



Full Length Article

Biodiesel production from soybean oil and dimethyl carbonate catalyzed by potassium methoxide



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ABSTRACT

A study of the soybean oil transesterification reaction with dimethyl carbonate (DMC) catalyzed by potassium methoxide prepared through recrystallization process in presence of methanol was done. Reaction variables were analyzed viz. temperature of 40, 60 and 80 °C, DMC to oil molar ratio of 2:1, 4:1, 6:1, 8:1 and 10:1, and catalyst concentration of 1, 1.5 and 2 wt% in relation to oil, aiming to obtain the best condition for reaction. Triglyceride conversion of 99% was achieved for 6:1 DMC:oil molar ratio, 2.0 wt% of catalyst concentration and 80 °C after 15 min of reaction. Experiments were carried out to investigate methanol effects in DMC/oil medium and also to compare reactions with recrystallized and heterogeneous catalysts. Potassium methoxide recrystallized in presence of methanol achieved a triglyceride (TG) conversion higher than 99% while only a 20% TG conversion was achieved from heterogeneous reaction at same condition. Potassium quantification in biodiesel phase was done in order to investigate the homogeneous pathway catalysis in recrystallized catalyst reaction.

1. Introduction

Nowadays, biodiesel is the most used renewable biofuel to replace petrodiesel in compression ignition engines [1]. Guided by government policies, implementation of biodiesel/petrodiesel blends in commercial fuels have brought biodiesel to the energetic matrix of many countries increasing dramatically its production in recent years [2].

Transesterification of vegetable oils in presence of methanol is the main production process to produce biodiesel, which is a mixture of fatty acid methyl esters (FAMES). However, this reaction also produces glycerin as byproduct. Glycerin has a big impact in profits for small and medium biodiesel industry because its market is deeply connected to the biodiesel market [3]. At the same time biodiesel production has increased, glycerin supply also increased and prices began to fall.

Many researches have been done aiming to increase the economic viability in biodiesel production compared to petrodiesel. Glycerol-free process is an alternative to overcome this challenge since it produces, instead of glycerol, another component that usually has higher market value, or that is miscible in biodiesel phase, preserving its physico-chemical characteristics and increasing global process yield.

According to this, Fabri et al. [4] presented a novel reaction pathway to produce biodiesel-like fuel from triglyceride (TG) and dimethyl carbonate (DMC) over several catalysts which yields, in addition to FAMES, fatty acid glycerol carbonate monoesters (FAGCs). FAGCs are

soluble in FAMES phase increasing the global yield production without changing the main biodiesel properties. Besides that, FAGCs can react with DMC producing one more FAME and one molecule of glycerol dicarbonate (GDC), which separates from the biodiesel phase naturally via decantation. The reactions mentioned above are illustrated in Fig. 1.

GDC is a poorly explored component so far and few information about it is found in literature. Ochoa-Gómez et al. [5] have synthesized GDC and reported that it is a crystalline yellowish white solid when pure at ambient temperature with melting point of 80 °C. On the other hand, a similar component named glycerol carbonate (GC) is widely known. GC can be formed in the transesterification reaction due to GDC decomposition when water is present in the medium as shown in Fig. 2. The increasing industrial attention for GC is based on its physical and chemical (reactivity) properties. GC is non-flammable, water soluble, readily biodegradable, non-toxic and slightly viscous liquid molecule with a very low evaporation rate. It is or can be used as solvent, component in beauty and personal care compositions, solid laundry detergents, building ecomposites, electrolytes for lithium and lithium-ion batteries, carrier in pharmaceutical preparations, and in the manufacturing of chemical intermediates and polymers [5]. Nowadays GC has high market value and GDC could have as well in the future.

Unlike methanol, DMC is very soluble in oil, which favors transesterification reaction, however many authors [4,6–12] have pointed out that common catalysts used in transesterification reactions like

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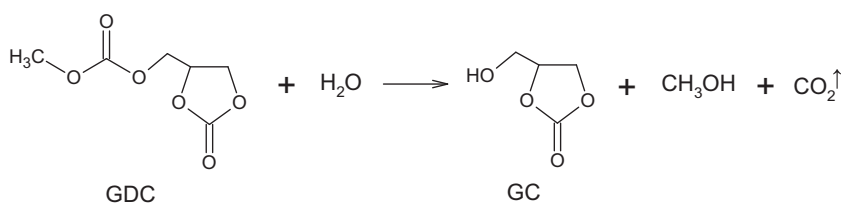
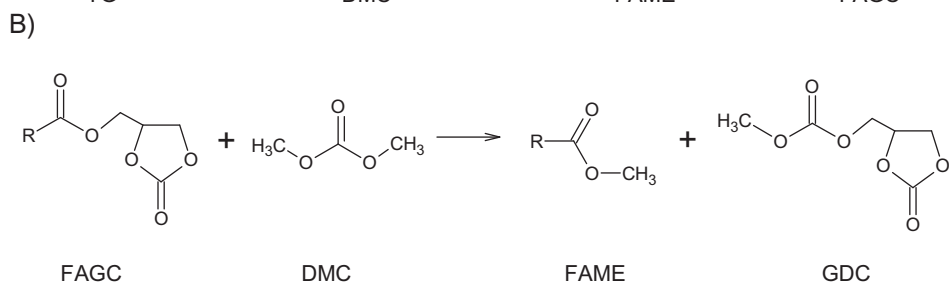
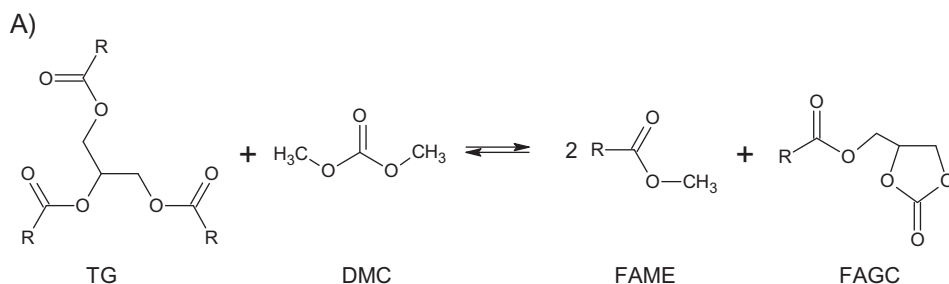


Fig. 1. A) Reaction between TG and DMC producing a mixture of FAMES and FAGCs. B) Reaction between FAGC and DMC yielding another FAME and GDC.

Fig. 2. Decomposition reaction of GDC in presence of water yielding GC, methanol and carbon dioxide.

hydroxides and methoxides of sodium and potassium are not soluble in DMC. This characteristic makes reactions with DMC heterogeneous, which decreases the reaction rate. To overcome this issue, Kai et al. [10] performed a transesterification with DMC catalyzed by sodium methoxide prepared by recrystallization process. According to these authors, this method increases dramatically the catalytic activity owing to the larger catalyst surface area of the very small particles generated.

Another similar problem was reported by Casas et al. [13] in their work of interesterification of vegetable oil with methyl acetate. As well as transesterification with DMC, the interesterification is a glycerol-free method to produce biodiesel, and methoxides are slightly soluble in the solvent/reagent methyl acetate. The authors used potassium methoxide as catalyst and noticed and enhanced reaction rate in the presence of methanol due to the greater quantity of catalyst that could be dissolved in methyl acetate, reducing heterogeneous catalysis.

Transesterification reaction from soybean oil and DMC using potassium methoxide in heterogeneous form was recently investigated by Dawodu et al. [6]. These authors related high triglycerides conversions but at high reaction times and catalyst loadings. Since soybean oil is the most widely feedstock used in biodiesel production in whole world, the aim of this work is to investigate the transesterification reaction of soybean oil with DMC catalyzed by potassium methoxide prepared by recrystallization with methanol.

2. Material and methods

2.1. Materials

Commercial refined soybean oil was obtained in a local marketplace. Dimethyl carbonate (99%) ReagentPlus® grade, potassium methoxide (95%), Heptane (99%), methyl heptadecanoate (internal standard), tricaprín (internal standard) and standard references for FAME analysis which include methyl palmitate, methyl oleate, methyl linoleate and methyl linolenate were purchased from Sigma Aldrich (Brazil). Methanol HPLC grade was acquired from Dinâmica (Brazil).

2.2. Oil characterization

Commercial soybean oil was characterized to determine the fatty acid profile based on a method described by Hartman and Lago [14] to convert all fatty acids in FAMES prior to analysis, based on the standard method EN 14103. Total esterificable matter was obtained after the sum of all present FAME peaks in chromatogram. Water content was determined by Karl-Fisher titration and acid value by potentiometric titration with methanolic solution of potassium hydroxide.

2.3. Catalyst preparation

The catalyst was prepared by a recrystallization process. The required amount of powder potassium methoxide was weighed in a beaker and after that methanol was mixed until complete dissolution. A methanolic catalyst solution of about 10 wt% was produced and transferred to a flask to evaporate part of the solvent in a rotary evaporator under 50 mbar vacuum, at 50 °C for 30 min. Then, a white catalyst slurry was produced composed by small recrystallized particles suspended in methanol solution (catalyst saturated methanolic solution). Total methanol removal was not intended due to reasons that will be discussed further. To control methanol quantity into the reaction, weighing was done before and after the solvent evaporation.

2.4. Experimental procedure

In the same flask used to catalyst preparation, DMC was weighed over the catalyst slurry prepared and immersed in a controlled temperature bath under magnetic stirring to reach the desired temperature of the reaction. In parallel, soybean oil was weighed in a beaker and heated to the same temperature. Since oil and slurry-DMC mixture reached the temperature, oil was dumped into slurry-DMC mixture to start the transesterification reaction. A condenser was used to avoid methanol and DMC evaporating. Temperature was controlled by a PID controller with a thermocouple immersed into the reactor, with ± 1 °C

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