Two-step supercritical dimethyl carbonate method for biodiesel production from Jatropha curcas oil

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ABSTRACT

This study reports on a novel two-step process for biodiesel production consisting of hydrolysis of oils in sub-critical water and subsequent supercritical dimethyl carbonate esterification. This process found to occur optimally at sub-critical water treatment (270 °C/27 MPa) for 25 min followed by a subsequent supercritical dimethyl carbonate treatment (360 °C/39 MPa) for 15 min to achieve a comparably high yield of fatty acid methyl esters, at more than 97 wt%. In addition, the fatty acid methyl esters being produced satisfied the international standard specifications for use as biodiesel fuel. This new process for biodiesel production offers milder reaction condition (lower temperature and lower pressure), non-acidic, non-catalytic and applicable to feedstock with high amount of free fatty acids such as crude Jatropha curcas oil.

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1. Introduction

To date, biodiesel has been widely produced and used in many countries. Biodiesel, a clean fuel commonly derived by transesterification of either edible or non-edible oils with alcohol, is a comparable match to petroleum diesel. The current commercial biodiesel production method called the alkali-catalyzed method, transesterifies triglycerides in the presence of alkaline catalyst with methanol to produce fatty acid methyl esters (FAME). However, this method does not suit feedstock with high content of free fatty acids, which consume the catalyst to form saponified substance and reduce the yields of fatty acid methyl esters (Hawach et al., 2008). In order to overcome these problems, the one-step non-catalytic supercritical methanol process (Saka process) and two-step process (Saka-Dadan process) have been developed (Kusdiana and Saka, 2004; Saka and Kusdiana, 2001).

Furthermore, the increasing trend towards biodiesel production has also led to an extreme increase of glycerol as by-product. In Europe, glycerol price decreased tremendously due to extensive supply in the market and glycerol-producing chemical companies were extremely affected (Wilkie and Vandep, 2004). Glycerol, accounts 10% of mass of the feedstock, is recovered together in mixture with methanol, water and residues of the alkaline catalyst after the transesterification process. Several complicated purification processes have to be conducted for this mixture to recover the pure glycerol, and this makes the price 10 times higher than the unpurified one. By considering the complicated processes and its cost, the pursuit to recover pure glycerol is not an economical one.

To balance glycerol’s availability and demand, attempts to utilize glycerol from biodiesel production in innovative new ways have been reported (Silva et al., 2009; Tang et al., 2009). However, it is superior if biodiesel production could produce less or no glycerol at all. In accordance to this, Saka and Isayama (2009) developed supercritical methyl acetate method to produce fatty acid methyl esters and tricetin, without producing glycerol. The mixture of fatty acid methyl esters and tricetin can be used entirely as biodiesel due to their miscibility and similar fuel properties (Saka and Isayama, 2009).

Similarly, our recent study has reported a new potential method for biodiesel production by utilizing supercritical dimethyl carbonate without using any catalyst. This one-step direct transesterification process could yield glycerol carbonate and citramalic acid as by-products apart from the abundantly available glycerol normally produced in the conventional method (Ilham and Saka, 2009). Although this method could produce the by-products with higher values, the severe reaction conditions may become a major concern in industrial application.

Therefore, in this study, a potentially new milder alternative route via two-step biodiesel production process has been investigated based on the hydrolysis of triglycerides in sub-critical water and subsequent supercritical dimethyl carbonate esterification of fatty acids in a non-catalytic manner. Briefly, the supercritical dimethyl carbonate was incorporated into a two-step process for biodiesel process. In this paper, the results obtained by utilizing Jatropha curcas oil in such a two-step process will be discussed.