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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# Clean and Green Procedure for the Synthesis of Biodiesel from the Esterification of Free Fatty Acids and Alcohol Catalyzed by 6-*O*-(sulfobutyl)-β-cyclodextrin[1]

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**Abstract**—The catalyst of 6-*O*-(sulfobutyl)-β-cyclodextrin (SB-CD) is renewable, non-toxic, environmentally benign and biocompatible, which could be used as efficient and recyclable catalyst for the synthesis of biodiesel from free long-chain fatty acids with low-chain alcohols as substrates. The reaction was accomplished at 60°C for 1.5 h, while the products were separated from the catalyst system by liquid/liquid at room temperature with good conversion of 91–98%. The catalyst can be reused for 10 times. The novel and clean procedure offers advantages including short reaction time, good conversion, operational simplicity, and environmentally benign characteristics.

**Keywords:** Cyclodextrin; biodiesel; esterification; free fatty acid; heterogeneous separation

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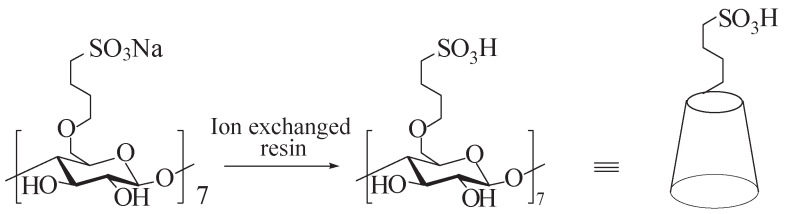
## INTRODUCTION

For several decades, energy crisis have being confronting the world due to the excessive utilization of the world's depleting oil reserves by the ever-increasing human population. Apart from the ever-increasing prices of petroleum fuels, more worrying issues associated with utilizing these fuels include deteriorating health standards and environmental degradations. These concerns have led to the search for sustainable biofuel alternatives [1]. A renewable and sustainable fuel currently receiving renewed interests and intensive experimentations since the work of Rudolf Diesel is biodiesel [2, 3]. Prominent amongst them is the simultaneous esterification and transesterification of feedstocks especially those containing high amounts of free fatty acids (FFAs) [4–6]. The product is fatty acid alkyl ester (FAME), the biodiesel fuel, is a perfect biodegradable and renewable clean fuel [7]. In order to reduce the production costs and to facilitate competition with petroleum diesel, low-cost feedstocks, such as waste fried oils and non-edible oils, can be used as raw materials, which were massive in China and other developing countries [8–10]. However, the low-cost feedstocks also contain significant amounts of free fatty acids, which pose significant processing problems in the standard biodiesel manufacturing. FFAs are saponifed by alkali catalysts, leading to a depletion of the catalysts as well as to increased purification costs [11]. Generally, the problem can be circumvented by an esterification pretreatment of FFAs to alkyl esters in the presence of an acid catalyst. However, the catalyst of $H_2SO_4$ involves high consumption of energy, and the separation of the catalysts from the homogenous reaction mixtures is costly and produces chemical wastes [12]. Solid acidic and basic catalysts also have such disadvantages as low activity, easy deactivation, and adsorption of products, which result in their limited application [13–20]. Functional acidic ionic liquids (FILs) are designed to replace traditional mineral liquid acids and used for the synthesis of biodiesel [21–32]. Accordingly, the aim of numerous recent research efforts is to develop novel catalysts. Certainly, these catalysts must be active, selective, reusable, stable and reproducible via simple viable procedures.

[1] The text was submitted by the authors in English.

**Scheme 1.** General structure of SB-CD.




β-Cyclodextrin (β-CD) is type of cyclic oligosaccharides consisting of seven glucose units with lipophilic central cavities and a hydrophilic outer surface, which bind substrates and catalyze reactions by supramolecular catalysis involving reversible formation of host-guest complexes by noncovalent bonding as seen in enzymes. In addition, there have been many reports about cyclodextrin as co-catalyst [33]. For instances, Rao et al. have used β-CD as co-catalyst for the addition reactions of olefins, ring-opening reaction, and oxidation reactions [34–35]. Cyclodextrins derivatives have been playing important roles in the artificial enzymes [36]. Thus, β-CD derivatives are attractive catalysts and they are highly desirable on the way to improve the catalytic activity.

As discussed above, many catalysts have been developed for the esterification reaction. However, it is still very interesting to develop efficient catalytic systems for the reaction using cheap and non-toxic reagents. In the present work, we designed and synthesized sulfonic acid functionalized β-CD as novel catalysts in an efficient and convenient procedure for biodiesel (Scheme 1). The esterification reaction that was studied can be summarized as follows:

$$\mathrm{R{-}COOH + R'OH \xrightleftharpoons{SB\text{-}CD} R\,COOR' + H_2O,}$$

where R and R' are the carbon chains. R' represents a primary alcohol.

## EXPERIMENTAL

**Preparation of SB-CD.** To a solution of 6-O-(sulfobutyl)-β-cyclodextrin sodium salt (2.4 g) in 30 mL of methanol was added Amberlite 732 resin (8 g). The mixture was then stirred for 2 h to give the solution of catalyst of SB-CD. The concentration of the SB-CD solution was titrated by standard KOH solution. The solvent was evaporated by evaporator and dried under vacuum at 40°C for 24 h to give a white powder, which was characterized by FTIR spectrum and NMR spectrum. SB-CD: $^1$H NMR (400 M, $D_2O$) (one glucose unit): δ = 1.53 (d, 4H), 2.71 (s, 2H), 3.10–3.62 (m, 8H), 4.91–5.25 (m, 1H); $^{13}$C NMR (100 M, $D_2O$): 20.90, 28.25, 36.58, 50.77, 60.49, 72.83, 81.51, 100.88; FTIR (KBr): 3421, 1159, 1043, 607, 533.

**General procedure for the synthesis of biodiesel.** To a flask was added different volume of SB–CD solution, the solvent was evaporated by evaporator and dried under vacuum at 40°C for 24 h, methanol and FFAs were added into the flask. The esterification was then typically carried out for a length of time at a specific temperature with vigorous stirring. After the reaction, the unreacted alcohol was recovered by distillation. After the residue was cooled and kept for a while, the reaction mixture became biphasic. The upper phase containing the desired biodiesel could be collected by decantation; the bottom phase, a mixture of catalyst and water generated from the reaction, could be reused after removal of water (Fig. 1). Conversion data were calculated based on FFAs through KOH titration [24].

## RESULTS AND DISCUSSION

**Synthesis and characterization of SB-CD.** The 6-*O*-(sulfobutyl)-β-cyclodextrin sodium salt can be changed into SB-CD by the resin of Amberlite 732 resin through ion-exchange (Scheme 1).

The structure of SB-CD was examined by NMR spectrum and FTIR spectrum, which are shown in Figs. S1–S3 in supporting information. The NMR spectrums indicate that SB-CD possesses glucose units. The vibrational bands at 1159 (O=S=O stretching in $SO_3H$), 1043 ($SO_3$-stretching) and 607 (C–$SO_3H$ stretching) in the FTIR spectrum indicate that the catalyst possesses –$SO_3H$ groups.

**Effect of the amount of methanol on esterification.** Generally, an excess of reactant methanol is necessary for the esterification of FFA because it can increase the

rate of methanolysis. The mole ratio of methanol to oleic acid varied from 2 : 1 to 16 : 1, and the conversions obtained are shown in Table 1. The more the methanol was added, the higher the conversion of oleic acid to methyl oleate was obtained in the same time (entry 1–6). The highest conversion of oleic acid achieved was 94.5% with methanol to oleic acid mole rate of 10 : 1 in 1.5 h. Further increase of methanol did not result in an increase in conversion. Unfortunately, the unmodified catalyst can not be realized the reaction (entry 7).

**Effect of the catalyst amount on esterification.** The catalyst amount was also of great importance for the esterification. Figure 2 shows the effect of the catalyst amount with increasing of the molar ratio of catalyst SB–CD. When the loading of the catalyst increased from 0.6 to 1.7 mol %, the conversion of product increased from 85.2 to 94.8%. At a catalyst loading of 1.3 mol %, the best result can be obtained. Further increasing the amount of catalyst, the conversion increase slightly, therefore 1.3 mol % was selected as the best loading of catalyst amount.

**Effect of reaction temperature.** The effect of reaction temperature on esterification is shown in Fig. 3. When the reaction temperature was 40°C, 90.4% of the oleic acid was converted into methyl oleate in 1.5 h. The conversion of oleic acid was found to increase with temperature from 40 to 60°C. Further increase temperature had no significant effect on conversion, at which the reaction system exhibited a slightly yellow color and a state of reflux. Considering conversion and cost, the optimum reaction temperature is 60°C.

**Effect of reaction time on esterification.** The effect of reaction time on oleic acid conversion is shown in Fig. 4. As shown in Fig. 4, SB-CD was very efficient for the reaction of methanolysis of oleic acid, over 78.9% of oleic acid was converted into methyl oleate within 0.5 h. The rate of methanolysis became slow, extending from 0.5 h to 1.5 h, and the conversion of oleic acid was 94.5%. The reaction of methanolysis approached equilibrium after 1.5 h, and the conversion of oleic acid did not increase when the reaction was prolonged. The trend was consistent with the previous report [21]. The optimum reaction time is 1.5 h.

**Reusability of SB-CD for esterification.** The recycling performance of SB-CD was investigated using the above model reaction. After the reaction, the products were isolated from the catalytic system by centrifugation and decantation, the catalyst was reused in the next time after removal of water under vacuum. As shown in Fig. 5, SB–CD could be reused at least ten times. The catalyst structure did not change after the reactions, according to the NMR and FTIR spectrum (Figs. S4 and Fig S5 in supporting information). Compared with traditional catalysts, efficient recycling performance is an attractive property of the proposed catalysts from the environmental protection and economic perspectives.

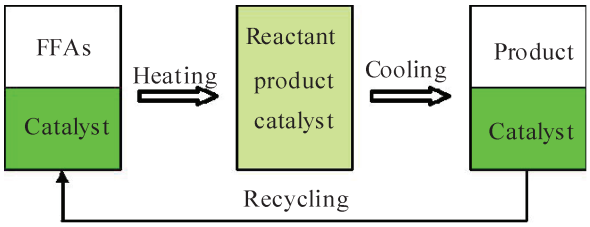



**Fig. 1.** Esterification reaction procedure.

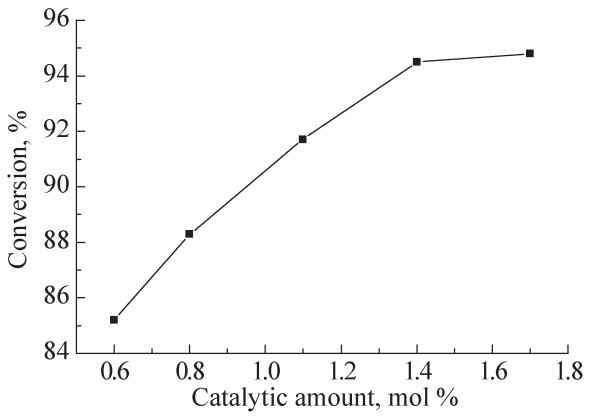



**Fig. 2.** Effect of the catalyst amount on esterification. Reaction conditions: 79 mmol methanol, 7.9 mmol oleic acid, 60°C, 1.5 h.

**Table 1.** Effect of the amount of methanol on esterification[a]

| Entry | Ratio of methanol to oleic acid | Conversion, % |
|---|---|---|
| 1 | 1 : 2 | 38.3 |
| 2 | 1 : 4 | 59.1 |
| 3 | 1 : 6 | 70.9 |
| 4 | 1 : 8 | 82 |
| 5 | 1 : 10 | 94.5 |
| 6 | 1 : 16 | 95.1 |
| 7[b] | 1 : 10 | NR |

[a] Reaction conditions: 7.9 mmol oleic acid, 0.11mmol SB-CD, 60°C, 1.5 h.
[b] Unmodified catalyst (I), no reaction.

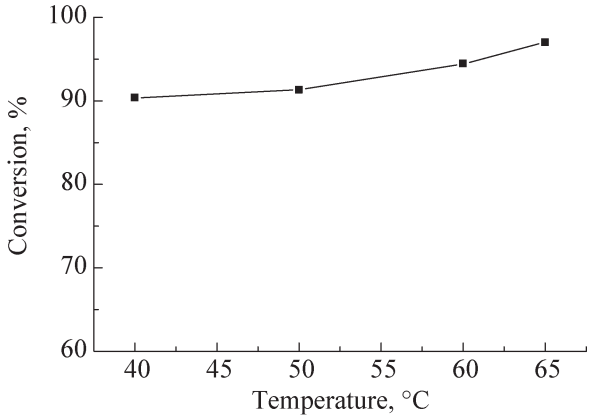



**Fig. 3**. Effect of reaction temperature on esterification. Reaction conditions: 79 mmol methanol, 7.9 mmol oleic acid, 0.11 mmol SB-CD, 1.5 h.

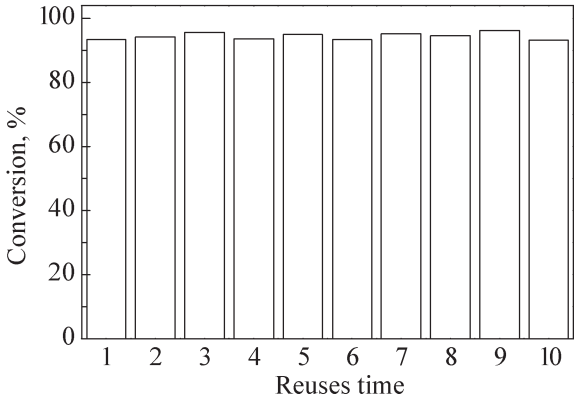



**Fig. 5**. Reusability of SB-CD for esterification with methanol. Reaction conditions: 79 mmol methanol,7.9 mmol oleic acid, 0.11 mmol SB-CD, 60°C, 1.5 h.

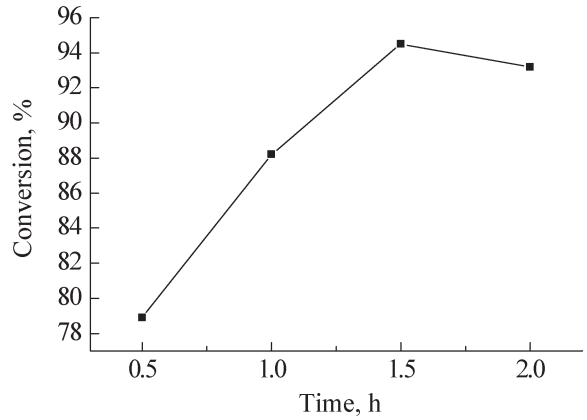



**Fig. 4**. Effect of reaction time on oleic acid conversion. Reaction conditions: 79 mmol methanol, 7.9 mmol oleic acid, 0.11 mmol SB-CD, 60°C.

**Catalytic performance of SB-CD for the esterification of other FFAs and short-chain alcohols.** To investigate the scope of SB-CD in terms of the preparation of FAME related to biodiesel production, stearic acid and palmitic acid, which are key components in waste oils for biodiesel production, as well as alcohols, were tested as the substrates. The results are listed in Table 2. Excellent conversion rates were obtained in all cases (entry 1–6). Notably, the length of the alkyl chains of alcohols had a significant effect on the conversion of FFAs (entry 1–3). Our investigation showed that SB-CD could be a good candidate for biodiesel production from non-edible oils.

**Table 2.** Results of esterification for different FFAs and alcohols[a]

| Entry | Fatty acids | Alcohol | Conversion, %[b] |
|---|---|---|---|
| 1 | Oleic acid | Methanol | 94.5 |
| 2 | Oleic acid | Ethanol | 93.8 |
| 3 | Oleic acid | Propanol | 90.7 |
| 4 | Lauric acid | Methanol | 97.0 |
| 5 | Stearic acid | Methanol | 92.4 |
| 6 | Palmitic acid | Methanol | 98.0 |

[a] Reaction conditions: 79 mmol alcohols. 7.9 mmol FFAs, 0.11 mmol SB-CD, 60°C, 1.5 h.

## CONCLUSIONS

In conclusion, the catalyst of SB-CD is renewable, non-toxic, environmentally benign and biocompatible, which was found to be novel catalyst for the synthesis of biodiesel from various FFAs and alcohols with satisfactory conversion of 91–98% under optimal reaction conditions. The catalyst has the advantages of high activity as well as practical convenience in the product separation from the catalytic system. The SB-CD can be reused for 10 times, which renders the method as a potential application in the production of biodiesel.

## ACKNOWLEDGMENTS

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## APPENDIX

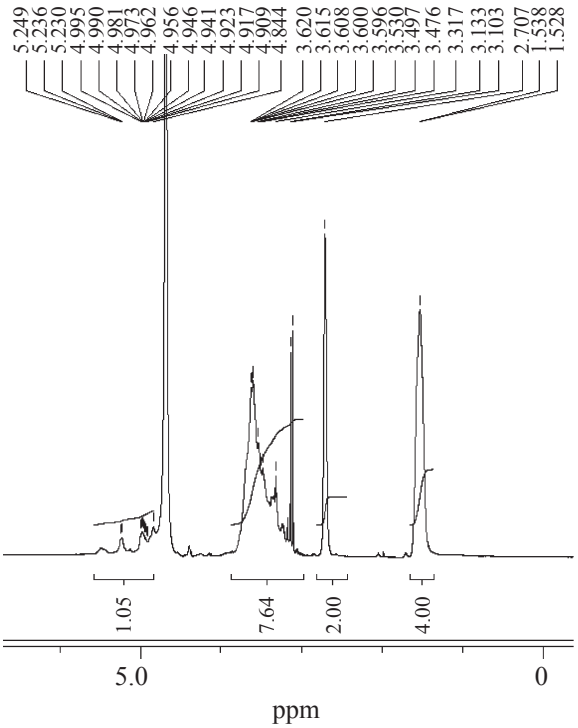


**Fig. S1.** The $^1$H NMR spectrum of SB-CD.

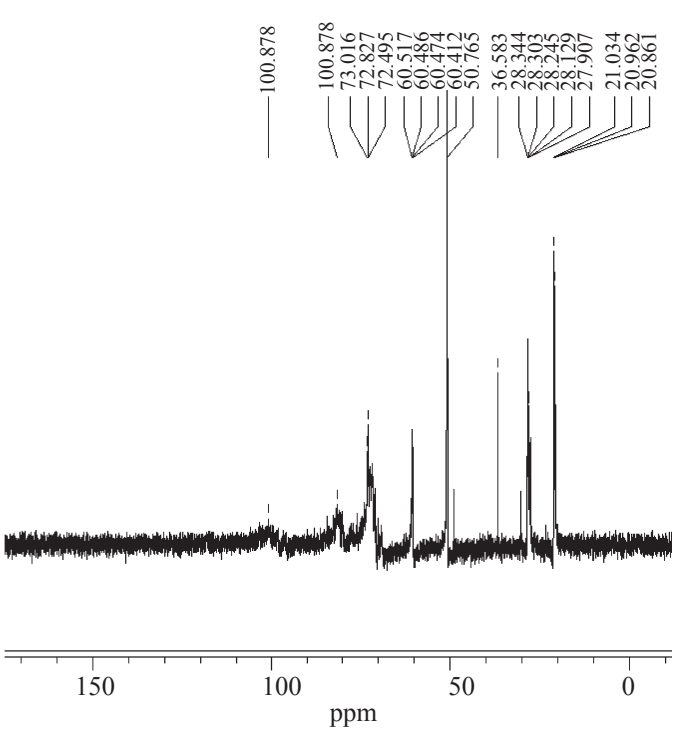


**Fig. S2.** The $^{13}C$ NMR spectrum of SB-CD.

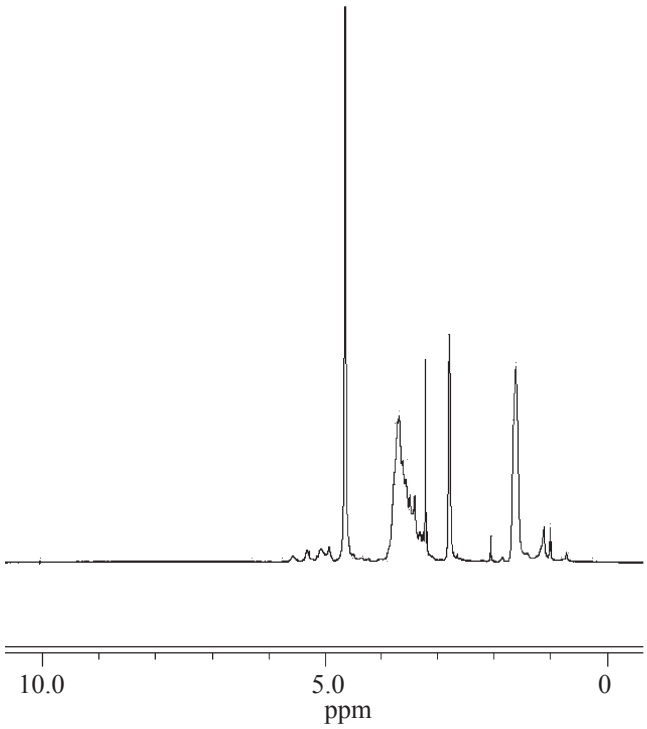


**Fig. S4.** The $^{1}H$ NMR spectrum of recycled SB-CD.

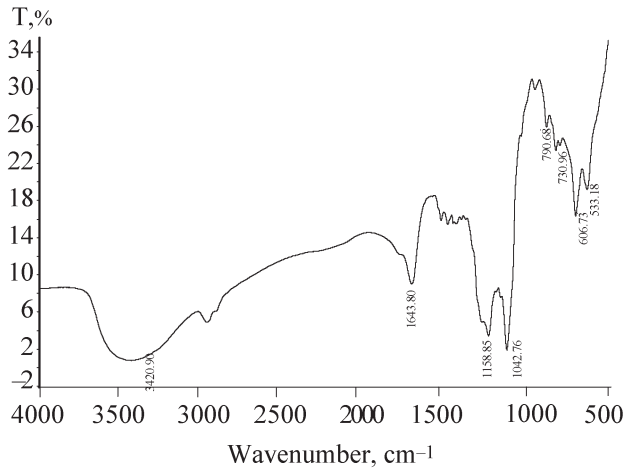


**Fig. S3.** The IR spectrum of SB-CD.

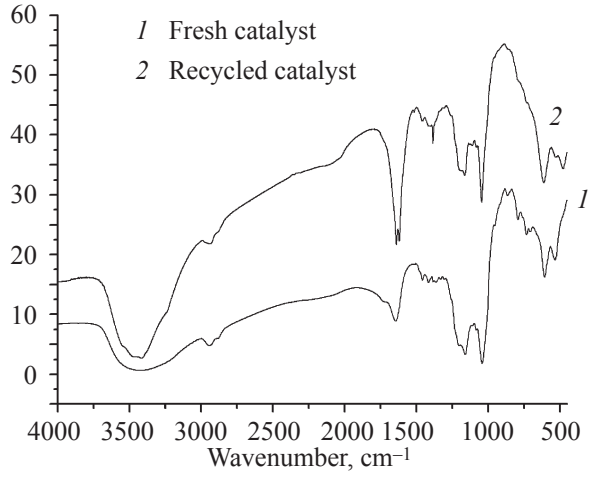


**Fig. S5.** The IR spectrum of fresh catalyst and recycled catalyst.