



# Transesterification of biodiesel byproduct glycerol and dimethyl carbonate over porous biochar derived from pyrolysis of fishery waste

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## ARTICLE INFO

### Keywords:

Dimethyl carbonate  
Fishmeal biochar  
Glycerol  
Glycerol carbonate  
Reusability

## ABSTRACT

Glycerol carbonate (GC), an oxygenated fuel additive was synthesized from oversupplied glycerol in transesterification with dimethyl carbonate (DMC) over fishmeal biochar. Fishmeal was carbonized at various temperatures (550–750 °C). The most suitable carbonization temperature based on GC yield was utilized in transesterification. Biochar was characterized to investigate textural and basic properties and surface functional groups. Thermal treatment, methanol washing, and solvent addition techniques were adopted to investigate biochar reusability after each reuse. At the most suitable reaction conditions of 85 °C, 2 wt% catalyst dosage, and DMC-to-glycerol molar ratio of 2, 99.5% GC yield and complete conversion of glycerol were attained over biochar carbonized at 650 °C. Strong basicity of biochar initiated decarboxylation reaction, which resulted in formation of glycidol (0.5%). Addition of methanol without catalyst treatment after each reuse sustained GC yield of 93% at the end of fifth reuse.

## 1. Introduction

As alternative to fossil fuels, biodiesel demand has considerably increased in the last decade. As such, biodiesel production via methanolysis of triglycerides has increased, thereby resulting in generation of abundant crude glycerol with low economic value because of constituent impurities [1]. Recently, research emphasis is directed toward the development of sustainable and environmentally friendly technologies to utilize and convert glycerol to valuable compounds. Glycerol is upgraded to platform chemicals by utilizing technologies, such as glycerol oxidation, etherification, esterification, transesterification, hydrogenolysis, and reforming [2–6].

Glycerol transesterification with dimethyl carbonate (DMC) synthesizes glycerol carbonate (GC) and represents a thermodynamically favorable route compared with that of ethylene carbonate [7,8]. The transesterification reaction mechanism proceeds via three steps. The catalyst alkaline sites deprotonates glycerol to form glyceroxide anion. Then the DMC carbonyl group reacts with the anion to form a hydroxyl alkyl carbonate and a methoxide anion. Further intermolecular reactions in the presence of the catalyst generated GC and two molecules of methanol as byproduct. GC, a water soluble and environmentally friendly chemical, is widely used in cosmetic industries as surfactant and agro-allied booster [9]. Studies revealed that transesterification

reaction of triglyceride with DMC as acyl acceptor produces a blend of one molecule of GC and three molecules of biodiesel (BD) without glycerol byproduct. Hence, GC also possesses fuel-like properties, and it can be blended with biodiesel to increase combustion efficiency [10]. The pathway via DMC and triglyceride reaction to synthesize GC mitigates the energy intensive purification steps encountered in BD synthesis via methanolysis. In fact, there is general research consensus that GC potential as anti-explosive additives for diesel and gasoline will result in an increasing demand of GC [10]. Irreversible glycerol transesterification utilizes excess DMC, relatively mild reaction conditions, and catalyst to promote forward reaction [11,12]. Hence, GC yield can be enhanced by controlling reaction-influencing parameters, such as temperature, DMC-to-glycerol molar ratio, catalyst dosage, and reaction time [13].

Studies have extensively investigated the use of heterogeneous catalysts to modify glycerol transesterification. Notably, calcium-based catalysts are known options for promoting reaction due to their abundance and appreciably high catalytic activity [14–16]. However, calcium is hygroscopic and unstable in glycerol. Reusability of such catalysts in successive experimental cycles is characterized with serious deactivation because of severe leaching and homogeneous catalysis. To stabilize calcium, alkali and alkaline earth metals, such as Na, K, and Mg, are utilized with relative success [16–18]. Their dispersion force

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and ionic bond interaction provide improved resistances to leaching, and such resistance is attributed to surface coverage by amorphous calcium carbonate generated in situ [16,17]. Hydrotalcites are double-layered hydroxides with memory effect and have been applied as alternative to avoid limitations encountered using calcium-based materials [19–21]. The use of hydrotalcites recorded considerable success with appreciable GC yield of > 90%. Nevertheless, their application often requires relatively high temperature (90–120 °C) to increase contact between catalyst and reacting species. Mg in hydrotalcites features the weakest reactivity among group II oxides, and it presents low solubility in reaction solution [22,23].

Sustainability is desirably achieved by shifting from conventional and fast-depleting synthetic chemicals to wastes (either industrial waste or biomass) as active catalytic materials. Functionalizing wastes for beneficial utilization will mitigate handling and disposal challenges. Catalytic conversion of glycerol and DMC to GC over functionalized wastes or abundant earth crust minerals has received limited research effort. To date, materials, such as gypsum, dolomite, ladle furnace steel slag wastes, and Na or K-zeolites from oil palm ash, have been reported to modify glycerol transesterification with DMC [12,24,25]. In most cases, high calcium content (especially predominantly calcium-based materials) still presents severe stability problems. To increase stability and consequent calcination, optimization must also be performed on energy-intensive steps involved in transforming oil palm ash to zeolites or functionalizations of ladle furnace slag [25].

Biochars are low-cost and efficient catalytic materials for transesterification reactions because of their tailored textural characteristics and relatively high surface area. They are usually activated and/or functionalized with mineral acids or alkaline metals to enhance their catalytic performance. Biochars derived from animal wastes presents even enhanced features for direct application with or without functionalization. This is because, animal wastes such as meat and bone contains variant minerals necessary to drive transesterification. Wang et al. [26], utilized meat and bone biochar as a catalyst to tailor biodiesel production. The meat and bone biochar displayed remarkable regeneration attributes and can be reused over ten successive cycles. Similarly, Guinea fowl bone was utilized as an efficient catalyst to promote biodiesel production [27]. The Guinea fowl bone contains calcium phosphate mineral that was transformed to hydroxyapatite at 900 °C and presents good resistance to acute deactivation. Thus, the utilization of bio-wastes to synthesize catalytic materials mitigates disposal problems and facilitates reduction of environmental pollution. Hence, synthesizing highly active, reusable and low-cost biochar catalyst for glycerol transesterification reaction is the motivation for this study.

Fishmeal is derived from sub-utilized fish species, unsold fish, and offal [28]. In the year 2015, 463 million metric tons of fishmeal were produced globally. As such, the high demand and consumption of fish as a food results in generation of abundant by-product fishmeal that requires utilization [29]. Depending on the parent material, mineral constituents of fishmeal vary [30,31]. These mineral elements, primarily a mixture of some alkali metals, phosphorus, fatty acids, and proteins, are suitable for base-catalyzed glycerol transesterification. No cost-effective and environmentally friendly method is available for preservation of fishmeal. Refrigeration or other known chemical preservation techniques (formaldehyde) are costly, and preventing generation of poisonous nitrosamines requires special control skills [32]. Hence, diversified utilization of fishmeal will reduce handling challenges and promote its viability. In the present study, GC was synthesized from glycerol and DMC over fishmeal-derived biochar. The as-obtained fishmeal was carbonized under inert conditions and utilized directly in glycerol transesterification without post-functionalization. Reaction conditions and reusability were investigated to obtain the most suitable conditions and probe stability, respectively.

## 2. Materials and methods

### 2.1. Materials

Fishmeal (mixture of fish offal and fish bone) was obtained from a local fishmeal company in Malaysia. Methanol (99%), DMC, NaOH pellets, and anhydrous glycerol were purchased from R & M Chemicals (Malaysia). Industrial grade nitrogen gas was used for carbonization (98.8% assay), and gas chromatography standards (99%) used were obtained freely from Huntsman Company (USA).

### 2.2. Fishmeal biochar catalyst preparation

Tubular stainless-steel reactor was used to carbonize fishmeal at a temperature range of 550–750 °C for 90 min under N<sub>2</sub> gas flow at 100 mL/min rate. Fishmeal carbonization was performed at different temperatures to investigate effects of heat treatment on catalyst performance. The obtained fishmeal biochar was cooled under the same nitrogen flow. Subsequently, grinding and sieving in a 100-mesh sieve (0.15 mm sieve size) were performed to obtain a powdered biochar. The powdered biochar was used in glycerol transesterification without any further treatment.

### 2.3. Characterization of fishmeal biochar

Composition of fishmeal biochar was investigated using field emission-scanning electron microscope (ZESIS SUPRA 35VP model) equipped with energy-dispersive spectroscope. Active site for leaching was investigated for solvent biochar reused for five times via energy-dispersive spectroscopy (EDX).

Acid–base (neutralization) titration technique was used to determine bulk base amount of sample [16]. Approximately 100 mg of biochar was dispersed in 10 mL of HCl (0.5 M) and stirred for 24 h. Afterward, suspension was filtered, and filtrate was titrated against NaOH (0.1 M). Phenolphthalein was used as indicator. Basic strength of biochar catalyst was determined by observing virtually color changes in utilized Hammett indicators (phenolphthalein ( $H_a = 9.3$ ), 2,4-dinitroaniline ( $H_a = 15.0$ ), 4-nitroaniline ( $H_a = 18.4$ ), and aniline ( $H_a = 27.0$ )). Typically, 50 mg of biochar was sonicated in 10 mL cyclohexane for 2 h. Indicators were prepared by dissolving in benzene (0.75 wt%) [16,23,25]. The indicator dissolved in benzene was added dropwise to cyclohexane solution, which contained suspended biochar catalyst. Sample was allowed to stand further for 2 h until no further color changes were virtually observed.

Nitrogen adsorption measurements were conducted using Autosorb I Quantachrome adsorption analyzer, which automatically reports surface area, pore volume, and adsorption isotherm. Multipoint Brunauer–Emmet–Teller equation was used between 0.05 and 0.20. The thermodynamic-based Barrett–Joyner–Halenda method was used to calculate pore size distribution from adsorption–desorption branches of N<sub>2</sub> isotherm. Total pore volume was determined from adsorption–desorption trend of N<sub>2</sub> isotherms.

Perkin Elmer Spectrum GX model of Fourier transform infrared spectrometer (FTIR) analyzer was used to study functional groups in biochar surface. IR spectra were recorded in the range of 4000–400 cm<sup>−1</sup> wavenumber at a resolution of 4 cm<sup>−1</sup>. Krypton–bromide (KBr) pelleting technique was used to prepare samples for analysis by mixing powdered KBr and catalyst (KBr:biochar) at 10:1 ratio. Afterward, powder mixture was ground in agate mortar and pressed in an evacuable pellet die to form transparent pellets.

### 2.4. Glycerol transesterification with DMC

Glycerol transesterification was conducted in a 250 mL three-neck glass reactor, which was attached with a thermocouple, condenser, and stopper. Reaction temperature, time, and agitation speed were

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