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In situ self-catalyzed reactive extraction of germinated oilseed with short-chained dialkyl carbonates for biodiesel production

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HIGHLIGHTS

- Germinated seeds and DMC were used for in situ biodiesel production.
- The extra uses of catalyst and oil extraction solvent were avoided.
- The maximum biodiesel yield was 87.41% under the optimized conditions.
- The overall processing steps for biodiesel production can be reduced.

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ABSTRACT

In order to eliminate the expense associated with solvent extraction and oil cleanup, and reduce the processing steps in biodiesel production, reactive extraction has become a focus of research in recent years. In this study, germinated castor seed was used as substrate and catalyst, dimethyl carbonate (DMC) was used as acyl acceptor and oil extractant to produce biodiesel. The optimum conditions were as follows: the germination time of castor seed was 72 h, DMC/germinated seed ratio was 12.5 ml/g, reaction temperature was 35 °C, and water content was 2.11%. The biodiesel yield could reach as much as 87.41% under the optimized conditions. This germinated oilseed self-catalyzed reactive extraction can be a promising route for biodiesel production.

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1. Introduction

Biodiesel, a renewable, biodegradable and non-toxic fuel, has emerged as one of the most potential candidates to replace current petro-diesel fuel (Shimada et al., 1999; Lam et al., 2010). Traditional methods for producing biodiesel from non-edible seeds oil involve various steps: oil extraction, purification, deacidification, dewaxing and a series of other processing, and subsequent esterification or transesterification. The requirement of these processing steps constitutes more than 70% of the total biodiesel production cost if refined oil is used as feedstock (Zeng et al., 2009; Shuit et al., 2010a). Recently, some researchers used "reactive extraction" technology for the production of biodiesel from oil-bearing materials, which can simplify the steps associated with solvent extraction and oil cleanup (Georgogianni et al., 2008; Qian et al., 2008; Ehimen et al., 2010; Kasim et al., 2010; Shuit et al., 2010b; Haas and Wagner, 2011a,b; Kiss and Bildea, 2012; Dong et al., 2013). Therefore, the reactive extraction is capable to replace traditional methods for biodiesel production.

According to the catalysts used in the reactive extraction process, the production methods of biodiesel can be broadly classified into two categories: chemical and enzymatic based transesterification (Su et al., 2009; Leung et al., 2010; El-Enin et al., 2013). Homogeneous acid or alkaline catalysts, such as H_2SO_4, NaOH, KOH and CH_3ONa, are mostly used in chemical reactive extraction thanks to the high catalytic efficiency, short reaction time and easy maneuverability. However, some disadvantages such as difficulties in products separation, equipments corrosion and wastewater pollution limit their applications (Leung et al., 2010). Enzymatic reactions can overcome these shortcomings, and have the advantages of low energy consumption, easy separation of products, mild reaction conditions and friendly to the environment (Su et al., 2009; Leung et al., 2010). However, the activity of lipase can be easily destroyed by the excessive use of short-chained alcohols (Shimada et al., 1999; Kumari et al., 2009). Su et al. have reported the production of biodiesel using dimethyl carbonate (DMC) as acyl acceptor, which could eliminate the risk of deactivation of lipase

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caused by short-chained alcohols (Su et al., 2007). Moreover, the reaction between oil and DMC is irreversible, and therefore enhance the reaction speed and improve the biodiesel yield (Su et al., 2007, 2009). However, the high cost and poor operational stability of the immobilized lipase become major bottlenecks of the enzymatic approach for biodiesel production (Shimada et al., 1999; Noureddini et al., 2005; Kumari et al., 2009). It is necessary to find a novel type of lipase for this enzyme-catalyzed reactive extraction technology. Recently, an environmentally friendly and low-cost in situ self-catalytic process for biodiesel production was developed (Gu et al., 2011). The highest fatty acid methyl ester (FAME) yield could reach 87.6% under the optimum conditions. Such a simple reactive extraction process without additional catalyst may greatly reduce the processing steps and costs of biodiesel production. In that work, *n*-hexane was used as co-solvent to accelerate the in situ transesterification. However, *n*-hexane was unfavorable to the lipase activity as well as to the separation of products. In order to avoid the extra use of extraction solvent and improve the stability of the lipase, DMC may be a better candidate, which can be used as acyl acceptor and extraction solvent at the same time.

Castor oil, extracted from the seeds of castor, is a non-edible plant oil source for biodiesel production, which ensures that biodiesel production does not compete with the food industry for resources (Ogunniyi, 2006; Berman et al., 2011; Hama and Kondo, 2013). Although there have been many studies reported on the production of biodiesel from castor seeds (Berman et al., 2011; Hincapié et al., 2011; Dias et al., 2013), there is no report on the in situ self-catalyzed process. Therefore, the main objective of the present work is to determine the feasibility of using reactive extraction without additional catalyst for the production of biodiesel from germinated castor seeds. DMC was used as acyl acceptor and extraction solvent. The optimal germination time of castor seed and reaction conditions (DMC dosage, reaction temperature, and water content) were investigated to obtain the maximum biodiesel yield.

2. Methods

2.1. Materials

The castor seeds (obtained from Fuao Seed Limited Company, Hebei Province, China) used in this study were standard products of Chinese agriculture. Anhydrous alcohol ($\geqslant$99.7% purity) and DMC were obtained from Tianjin Jiangtian chemical factory, Tianjin, China. Formaldehyde (37–40%) was obtained from Jinan Baiyun Chemical Limited Company, Jinan, China. All other chemicals and reagents were analytical pure and obtained commercially. All the organic solvents were treated with 4 Å molecular sieves for several days before use.

2.2. Preparation of germinated castor seed powder

Germinated castor seed powder was prepared according to the method of Gu et al. (2011). Castor seeds were soaked in 2% formaldehyde solution for 30 min to avoid fungal contamination and then washed several times with distilled water until the residual formaldehyde was removed thoroughly. Then, the disinfected seeds were soaked in tap water for 12 h to adequately absorb moisture. Thereafter, the seeds were placed in a culture dish paved with sheets of moist gauze, and were germinated at 27 °C in dark. Water was added at every 12 h to keep the gauze wetting. An amount of the germinated seeds were collected at every 24 h after seeding, and the water was removed through freeze-drying. Finally, the germinated seeds were milled to powder (particle size less than 1 mm) under 10 °C and stored at 4 °C.

2.3. Water and oil content of castor seeds

The castor kernels of different germination stages were milled to powder (particle size less than 1 mm) in advance and the obtained powder was used as the test sample.

Water content of castor seeds was measured gravimetrically using the official method of American Oil Chemists' Society (AOCS) Ai2-75 at 103 °C.

The theoretical oil content of castor seeds was determined according to AOCS Am2-93 using a soxhlet extractor with light petroleum as solvent. The amount of test sample and light petroleum was 4 g and 80 ml, respectively. The extraction process was carried out at 80 °C for 4 h. Light petroleum was removed by using a rotary evaporator after the extraction process and then the extracted oil was measured. The percentage yield was calculated on a dry weight basis.

2.4. Activity assay of the castor seed lipase

The germinated castor seed powder was washed with cold acetone for several times and the obtained white powder was named crude lipase. The hydrolytic activity of castor seed lipase was detected using an olive oil emulsion which contains 2% (w/v) polyvinyl alcohol as substrate. A mixture of 4 ml emulsion and 5 ml phosphate buffer (0.025 M, pH 5.0) was preheated at 37 °C for 10 min, and then a certain amount of the crude lipase was added into the mixture for another 30 min. The reaction was terminated through an addition of a mixture of ethanol and acetone (1:1, 15 ml) to inhibit the lipase activity (Kanwar et al., 2005). The quantity of the released fatty acid was measured by titration with 0.1 M KOH solution. One unit of lipase activity was defined as the amount of lipase that needed for olive oil to liberate 1 μmol of fatty acids per minute at 37 °C and pH 5.0.

2.5. Production of biodiesel

The oilseed powder (4 g) was mixed with a certain amount of DMC and the reaction system was kept tightly closed. The reaction was carried out at particular temperature with shaking speed of 180 r/min on a water bath shaker. Samples (200 μl) taken from the reaction mixture at specified times were analyzed quantitatively by gas chromatography (GC).

2.6. GC analysis of FAME yield

A gas chromatograph (SP-1000) which equipped with a hydrogen flame ionization detector (FID) was used in this study to detect the yield of FAME, and a capillary column (SE-30, 30 m × 0.25 mm) was employed for chromatographic analysis. The column temperature was kept at 160 °C for 2 min, and then heated to 200 °C at 15 °C/min. After that the heating process continued at 8 °C/min to 260 °C, with a holding time of 10 min. The temperature of the injector and detector were 240 and 280 °C, respectively. The yield of FAME can be calculated using the following equation:

$$\text{FAME yield}\ (\%) = \frac{(\sum \text{Concentration of each FAME}) \times (\text{Volume of upper layer})}{\text{Theoretical quantity of FAME}} \times 100\%$$

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