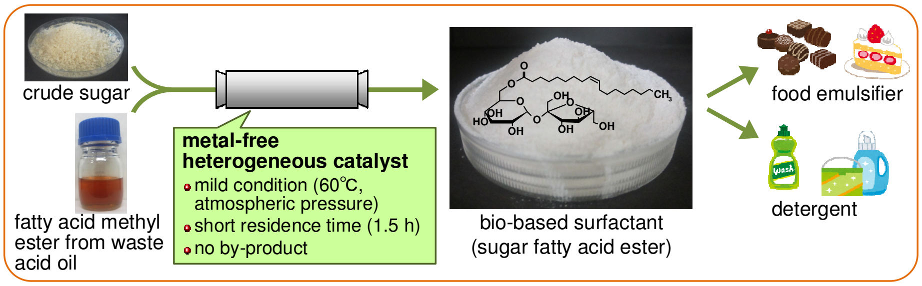


Fig. 6. Concentration profiles of each component in effluent during long-term continuous experiment with supply of 0.23 mol/dm3 sucrose during the reaction

Graphical Abstract



Highlights

- Bio-based surfactant, sugar ester was efficiently produced by porous resin catalyst.
- It was produced under the mildest condition, 60℃ and atmospheric pressure.
- Downstream operations to separate by-product and catalyst were unnecessary.

Table captions

Table 1 Experimental conditions for batch transesterification

Table 2 Product concentrations and yields in effluent in continuous system

Table 3 Comparison of new method using resin catalyst and various methods

Table 1 Experimental conditions for batch transesterification

	run1	run2	run3	run4	run5	run6
catalyst	PA306S	PA306S	PA306S	PA306S	PA306S	Na_2CO_3
catalyst conc. (wt%)	20	20	20	20	20	3.75
initial sucrose conc. (mol/dm^3)	0.10	0.20	0.30	0.10	0.10	0.10
initial OAMe conc. (mol/dm^3)	0.10	0.10	0.10	0.10	0.10	0.10
adsorption time (h)	0.50	0.50	0.50	0.50	-	-

underline: adsorption component

Table 2 Product concentrations and yields in effluent in continuous system

feed solution during reaction		effluent solution	
sucrose conc. (mol/dm^3)	OAMe conc. (mol/dm^3)	OASuc conc. (mol/dm^3)	OASuc yield (%)
0	0.10	0.0269 (max)	26.9 (max)
0.12	0.10	0.0329	32.3
0.23	0.10	0.0486	47.4

Table 3 Comparison of new method using resin catalyst and various methods

	this method	conventional method [23]	microemulsion method [40]	ultrasound method [41]	microwave method [42]
FAME : Suc molar ratio	1:2.3	1:4	1:0.5	1:2	1:1
catalyst	strongly basic resin	potassium carbonate	potassium carbonate	potassium carbonate	none
solvent	DMSO	DMSO	none (emulsifier : SE)	DMSO	water (emulsifier : SE)
temperature (°C)	60	90	120	70	90
pressure (kPa)	atmospheric pressure (100)	2.7	0.70	11	atmospheric pressure (100)
yield or conversion (%)	47 (SE yield)	100 (FAME conv.)	98 (FAME conv.)	78 (SE yield)	33 (SE yield)
reaction time (h)	1.5	3.0	4.0	2.0	10
mono ester mass fraction (wt%)	87	81	15	95	no data
soap formation	none	form	form	form	none