



## Dimethyl carbonate mediated production of biodiesel at different reaction temperatures



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### ABSTRACT

Methanol was replaced by dimethyl carbonate for biodiesel production. In the process, fatty acid methyl ester (FAME) was produced through transesterification of soybean oil with dimethyl carbonate (DMC) using potassium methoxide as a catalyst. This method produced a more attractive by-product, glycerol carbonate (GC). Factors affecting the reaction such as vegetable oil to DMC molar ratio, catalyst concentration, reaction time and reaction temperature were optimized. Triglyceride conversion of 95.8% was obtained at the optimized condition. This process provided an insight into the reactivity of DMC at different temperature. Co-production of FAME and glycerol carbonate (GC) proceeded through carboxymethylation reaction because methoxyl group and carbonyl group are generated which subsequently attacked the carbonyl moiety in glyceride molecules to form the required products.

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### 1. Introduction

At present, biodiesel is produced majorly from the reaction of triglyceride and methanol with glycerol as a by-product. The over-production of glycerol has caused a drastic reduction in price due to extensive supply in the market and glycerol-producing companies were extremely affected [1]. Even though glycerol currently has a large number of applications in various fields such as cosmetics, pharmaceuticals, foods and drinks industries [2], over-production of glycerol exceeds the current demand of this compound for chemical production and thus, new technologies for the large-scale usage of this feedstock will be required. The current production of glycerol has currently reached a plateau due to competition with food production, although the expected growth of biodiesel production levels both in Europe and in the US will stimulate researchers to find new applications for crude glycerol. One of the possibilities for large-scale consumption of glycerol would be to utilize glycerol as fuel for the transportation sector. Unfortunately, unlike ethanol, glycerol cannot be directly added to conventional fuels due to its low solubility in hydrocarbons [2]. Additionally, the high viscosity and instability (at high temperatures) of this

compound strongly discourage its use as an additive in combustion engines [3,4]. Therefore, glycerol must be chemically transformed (e.g. deoxygenated) to adjust its properties to those of liquid hydrocarbon fuels. In this respect, a promising route for glycerol conversion involves the production of syngas through Aqueous-Phase Reforming (APR) processes [5].

Researchers are also finding alternative methods of revalorizing glycerol into value-added commodities [6]. One of the various ways of utilizing glycerol is through the reaction of glycerol with dimethyl carbonate to produce glycerol carbonate (GC) which is currently utilized in the pharmaceutical, cosmetics and plastic industries [7]. Various ways of producing glycerol carbonate (GC) have been reported in the literature [8,9]. But these methods have been greatly limited due to catalysts short lifespan and long reaction time ( $\geq 30$  h).

Although, methanol mediated transesterification reaction only requires a small amount of alkali catalyst for biodiesel production and the reaction is completed within a short time but there are limitations. Since the reaction is homogeneous, the catalyst is removed by washing with water leading to loss of fatty acid methyl ester (FAME) through saponification of unreacted triglycerides. Also, the glycerol produced as by-product is lost to the washing step and some of the glycerol are even discarded as wastes, which is environmentally unfriendly [10]. These limitations could be solved using DMC as reactant in the presence of alkali. Since alkali acted as a solid catalyst in DMC solution, separation could be simply done by

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filtration or centrifugation thereby yielding high biodiesel purity and higher valued by-product, glycerol carbonate. In his pioneering work, Fabbri et al. [11], utilized dimethyl carbonate (DMC) both as the solvent and reactant in transmethylation of soybean oil in the presence of sodium methoxide. Since then, various research works have been reported on concomitant production of biodiesel and glycerol carbonate (GC). Ilham and Saka [7] reported a non-catalytic supercritical dimethyl carbonate process to produce biodiesel and GC from rapeseed oil while Tan and co-workers [12] also optimized the supercritical dimethyl carbonate technology for the production of biodiesel and glycerol carbonate (GC) from purified palm oil. Lipase catalysed production of biodiesel and glycerol carbonate (GC) have also been reported in literature [13–15].

DMC has a wide range of physical properties and chemical reactivities [10,16]. Also, DMC are being produced from methanol and carbon dioxide thereby making it a true green reagent. It exhibits low toxicological and ecotoxicological properties (Table 1). According to Tundo and Selva [16], the reactivity of DMC is tuneable, at the boiling point of DMC; methoxycarbonylations take place, whereas at higher reaction temperatures ( $\geq 160$  °C), methylation reactions are observed in the presence of a suitable catalyst. Methoxide ions are generated in the two reactions which subsequently start transesterification process. Most literatures on DMC-mediated production of biodiesel are either centred on supercritical methods or lipase catalysed processes. These methods are expensive and complex, thus making commercialization extremely difficult. Thus, this paper fully investigates the reactivity of DMC at different temperature in a simple batch system and the parameters affecting production of biodiesel were optimized in the presence of potassium methoxide.

## 2. Materials and methods

### 2.1. Materials

Refined soybean oil with low free fatty acid (0.06%, determined by acid titrimetry method) was purchased from Beijing Eisen-Lubao oil Co, Ltd, China and result of the fatty acid composition by gas chromatography-mass spectrometer (GC-MS) is shown in Table 2. Dimethyl carbonate (99.95%) was supplied by Liao Yang Kong Lung Chemical Industry Ltd, China. Methanol (99.5%), hydrochloric acid (~68.0%), potassium carbonate (99.0%) was obtained from Beijing Chemical Works, China while potassium hydroxide (85.0%), sodium hydroxide (99.0%) and n-hexane (95.0%) was purchased from Guangdong Xilong Chemical Co. Ltd., China. Sodium aluminate ( $\text{Al}_2\text{O}_3$  content;  $\geq 41.0\%$ ) was acquired from Sinopharm Chemical Reagent Co. Ltd., China. Acetone (HPLC grade) was supplied by J.T.

**Table 2**

Fatty acid composition of soybean oil.

| Fatty acid       | Formula | Composition (%) |
|------------------|---------|-----------------|
| Palmitic acid    | C16:0   | 11.9            |
| Palmitoleic acid | C16:1   | 0.1             |
| Stearic acid     | C18:0   | 4.8             |
| Oleic acid       | C18:1   | 32.8            |
| Linoleic acid    | C18:2   | 49.7            |
| Linolenic acid   | C18:3   | 0.6             |

Baker (USA). Sodium methoxide (99.0%) and methyl oleate (99.0%, J&K Scientific Ltd., China), methyl linoleate (99.4%), methyl stearate (99.0%), methyl palmitate (99.0%), methyl linolenate (99.0%) and methyl heptadecanoate (98.7%) was purchased from AccuStandard, China. All chemicals and reagents used were of analytical grades and used without further purification.

### 2.2. Transesterification of soybean oil and DMC over alkali catalysts

Some alkalis such as potassium carbonate ( $\text{K}_2\text{CO}_3$ ), potassium hydroxide (KOH), sodium aluminate ( $\text{NaAl}_2\text{O}_3$ ), sodium methoxide ( $\text{NaOCH}_3$ ), potassium methoxide ( $\text{KOCH}_3$ ) and sodium hydroxide (NaOH) were screened for the conversion of soybean oil and dimethyl carbonate (DMC) to fatty acid methyl ester (FAME). The reaction was conducted in a reactor consisting of reflux condenser, thermocouple and a sample dropper. 25 g of the oil was initially charged into the glass reactor and heated in an oil bath to 90 °C. DMC and catalysts were added into the reactor and the reaction was allowed to proceed for 300 min. After completion, unreacted DMC, methanol and GC were removed via vacuum and the product was centrifuged at 3000 rpm to remove the catalyst.

The reaction carried out at 200 °C, autoclave made of stainless steel capable of withstanding high pressure was used. The Teflon-lined autoclave is thermostatically controlled and is equipped with a stirrer. Predetermined amounts of vegetable oil, DMC and catalyst were added into the Teflon-lined reactor and pressurized to ensure that the reactant is in a liquid phase throughout the reaction. The reactor was then mounted onto the heating chamber and timed immediately. A blank experiment in the absence of catalyst was initially carried to eliminate the possibility of the reaction taking place under supercritical condition.

#### 2.2.1. Optimization studies

In the optimization work, the effect of oil to DMC molar ratio, catalyst concentration and temperature on triglyceride conversion

**Table 1**  
Toxicological and ecotoxicological profile of DMC.

| Property  | DMC <sup>d</sup>                              | Methanol <sup>e</sup>                              |
|---|---|--|
| Oral acute toxicity (rats)  | <sup>a</sup> LD <sub>50</sub> 13.8 g/kg       | LD <sub>50</sub> 13 g/kg                           |
| Acute toxicity per contact (cavy)   | LD <sub>50</sub> > 2.5 g/kg                   | LD <sub>50</sub> > 5 g/kg                          |
| Acute toxicity per inhalation (rats)                                      | <sup>b</sup> LC <sub>50</sub> 140 mg/L; (4 h) | LC <sub>50</sub> 8800 mg/L; (8 h)                  |
| Mutagenic properties  | none  | none   |
| Irritating properties (rabbits, eyes, skin)                               | none  | Skin dryness and redness, causes death in children |
| Biodegradability (OECD 301 C) <sup>c</sup>                                | >90% (28 days)                                | >50% (7–18 days)                                   |
| Acute toxicity (fish) (OECD 203)  | <sup>d</sup> NOEC 1000 mg/L                   | NOEC 23.75 mg/L                                    |
| Acute toxicity on aerobic bacteria of wastewaters (OECD 209) <sup>c</sup> | <sup>e</sup> EC <sub>50</sub> > 1000 mg/L     | EC <sub>50</sub> > 7690 mg/L                       |

<sup>a</sup> LD<sub>50</sub> = The dose that kills half (50%) of the animals tested.

<sup>b</sup> LC<sub>50</sub> = A calculated concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population.

<sup>c</sup> OECD = International body on guidelines for the testing of chemicals.

<sup>d</sup> NOEC = Concentration which does not produce any effect.

<sup>e</sup> EC<sub>50</sub> = The concentration of a compound where 50% of its maximal effect is observed.

<sup>f</sup> Tundo and Selva [16].

<sup>g</sup> IPCS [17].

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