



Technical Note

Boosting the value of biodiesel byproduct by the non-catalytic transesterification of dimethyl carbonate via a continuous flow system under ambient pressure

Eilhann E. Kwon^a, Haakrho Yi^{b,*}, Young Jae Jeon^{c,*}^a Department of Environment and Energy, Sejong University, Seoul, South Korea^b Bioenergy Research Team, Research Institute of Science and Technology (RIST), 813-1 Keumho-Dong, Kwang-Yang, Cholla-Nam-Do, South Korea^c Department of Microbiology, Pukyong National University, Busan, South Korea

HIGHLIGHTS

- Biodiesel production via the continuous flow system.
- Enhanced conversion of biodiesel in the presence of porous material.
- Transesterification of coconut oil with dimethyl carbonate.

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ABSTRACT

Transformation of coconut oil into biodiesel by using dimethyl carbonate (DMC) via a non-catalytic transesterification reaction under ambient pressure was investigated in this study. The non-catalytic transformation to biodiesel was achieved by means of a heterogeneous reaction between liquid triglycerides and gas phase DMC. The reaction was enhanced in the presence of porous material due to its intrinsic physical properties such as tortuosity and absorption/adsorption. The numerous pores in the material served as micro reaction chambers and ensured that there was enough contact time between the liquid triglycerides and the gaseous DMC, which enabled the completion of the transesterification. The highest fatty acid methyl esters (FAMES) yield achieved was $98 \pm 0.5\%$ within 1–2 min at a temperature of 360–450 °C under ambient pressure. The fast reaction rates made it possible to convert the lipid feedstock into biodiesel via a continuous flow system without the application of increased pressure. This suggested that the commonly used supercritical conditions could be avoided, resulting in huge cost benefits for biodiesel production. In addition, the high value of the byproduct from the transesterification of the lipid feedstock with DMC suggested that the production biodiesel using this method could be more economically competitive. Finally, the basic properties of biodiesel derived from the non-catalytic conversion of rapeseed oil with DMC were summarised.

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1. Introduction

Alternative energy sources, such as biofuels for transportation, are highly desired because of their well-known carbon neutrality

among the various known biofuels. Biodiesel has been highlighted as a potential alternative due to its compatibility with current diesel engines without the need for any modifications (Basha et al., 2009; Atadashi et al., 2010). For instance, biodiesel has similar fuel properties. Moreover, the emission profiles including arrayed particulate matters (PM), have been shown to be superior to petroleum-based diesel (Basha et al., 2009; Kohse-Höinghaus et al., 2010; Hoekman and Robbins, 2012). The current distribution networks for petroleum-based fuels by means of blending can be directly implemented for biodiesel (Lardon et al., 2009).

The alkali-catalysed transesterification reaction has been previously used in the biodiesel industry (Hara, 2009; Atadashi et al.,

* Corresponding authors. Address: Bioenergy Research Team, Research Institute of Industrial Science and Technology (RIST), 813-1 Kumho-Dong, Kwangyang-City, Chollanam-Do 540-090, South Korea. Tel.: +82 061 799 2707; fax: +82 061 792 0768 (H. Yi). Address: Department of Microbiology, Pukyong National University, 45 Yongso-ro, Nam-gu, Busan 608-737, South Korea. Tel.: +82 51 629 5612; fax: +82 51 629 5619 (Y.J. Jeon).

E-mail addresses: haakrho@yahoo.com (H. Yi), youngjaejeon@pknu.ac.kr (Y.J. Jeon).

2010; Singh and Singh, 2010; Zinoviev et al., 2010; Mekhilef et al., 2011). However, it exhibited low tolerance of water and free fatty acids (FFA) derived from the crude lipid feedstock (Kusdiana and Saka, 2004; Minami and Saka, 2006; Isayama and Saka, 2008; Ilham and Saka, 2010; Goembira et al., 2012). This resulted in decreased fatty acid methyl esters (FAME) yield and complicated the purification process for biodiesel. In order to make biodiesel more economically viable and competitive, the utilisation of inexpensive lipid feedstock would be highly advantageous, as 70–75% of biodiesel cost arises from the lipid feedstock (Abbaszaadeh et al., 2012; Lou et al., 2012). However, inexpensive lipid feedstock generally contains a large amount of water and FFA, making additional purification processing necessary (Zabeti et al., 2009; Lam et al., 2010). Thus, economically and technically reliable biodiesel production methodology that can tolerate the high amount of water and FFA derived from the lipid feedstock must be developed. One such potential method is the non-catalytic transesterification of triglycerides.

Up to now, non-catalytic biodiesel conversion methods have been limited to the use of supercritical conditions (i.e. temperatures above 250 °C and pressures above 10 MPa) (Kusdiana and Saka, 2004; van Kasteren and Nisworo, 2007; Isayama and Saka, 2008; Tan et al., 2010a; Alexandre et al., 2012; Ilham and Saka, 2012). In spite of the numerous advantages, the operational and equipment costs for producing biodiesel under supercritical conditions are huge obstacles (Tan and Lee, 2011). In this regard, non-catalytic biodiesel conversion with the conditions under ambient pressure must be developed.

In addition, the level of surplus glycerol byproduct from biodiesel production gives rise to environmental problems (Pagliaro et al., 2007; Katryniok et al., 2009; Ayoub and Abdullah, 2012). This needs to be further separated before use due to its low purity (~67%). In practice, most crude glycerol is discarded or incinerated due to the high cost of purification. Thus, the non-catalytic transformation of lipids to biodiesel can be further justified as an economically viable process due to the high purity of glycerol that can be produced via this technology.

Recently, dimethyl carbonate (DMC) has been investigated as an alternative reactant for transforming lipid feedstock into biodiesel (Fabbri et al., 2007; Ilham and Saka, 2009; Zhang et al., 2010a,b; Tan et al., 2010c; Seong et al., 2011; Ilham and Saka, 2012; Jung et al., 2012). The economic value of byproducts such as glycerol carbonate and glycerol dicarbonate, from the non-catalytic transesterification using DMC as a methyl donor, is higher than that of glycerol (Ilham and Saka, 2009, 2010, 2012). In general, DMC is a versatile chemical due to its eco-friendliness, chemical reactivity, and superior physical properties compared to MeOH (Fabbri et al., 2007).

The main goal of this study was to describe the transesterification of a lipid feedstock with DMC to form biodiesel via a continuous flow system under ambient pressure. The optimal experimental parameters (i.e. temperature and molar ratios of raw materials) for producing biodiesel were determined, with coconut oil used as an example feedstock. The economic advantages of the byproducts were considered to justify the employment of DMC instead of primary alcohols, such as MeOH, for the biodiesel formation. Finally, the basic properties of biodiesel derived from the non-catalytic transesterification with DCM are summarised.

2. Materials and methods

2.1. Characterisation of coconut oil and sample preparation

Pure natural coconut oil and rapeseed oil were purchased from the local market. The crude fatty acids were purchased from

Sam-Chun Chemical (Pyeongtaek-City, South Korea). MeOH, DMC and H₂SO₄ were purchased from Sigma–Aldrich (St. Louis, USA).

In order to analyse the fatty acid composition of the coconut oil, acid esterification was carried out with H₂SO₄ for 65 h at 60 °C. The composition of the coconut oil is summarised in Table 1, and it can be seen that the main fatty acid present was in the C_{14–16} carbon range.

2.2. Experimental setup for the non-catalytic transesterification reaction

A tubular reactor (TR) made of 2.54 cm outer diameter quartz tubing (Chemglass CGQ-0800T-13) and a 2.54 cm stainless Ultra-Torr vacuum fitting (Swagelok SS-4-UT-6-400) was used, with a maximum possible pressure of 150 kPa. Activated alumina purchased from Dae-Jung Chemicals (Incheon, South Korea) was packed into the reactor. A BELSORP-mini II (BEL Japan) was used to characterise the surface area (297.350 m² g⁻¹) and pore distribution (average pore diameter: 5.41 nm) of the alumina. In addition, the coconut oil was transformed into biodiesel within the customised pressure reactor in order to investigate the effect of pressure in the presence of the activated alumina. The volumetric flow rate of the coconut oil to DMC used in this experiment was 10–3 mL min⁻¹ respectively which is equivalent to 1: 8–10 M ratios. An illustration of the pressure reactor is shown in Fig. SM-1 in the Supplementary material (SM). The experimental procedures followed those of previous reports by other authors (Ilham and Saka, 2009, 2012).

The experimental temperature in the range 250–450 °C was achieved using a split-hinged furnace (AsOne, Japan), and was monitored simultaneously by an S-type thermocouple to ensure that the target temperature had been achieved. An insulation collar (high-temperature Duraboard insulation) at the end of the furnace was used to block heat transfer during operation and to protect the quartz tubing. The lipids and DMC were continuously fed into TR using a gear pump (micro annular gear pump MZR-2905, Germany) and a high-performance liquid chromatography (HPLC) pump (Lab Alliance ON#F40SFX01, USA).

After the reaction, the mixture was allowed to settle for 2 h before the glycerin layer and the top layer including the biodiesel fraction were separated and removed into separate bottles. The samples collected from each layer were weighed and analysed using a gas chromatograph–mass spectrometer (GC/MS; HP-790A/5975C MSC) and a GC/flame ionisation detector (HP-7890A) calibrated with a Supelco mixture (Lot# LB-80557). DB wax (J&W 127-7012) and HP-5MS (19091S-413E) GC columns were used for the GC/MS analysis. The FAME yield was calculated according to our previously reported methods (Kwon et al., 2012a,b,c) and compared to those obtained by other authors (Tan et al., 2010a,b).

Table 1
Fatty acid composition in coconut oil.

Common name	Composition	Weight percent (%)
Caproic acid	C _{6:0}	0.7
Caprylic acid	C _{8:0}	4
Capric acid	C _{10:0}	8
Lauric acid	C _{12:0}	58
Myristic acid	C _{14:0}	17.4
Palmitic acid	C _{16:0}	8.2
Stearic acid	C _{18:0}	0.4
Oleic acid	C _{18:1}	3.1
Linoleic acid	C _{18:2}	0.2

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