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Kinetic study of free fatty acid esterification reaction catalyzed by recoverable and reusable hydrochloric acid

Chia-Hung Su *

Graduate School of Biochemical Engineering, Ming-Chi University of Technology, No. 84 Gungjuan Rd., Taishan, Taipei 24301, Taiwan, ROC

HIGHLIGHTS

- Biodiesel synthesis catalyzed by a recoverable and reusable catalyst was studied.
- The catalyst reusability for the reaction could be predicted by a kinetic model.
- High yield of biodiesel can be achieved in each reuse cycle.

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ABSTRACT

The catalytic performance and recoverability of several homogeneous acid catalysts (hydrochloric, sulfuric, and nitric acids) for the esterification of enzyme-hydrolyzed free fatty acid (FFA) and methanol were studied. Although all tested catalysts drove the reaction to a high yield, hydrochloric acid was the only catalyst that could be considerably recovered and reused. The kinetics of the esterification reaction catalyzed by hydrochloric acid was investigated under varying catalyst loading (0.1–1 M), reaction temperature (303–343 K), and methanol/FFA molar ratio (1:1–20:1). In addition, a pseudo-homogeneous kinetic model incorporating the above factors was developed. A good agreement (r^2 = 0.98) between the experimental and calculated data was obtained, thus proving the reliability of the model. Furthermore, the reusability of hydrochloric acid in FFA esterification can be predicted by the developed model. The recoverable hydrochloric acid achieved high yields of FFA esterification within five times of reuse.

1. Introduction

Increasing global demand for petroleum-based fuel leads to energy shortage and environmental pollution. To solve this problem, many countries are taking steps to develop alternative fuels (Ryan et al., 2006). Biodiesel, which contains fatty acid methyl esters, is a biomass-derived fuel that can replace petro-diesel because both have similar properties (Melo-Junior et al., 2009). The usage of biodiesel as a petro-diesel alternative has recently received considerable attention because it is technically feasible, environmentally acceptable, and fully compatible with existing diesel engines (Feng et al., 2010; Shibasaki-Kitakawa et al., 2007). In addition, biodiesel is a sustainable biofuel because it can be derived from a variety of edible and nonedible oil feedstock (Dizge et al., 2009; Fu et al., 2010; Hayyan et al., 2011; Subhash and Mohan, 2011). On the basis of such merits, numerous studies have focused on developing more efficient, economical, and safer processes for biodiesel production.

Biodiesel is commonly produced via alkaline transesterification of oil (triglyceride), which is extracted and refined from oleaginous plant seeds (Su et al., 2008). However, using refined oils as feedstock increases the total production cost of producing biodiesel (Boucher et al., 2008), thus making the process less competitive. To circumvent this problem, crude or waste oils have been used as feedstock because they are less expensive (Deshmane et al., 2009); however, they contain a considerable amount of water and free fatty acid (FFA), which can inhibit alkaline transesterification (Su et al., 2008). In alkaline transesterification of such acid oils, FFA also reacts with alkali catalysts to form soap, which causes catalyst loss and difficulties in purifying the biodiesel product (Talukder et al., 2010; Ting et al., 2008).

Besides transesterification, other methods for converting acid oil into biodiesel have been gaining interest. Talukder et al. (2010) developed a two-step process for biodiesel production involving enzyme-catalyzed hydrolysis followed by acid-catalyzed esterification. In the first stage, 100% FFA can be prepared through the hydrolysis of tri-, di-, and monoglycerides by using lipase (Talukder et al., 2010). The hydrolyzed FFA is then esterified in the second step to biodiesel by acid catalysts (de Sousa et al., 2010; Talukder et al., 2010). The advantage of this process is feedstock flexibility, unlike conventional transesterification, which requires strict feedstock specification (de Sousa et al., 2010;

* Tel.: +886 2 29089899x4665; fax: +886 2 29083072.
E-mail address: chsu@mail.mcut.edu.tw

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