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CaO-loaded alginate capsule modified with silane coupling agents for transesterification of rapeseed oil with methanol

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HIGHLIGHTS

- The capsule shell modification improved the rigidity of alginate capsules.
- A different FAME yield was obtained depending on the type of shell.
- The triglyceride methanolysis was the rate determining step.
- Methanol permeation was important for FAME synthesis with CaO-loaded capsules.

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ABSTRACT

The methanolysis of rapeseed oil to fatty acid methyl esters (FAME) using CaO-loaded alginate capsules modified with silane coupling agents is reported. A FAME yield of 87% was obtained with CaO-loaded alginate capsules after 6 h at 333 K. However, capsule breakage reached 18.8% after the first run. In contrast, the breakage was reduced to 2.6% by extra alginate shells modified with n-butyltrimethoxysilane. Consequently, the amount of Ca leaching into the FAME phase was decreased substantially, whereas the reaction induction and completion times were increased. Static diffusion experiments and analyses of the liquid phases inside and outside the capsules at each time interval indicated that the permeability of methanol is the most important factor for determining the induction and completion times.

1. Introduction

Biodiesel fuel (BDF) is as an alternative to diesel fuel owing to BDF's low sulfur content, lack of aromatic hydrocarbons, and carbon neutral characteristics. Waste edible oil, animal fat, and non-edible oil are used as feedstocks for producing BDF [1–3]. However, the amount of feedstock is limited in Japan. Thus, waste edible oil, which contains water, free fatty acids, and triglycerides, has been recycled for BDF. In commercial BDF production, after water removal free fatty acids are esterified with an acid catalyst and triglycerides are then transesterified with a base catalyst [4–7]. Various types of catalysts have been developed for these reactions [7–10]. Solid base catalysts are suitable for the transesterification of triglycerides owing to the mild reaction conditions and easy recovery of the catalyst. However, the active species dissolve in the BDF and glycerol phases during the reaction, particularly the CaO catalyst [4,11–22]. Catalyst stability has been improved by the preparation of solid supported CaO or binary complex oxides [17–20,22], and a purification step to remove the leached Ca with cation-exchange resin [23].

In our previous works [24,25], when capsule was used as a reaction field for the methanolysis of rapeseed oil to improve the performance of the CaO catalyst, CaO-loaded alginate capsules hindered the dissolution of Ca species and could be reused three times without loss of activity [24]. Moreover, capsules containing CaO and active carbon powders gave a BDF yield of about 80% after 6 h for the transesterification of rapeseed oil using xenon lamp as a light source, and the amount of Ca leaching into the BDF phase was reduced considerably owing to a lower reaction temperature [25]. However, mechanical capsule breakage of the alginate shell through stirring shear force was unavoidable.

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Recently, organic/inorganic hybrid composite materials, which consist of an organic polymer and an inorganic nanoscale controlled unit, have been developed to offer desirable tunable properties such as rigidity, thermal stability, flexibility, and elasticity [26]. Inorganic solids (silane coupling agent, metal, and sodium silicate) were incorporated or deposited into or on the organic microcapsule shell to form rigid and stable organic-inorganic hybrid shells [27–29]. We reported that 3-aminopropyltriethoxysilane (APTES) is incorporated into the framework of the alginate shell via the electrostatic interactions between the APTES amino groups and alginate carboxyl groups to form a dense shell structure that efficiently encapsulates enzymes [30].

Alginate-shells could be reinforced with a silane coupling agent to prevent mechanical breakage. However, the permeation rates of reactants and products are expected to be smaller compared with the alginate-shell capsule system because a closed dense shell would be formed via the bonds between the alginate OH or COOH groups and the hydrolyzed silane coupling agent OH groups. Therefore, a calculation method using enzyme-immobilized capsules was used to evaluate the permeation rates through the shell because that is rarely reported for BDF synthesis. Mei et al. [31] reported that the transmembrane mass-transfer characteristics of vitamin B_{12} (VB_{12}) diffusion across alginate capsules could be estimated by measuring the increase in the VB_{12} concentration in the surrounding media. They also proposed that the permeability coefficient of VB_{12} across the capsule shell could be calculated. Although various equations have been used to estimate the transfer coefficients of substances across capsule shells [32,33], the equation used by Mei et al. was used in the present study. In this study, alginate capsules are modified with silane coupling agents to prevent capsule breakage and the permeability coefficients of reactants and products are determined. The capsules are used for the methanolysis of rapeseed oil to discuss the performance of different shell types.

2. Materials and methods

2.1. Materials

CaO powder (BET surface area: $7\ m^2\ g^{-1}$) was purchased from Wako Chemical Co. and used as received [25]. Sodium alginate (Kanto Chemical Co.), $CaCl_2$ (Kanto Chemical Co.), and a modifier (tetramethoxysilane (TMOS); Tokyo Chemical Industry Co. Ltd., n-butyltrimethoxysilane (BTMS); Gelest Inc., n-octyltrimethoxysilane (OTMS); PCR Inc.) were used to prepare the capsules. Sesame oil (Nacalai Tesque) was used to test the permeation of oil through the capsule shells. Rapeseed oil (Nacalai Tesque) and methanol (Kanto Chemical Co.) were used for FAME synthesis. The properties of the rapeseed oil have been reported in a previous paper [24]. Hexane (Kanto Chemical Co.) and methyl heptadecanoate (Tokyo Chemical Industry Co. Ltd.) were used for sample preparation prior to gas chromatography-flame ionization detector (GC-FID) analysis. All other chemicals were of analytical grade and used as received.

2.2. Capsule preparation

CaO powder was encapsulated in an alginate shell by the co-extrusion method using a coaxial needle with concentric nozzles [24,25]. Commercial CaO powder was suspended in rapeseed oil at a concentration of 20 wt% and 2% (w/v) sodium alginate was dissolved in water. The CaO-rapeseed oil suspension and sodium alginate solution were supplied through inner and outer nozzles at flow rates of 7.5 and $50\ mL\ h^{-1}$, respectively, by syringe pumps. The two-phase droplets were dropped into a 0.1 M $CaCl_2$ solution and stirred at 300 rpm for 30 min. In this process, spherical-shaped capsules with CaO-rapeseed oil core and calcium alginate shell were obtained by a one step gelling technique. The capsules were recovered and washed thoroughly with distilled water. Finally, the capsules were dried in an oven at 323 K for 10 h to obtain Alg capsules that were used for FAME synthesis.

The second type of capsule was obtained by putting the Alg capsules collected from the 0.1 M $CaCl_2$ solution into 1% (w/v) sodium alginate solution and stirring them at 300 rpm for 5 min to form second alginate layer on the Alg capsule shell. The residual Ca^{2+} in the first alginate layer formed the second alginate layer. The capsules were collected, washed with distilled water, and then dried in an oven at 323 K for 10 h to obtain dAlg capsules that were used for FAME synthesis. dAlg capsules collected from sodium alginate solution were treated by immersion in 0.1 M TMOS/hexane solution for 24 h followed by recovery and washing with hexane. The capsules were dried in an oven at 323 K for 10 h to obtain dAlg-T capsules. dAlg-T capsules collected from TMOS/hexane solution and washed with hexane were immersed in 0.01 M BTMS/hexane solution or 0.01 M OTMS/hexane solution for 24 h to prepare dAlg-T-B or dAlg-T-O capsules, respectively. After washing with hexane, the capsules were dried at 323 K for 10 h.

2.3. Permeability experiments

Sesame oil-loaded or FAME-loaded capsules were prepared to conduct permeability tests for oil or FAME across the modified capsule shells. Sesame oil was used instead of rapeseed oil because it can be observed by UV–Vis spectroscopy. The FAME products from the transesterification of rapeseed oil with methanol by using CaO-loaded capsules for 6 h at 333 K were used as the core material of FAME-loaded capsules. The permeability test was performed as follows. 1-Butanol (20 mL) was placed in a 50 mL bottle and stirred at 200 rpm. Sesame oil-loaded capsules (0.065 g) were added to the bottle and the permeability test was started. Samples (1 mL) were taken at regular intervals and the concentration of sesame oil in 1-butanol was measured with a UV–Vis spectrometer (V-630, Jasco) at a wavelength of 284 nm. The permeability coefficient (P) of sesame oil across the capsule shells was determined by the increase in concentration of sesame oil in the surrounding medium with time, and calculated with the equation [31]:

$$P = \frac{VbVm}{A(Vb + Vm)t} \ln\left(\frac{Cf - Ci}{Cf - Ct}\right) \tag{1}$$

Here, Ci, Ct, and Cf are initial, intermediate at time t, and final concentrations ($mol\ L^{-1}$) of sesame oil in 1-butanol, respectively, Vb is the volume (L) of 1-butanol, Vm is the total volume (L) of capsules, A is the total external surface area (m^2) of capsules, and t is the time (s). The permeability coefficient of FAME across the capsule shells was also determined by the same method with FAME-loaded capsules (0.038 g). The concentration of FAME in 1-butanol was measured by UV–Vis spectrometry (228 nm).

2.4. FAME synthesis

The transesterification of rapeseed oil with methanol by using CaO-loaded capsules was performed in a batch reactor. Rapeseed oil (20 mL) and capsules (0.48 g; total CaO loading, 0.096 g) were placed in a spinner flask (50 mL) and sealed with a cap. The rapeseed oil was heated to 333 K with a mantle heater and stirred at 300 rpm. After reaching 333 K, the reaction was started by adding methanol (10 mL; methanol/oil molar ratio, 12) to the mixture. The reaction mixture was sampled (1 mL) at 1 h intervals and the sample was centrifuged (CF15RX, Hitachi) at 5000 rpm for 10 min. The supernatant was dried under vacuum at 323 K for 2 h, and the