A novel process for repeated biodiesel production from waste coffee grounds: employing a paper-cartridge containing solid catalysts manufactured from waste scallop shells

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1. Introduction

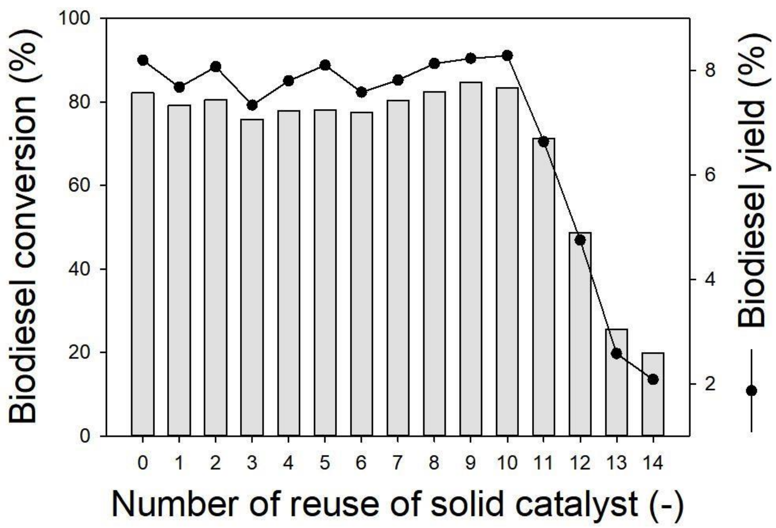
As the price of feedstock for biodiesel has risen, cheap, non-edible and renewable feedstock such as waste cooking oil and sewage sludge have been extensively explored [1]. The consumption of coffee in Korea dramatically has increased in recent years, accordingly, the discharge of waste coffee grounds (WCGs) are also significantly increased [2]. As for catalysts, homogenous chemical catalysts such as acid and alkaline ones have been conventionally used in the biodiesel production. However, they cannot be reused and thus should be repeatedly added to each batch operation, which requires large amounts of water for the neutralization and washing of biodiesel and increase biodiesel production cost substantially [3,4]. Unlike homogenous chemical catalysts, heterogeneous solid catalysts can be reused in a conventional two-step process (TSP) for biodiesel production by simply separating them from the reaction mixture, decreasing catalyst requirement and wastewater discharge [3-5]. However, they can be hardly reused in the one-step direct process (OSDP) where lipid extraction and transesterification of the lipids with methanol occurs simultaneously in a reactor due to the difficulty in the separation of solid catalysts from biomass debris, although this process has many advantages over TSP [6]. The city of Gangneung to which authors' university belongs is famous for its annual coffee festival and nationwide well-known coffee cafes. In addition, Gangneung located at the eastern seashore of Korea has many seafood restaurants, discharging a large volume of waste scallop shells. In this study, we manufactured solid catalysts from the waste scallop shells, and proposed a novel version of OSDP employing a papercartridge containing the solid catalysts for repeated biodiesel production. WCGs were used as the feedstock of biodiesel, and the reaction conditions of the novel OSDP were optimized with statistical tools.

2. Experimental

Waste coffee grounds (WCGs) and waste scallop shells (WSSs) were collected from a cafe and a seafood restaurant in Gangneung, respectively. After dried at 105°C for 6 h, WCGs were used as the feedstock of biodiesel. The composition of WCGS including lipid content and FFA content of the lipids were determined according to AOAC official method [1,7]. After washed carefully and dried, WSSs were ground to small pieces by a commercial electronic mixer, and calcined in an electronic furnace (FX-03, DAIHAN, Korea). Biodiesel was produced in 30 mL bottles tightly closed with Teflon-coated caps via OSDP. One gram of WCGs was placed in each bottle, and the amounts of solid catalyst in a papercartridge, methanol, and an organic solvent, reaction time and temperature were varied according to experimental design. The repeated operation of OSDP with a paper-cartridge was conducted as follows: As soon as the first round of OSDP finished, the paper-cartridge containing solid catalysts was simply removed from a bottle, and transferred to another bottle containing fresh WCGs, methanol, and the organic solvent for the second biodiesel production. The same procedure was repeated for the subsequent round of biodiesel production. The composition of solid catalyst from WSSs was analyzed by XRF (ZSX100e, Rigaku, Japan). Biodiesel was analyzed using a GC (7850A, Agilent, USA) with a FID detector [1,2]. Mixture design, factorial design, and analysis of data were conducted by Minitab 18.

3. Results and Discussion

The composition of WCGs used in this study was 12.9% of lipids, 13.3% of protein, 72.7% of carbohydrate, and 1.1% of ash. The FFA content of the lipids was 1.8%, which would allow alkaline catalysts to be used in the biodiesel production using the lipids from WCGs [2]. The major composition of solid catalyst was CaO (98.3%) followed by Na_2O (0.73%) and SO_3 (0.60%). Preliminary experiments indicated that an alkaline catalyst (NaOH) was readily used as a catalyst for biodiesel production from WCGs via OSDP due to a relatively low FFA content, and that the optimum calcination conditions for the preparation of solid catalysts were 700℃ and 3 hr. OSDP requires methanol and an organic lipidextraction solvent as well as catalysts (here, solid catalysts). Seven combinations of methanol with an extraction solvent (acetone, chloroform, diethyl ether, ethanol, isopropanol, n-hexane, toluene), and sole methanol were evaluated in terms of biodiesel conversion and yield, and the mixture of methanol and nhexane was found to be the best combination. The effect of factors including catalyst concentration, methanol loading, n-hexane loading, temperature, time and agitation speed were investigated on biodiesel production. Unlike homogenous reaction, agitation speed strongly related to mixing could be an influential factor because mass transfer of reactants and products into and from the paper-cartridge could be a crucial step in OSDP. The results showed the agitation at least 200 rpm was required to achieve high biodiesel conversion in the OSDP with a paper-cartridge containing solid catalysts while 50 rpm was enough to obtain comparable biodiesel production in the OSDP with free solid catalysts. The effect of total amount and mixing ratio of methanol and n-hexane was investigated using statistical mixture design. The optimum total volume was 9 mL/g-WCGs, and the mixing ratio of methanol to n-hexane was 1 to 3. Effect of remaining factors was statistically analyzed using factorial design. Catalyst concentration was the most significant, and temperature, previously insignificant in the OSDP with a homogenous alkaline chemical catalyst, was also significant. Based on these results, the optimal operating conditions were determined as 100%(w/w) catalyst relative to WCGs, 2.25 mL-methanol/g-WCGs, 6.75 mL-hexane/gWCGs, 45℃, 9 h and 200 rpm. The biodiesel conversion and yield at these optimal conditions were 82.1% and 8.19%, respectively. Finally, repeated operation of OSDP with a paper-cartridge was conducted and high biodiesel yield was stably obtained until 10th round of operation as shown in Fig. 1. Biodiesel yield was comparable to that obtained in the previous study where each step of a conventional two-step process was statistically optimized for biodiesel production [2].



<Fig. 1> Reuse of solid catalyst for biodiesel production via one-step direct process

4. Conclusions

The lipid content of WCGs and FFA content of the lipids was 12.9% and 1.8%, respectively. The optimal calcination condition of WSSs was 700℃ and 3 h, and calcium oxide (CaO) occupied 98.3% of the solid catalysts manufactured. A novel version of OSDP with a paper-cartridge containing the solid catalysts was proposed to reuse the solid catalysts. The mixture of methanol and n-hexane with the volume ratio of 3:1 was the best combination for the OSDP. Catalyst concentration was the most influential factor, and unlike homogenous catalysts, temperature and agitation speed were also critical factors. Under the optimal conditions, 82.1% and 8.19% of biodiesel conversion and yield were obtained, comparable to those obtained in the previous study using a TSP with homogenous chemical catalysts. Until 10th round of operation, biodiesel was stably produced without a noticeable decrease in biodiesel conversion and yield.

In this study, WCGs and WSSs were recycled as a valuable feedstock of biodiesel and a source of solid catalysts, respectively. In addition, it is believed that the novel OSDP with a cartridge containing solid catalysts could be a promising alternative to conventional TSP as well as OSDP in that it could save cost greatly in biodiesel production.

5. References

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