



Full paper/Mémoire

Coupling transesterifications for no-glycerol biodiesel production catalyzed by calcium oxide

Ying Tang*, Qitong Cheng, Hui CaO, Li Zhang, Jie Zhang, Huafeng Li

College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an Shaanxi 710065, China

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ABSTRACT

In this study, a method consisting in coupling transesterifications for no-glycerol biodiesel production catalyzed by CaO was put forward. The transesterification between rapeseed oil and methanol was greatly improved by integrating glycerol and dimethyl carbonate (DMC) transesterification. From this result, it was found that the high fatty acid methyl ester (FAME) yield of 92.6% (with ultra-traces of glycerol as a by-product) was obtained at 65 °C under normal pressure, which is as high as the previously reported supercritical DMC method for no-glycerol biodiesel production at a reaction temperature of 350 °C and under pressures up to 17.8 MPa. Moreover, this new method has high water tolerance, and a yield of over 82% of FAME is still achieved in the presence of 0.2% of water. The optimized reaction conditions, such as the molar ratio of DMC to methanol, the catalyst dosage and the reaction time, were investigated to produce high-quality biodiesel. The fuel properties determined and discussed in light of EN 14214 (European standards) demonstrate that the biodiesel produced using this new method has good flow properties with a cloud filter plugging point of –10 °C and a pour point of –9.4 °C. Furthermore, the amount of free glycerol was found to be as low as 0.018% in the biodiesel obtained directly from this new method without any further processing. The results of this study indicate the feasibility of producing quality biodiesel fuels without glycerol by coupling transesterifications.

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1. Introduction

Biodiesel is defined as the mono alkyl esters of fatty acids without aromatics; its low SO_x content has revealed its promise as an alternative fuel for diesel engines [1,2], and now it has been used as blended with diesel. Conventionally, biodiesel is produced by transesterification of glycerol triglyceride with short-chain alcohols, such as methanol and ethanol, in the presence of inorganic homogeneous base catalysts, which results in many problems, such as the recovery of the catalysts and the treatment of wastes [3,4]. Transesterification using

heterogeneous catalysts has been established to simplify the process of catalyst separation from liquid products and eliminate large consumption of water [5,6]. However, a by-product, crude glycerol, produced in the conventional transesterification process in excessive amounts, is an oversupplied chemical, as biodiesel production has kept growing in recent years. The current utilization of glycerol is not efficient enough to support its predicted increase. Therefore, it becomes imperative to find new convenient uses for glycerol and more perspectives for increasing the economy of biodiesel production [7]. With this purpose, alternative strategies to transform glycerol into high-value glycerol derivatives are under investigation, and some new technologies for the use of glycerol have been developed, such as glycerol hydrochlorination and dehydration of glycerol to acrolein [8].

* Corresponding author.

E-mail address: tangying78@xsyu.edu.cn (Y. Tang).

Recently, great interest has risen to promote the economic feasibility of the use of glycerol in biodiesel production by using DMC, an eco-friendly and chemical reactive reagent, as an acyl acceptor for transesterification to produce biodiesel and glycerol carbonate (GC) simultaneously [9,10]. By this new transesterification process, glycerol carbonate with higher commercial value, instead of glycerol, is obtained as a by-product. Fabbri et al. prepared biodiesel and GC simultaneously from transesterification between soybean oil and DMC by utilizing NaOH as a catalyst [11]. In this work, a high soybean oil conversion rate, 99%, was obtained at 90 °C after 6 h, but it suffers from tedious separation and purification procedures. Consequently, Saka and Tan conducted a non-catalytic DMC process to produce biodiesel and GC by using supercritical DMC technology under critical reaction conditions [12,13]. The transesterification rate between oil and DMC is accelerated dramatically and it is easy to get a high yield of FAME over 97% in less than 30 min [14]. However, its large-scale application is limited, due to the high temperature and pressure needed, since 350 °C and 17.8 MPa are required. Furthermore, in this procedure, the yield of FAME goes on decreasing with the reaction time due to its poor thermal stability under high temperatures and pressures. In recent years, biocatalytic production of biodiesel in mild reaction conditions has attracted much attention to overcome the problems encountered with the chemical method. Min and Lee employed lipase to perform biodiesel biosynthesis and GC from corn oil and DMC [15]. Although a high yield of biodiesel, nearly 94%, is attained, and although good stability of lipase with over 80% yield of FAME after seven recycling operations is observed, large dosage of enzymes (75–100 g/l) and long reaction times (24–48 h) limit its wide application [16,17].

Typical transesterification for biodiesel production from oil and methanol is catalyzed by basic catalysts, and solid bases such as CaO and CaO-supported catalysts have been used to avoid the problem caused by catalyst separation [18,19]. Among all kinds of solid bases, CaO has exhibited excellent catalytic performance with yields of over 92% of FAME after 4–6 h at 65 °C, which contributed to its strong basicity and low cost [20,21].

In this paper, in order to develop a new efficient process for biodiesel production without any issue concerning the crude glycerol by-product under mild reaction conditions, a new coupling transesterification process was designed and applied to prepare biodiesel and GC. The effects of individual reaction parameters and their interactions with the yield of FAME have also been screened to obtain the optimum reaction conditions. Some of the major biodiesel properties were measured according to the European standard EN 14214 at last.

2. Method

2.1. Materials

Rapeseed oil was purchased from a coal market (Xi'an, China). Before the reaction, the oil was treated by sodium hydroxide and bentonite; after that, the acid content

lowers to less than 1 mg KOH/g and the water concentration is below 1 mg/g. Analytical-reagent-grade dimethyl carbonate, methanol, and CaO were purchased from Sinopharm Chemical Regents Co., Ltd. (Beijing, China), and used without further purification.

2.2. Catalytic testing

For transesterification, a given amount of commercial CaO catalysts was added into the mixture of methanol, rapeseed oil and dimethyl carbonate in a three-necked round-bottomed flask equipped with a reflux condenser and a thermometer. The mixture was heated at a certain temperature under stirring and samples were taken out from the reaction mixture every 1 h. Then, the catalyst was separated by centrifugation and the excess methanol was distilled off under vacuum.

2.3. Product analysis and fuel properties of biodiesel

The FAME yield was defined as the ratio of the weight of FAME determined by GC (HP-6890) to the weight of fatty acid methyl esters that the oil used in the reaction, assuming that only traces of esters were transferred to the polar phase and that the extraction of methanol and glycerin only takes place. The products were analyzed by GC equipped with an HP-5 capillary column using an inner standard method. The nitrogen was used as a carrier gas at a flow rate of 20 mL/min. The oven temperature was kept at 280 °C in isothermal conditions [18–20]. The relative density of FAME at 15 °C was determined using an Anton Paar density meter (DMA 4500 M). The cloud, pour points and flash point were determined using the ASTM standard test methods.

3. Results and discussion

3.1. Design of bitransesterification for no-glycerol biodiesel production

As suggested by Fabbri et al. [11], the transmethylation reaction of vegetable oil and DMC under mild reaction conditions (90 °C, 5 h, 5% catalyst) only effectively proceeds over the base catalyst, while the heterogeneous catalysts tested in their study (hydrotalcite, titanosilicate, and zeolite) provided less than 5% conversion of triglyceride under the same conditions. Similarly, in our research, 65 °C, normal pressure and 15% CaO catalyst, the transesterification between vegetable oil and DMC has hardly any possibility to take place. But a comparable FAME yield of 84.5% was obtained when CaO was replaced with KOH. However, the separation of biodiesel is very complex due to the serious saponification caused by KOH. In contrast, the clear phase surface between CaO and the product is in favor of a consequent separation process.

The transesterification of vegetable oil and methanol is well known to be proceeded rapidly over a solid base, such as CaO, to produce FAME and glycerol under mild reaction conditions [22–24]. Additionally, previous reports have revealed that CaO also exhibits good catalytic performance in the transesterification of DMC and glycerol, showing a

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