



Research article

Continuous production of biodiesel from soybean flakes by extraction coupling with transesterification under supercritical conditions



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ABSTRACT

A continuous process of supercritical extraction coupling with supercritical methanol transesterification was put forward to prepare biodiesel directly from full-fat soybean flakes. This method is meaningful to the industrialized production of biodiesel. It can lower the high cost of the refined vegetable oil as feedstock. Furthermore, it gives a possibility that a mobile biodiesel processor could be easily moved to various locations where raw materials are available and produce biodiesel in situ. The experimental results indicated that a residence time of more than 2.5 h was required to obtain a stable fatty acid methyl ester yield. The maximum biodiesel yield of 86% was obtained at 350 °C, 20 MPa and 3 h, with the molar ratio of methanol-to-oil of about 42:1. In addition, based on the investigation of the process optimization, oil extraction was found to be the crucial step for the coupling process and other promising routes were proposed to improve both the production efficiency and the capacity.

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1. Introduction

Biodiesel is a renewable energy carrier produced from natural oils and fats, and is regarded as one of the most promising substitutes for petroleum diesel [1,2]. A widely used method of preparing biodiesel in industry is transesterification of triglycerides with alcohols using acid or basic catalysts [3–6]. However, a high purity of raw materials is usually required in these processes and separation of the catalysts at the end of the processes adds extra burden to the product purification [7]. These limitations of catalytic transesterification processes drive up the cost of biodiesel and have led to the development of non-catalytic processes [7]. In 2001, Saka et al. [8] first reported preparation of biodiesel using rapeseed oil in supercritical methanol in a tubular reactor without any catalysts. This method has the advantage of allowing a greater range of water content for the feedstock, especially for low-cost feedstocks, for example, waste cooking oil [7]. Furthermore, the product does not need to be washed to remove the catalysts, facilitating a continuous process. Lately, supercritical methanol (scMeOH) method has attracted increasing attention by many researchers [9–14].

However, this method requires a temperature as high as 350 °C and a pressure of 10–50 MPa, which adds to the cost of the apparatus [7]. Many efforts have been made to improve the scMeOH method, mainly in two directions. Yin et al. [15,16] used a small amount of alkali catalyst to intensify the scMeOH process, aiming at reducing the operating temperature and pressure while keeping the advantage of high fatty acid methyl esters (FAME) yield in this method. Only 0.1 wt.% KOH was

used, the reaction temperature was reduced to 160 °C, while the reaction pressure was less than 10 MPa and the reaction time was 20 min. Yin et al. [17,18] also reported intensification of the scMeOH process by applying recyclable solid catalysts such as Na₂SiO₃ and K₃PO₄, and a FAME yield of more than 95% was obtained in 30 min at 220 °C. The other direction is to improve the production efficiency by using a continuous-type process to instead of the batch-type [19–22]. Besides the scMeOH method, supercritical methyl acetate has also been investigated as a replacement solvent for alcohol in supercritical biodiesel synthesis [23–27]. In this process, an inter-esterification process takes place instead of the conventional transesterification, since the two different ester compounds exchange their acyl groups to produce new product compounds. The reaction produces FAME as well as triacetin as the co-product and avoids the over-production of glycerol as the by-product. However, in all these processes refined commercial oils are required as feedstocks to produce biodiesel, which adds to the cost of biodiesel production (e.g. transport and storage of oil-containing raw materials, oil refinement).

As is well known, supercritical CO₂ extraction is an environmentally benign and efficient method to obtain seed oil, and represents an alternative to the traditional liquid solvent technique [28]. In the present study, a continuous coupling process of supercritical extraction and a non-catalytic scMeOH transesterification method for preparing biodiesel are assessed, for the purpose of obtaining biodiesel directly from the oil-containing raw materials. It is possible that a mobile integration system, combined with extraction and transesterification, will be developed in the future, which can be easily moved to various places of raw materials availability, and produce biodiesel locally. The extraction, transesterification and coupling processes were investigated and

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correlated, in order to determine the crucial step in the coupling process, and to guide the design and optimization of the extraction and transesterification reactor.

2. Experimental

2.1. Materials

Soybean flakes with a thickness of 2 mm were brought from Linyi city, Shandong province, China. Soybean oil was obtained from Shanghai Fulinmen Food Co. Ltd. Both methanol (Tianjin Damao Chemical Reagent Factory) and n-hexane (Beijing Chemical Works) were of analytical grade. CO₂ was supplied by Dalian Guangming Special Type Gas Co., Ltd.

2.2. Methods

As shown in Fig. 1, the experimental apparatus consists of two units. One is for supercritical extraction and the other is for scMeOH transesterification. In a typical continuous scMeOH process (defined as CSM process), methanol and soybean oil at flow rates of 0.14–0.18 mL/min and 0.10–0.70 mL/min (molar ratio of methanol to oil of 12:1–50:1), were fed by pumps from container 12 and container 8 respectively. The preheated two materials were mixed, and then the reaction of transesterification was carried out in the tubular reactor 16 ($\phi 8 \times 250$ mm) at temperature of 220–350 °C and pressure of 14–22 MPa. The products were obtained in the collector 22 by depressurization using a back pressure valve 21. The samples were collected every 30 min for analysis after the post-treatment. The excess methanol in the product was removed using rotary evaporation, then the treated product was allowed to stand for about 30 min to have phases separated. The samples from the upper layer were washed by deionized water for several times and dried by anhydrous sodium sulfate, then diluted by n-hexane for gas chromatography analysis.

In a typical coupling process of extraction and scMeOH transesterification (defined as CPSM process), 40 g soybean flakes were first put into extractor 10. Then CO₂ was charged into the extractor by pump 5 until the pressure got up to 20 MPa, while n-hexane (flow rate 0.4 mL/min) was fed by pump 9 as a co-solvent. The mixture of extracts, n-hexane and CO₂ from extractor 10, and the methanol provided from container 12 were then used as the feed materials for the scMeOH transesterification reaction, which was conducted in reactor 16. The consequent procedures of collecting biodiesel samples were the same as those in the continuous scMeOH process. The pump 9 and pump 13 involved in the experimental apparatus are high performance liquid chromatography (HPLC) pumps. It has a flow rate ranged from 0.001 to 9.999 mL/min with an accuracy of $\pm 0.3\%$.

2.3. Analysis

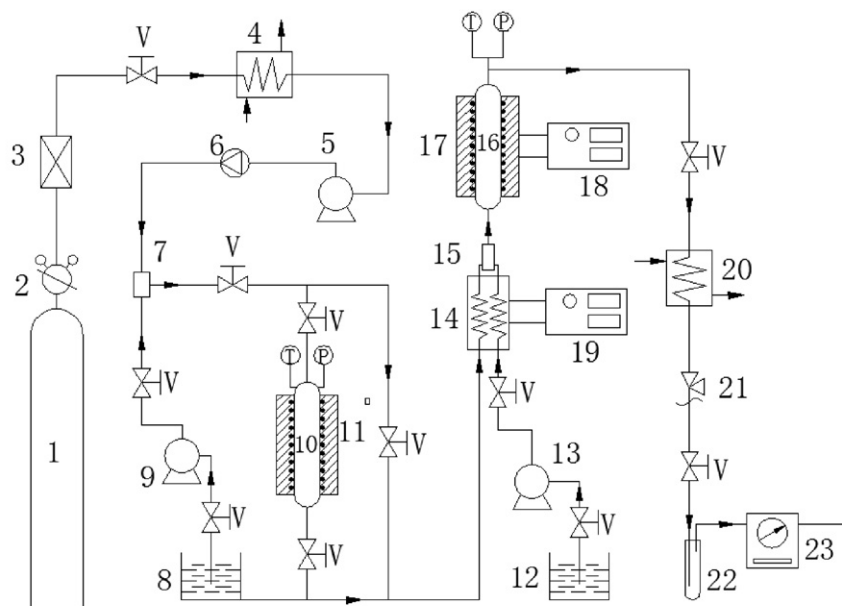
The FAME content of the biodiesel samples was determined by an Agilent 6890N gas chromatograph, equipped with a HP-5 capillary column (30 m \times ϕ 0.32 mm \times 0.25 μ m). The column temperature was increased from 160 °C to 225 °C at a rate of 3 °C/min, held at 225 °C for 0.5 min, before it was increased to 270 °C at a rate of 15 °C/min, then held at this temperature for 4 min. Because the FAME yield of the biodiesel prepared using strong-basic catalysis method is nearly 100%, the sample prepared using potassium hydroxide as a catalyst was considered as a standard sample to determine the FAME content of the products in this study.

3. Results and discussion

3.1. Continuous scMeOH transesterification process (CSM process)

3.1.1. Reaction time

There are four important factors that influence the yield of FAME when biodiesel is prepared using the CSM process: 1) temperature,



- 1) CO₂ cylinder; 2) regulator; 3) filter; 4) cold trap; 5) high pressure pump; 6) check valve; 7) mixer; 8) n-hexane (soybean oil) container; 9) HPLC pump; 10) extractor; 11) water bath; 12) methanol container; 13) HPLC pump; 14) preheater; 15) mixer; 16) reactor; 17) furnace; 18) temperature control unit; 19) temperature control unit; 20) cold trap; 21) back pressure valve; 22) collector; 23) flow meter; V: needle valve; T: thermocouple; P: pressure gauge

Fig. 1. Schematic diagram of preparing biodiesel using coupling process under supercritical conditions.

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