Energy Conversion and Management 88 (2014) 60–65

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Improvement in biodiesel production from soapstock oil by one-stage lipase catalyzed methanolysis

Erzheng Su [a,b,c,*], Dongzhi Wei [d]

[a] Enzyme and Fermentation Technology Laboratory, College of Light Industry Science and Engineering, Nanjing Forestry University, Nanjing 210037, PR China
[b] Jiangsu Provincial Key Lab of Pulp and Paper Science and Technology, Nanjing Forestry University, Nanjing 210037, PR China
[c] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[d] State Key Laboratory of Bioreactor Engineering, New World Institute of Biotechnology, East China University of Science and Technology, Shanghai 200237, PR China

ARTICLE INFO

Article history:
Received 19 May 2014
Accepted 17 August 2014
Available online 2 September 2014

Keywords:
Soapstock
Biodiesel
Lipase
Methanolysis
One-stage

ABSTRACT

A major obstacle in the commercialization of biodiesel is its cost of manufacturing, primarily the raw material cost. In order to decrease the cost of biodiesel, soapstock oil was investigated as the feedstock for biodiesel production. Because the soapstock oil containing large amounts of free fatty acids (FFAs) cannot be effectively converted to biodiesel, complicated two-stage process (esterification followed by transesterification) was generally adopted. In this study, simple one-stage lipase catalyzed methanolysis of soapstock oil was developed via one-pot esterification and transesterification. Water produced by lipase catalyzed esterification of FFAs affected the lipase catalyzed transesterification of glycerides in the soapstock oil severely. Addition of tert-alcohol could overcome this problem and enhance the fatty acid methyl ester (FAME) yield from 42.8% to 76.4%. The FAME yield was further elevated to 95.2% by optimizing the methanol/oil molar ratio, lipase amount, and water absorbent. The developed process enables the simple, efficient, and green production of biodiesel from soapstock oil, providing with a potential industrial application.

1. Introduction

Biodiesel fuel is an alternative to classic diesel fuel. It consists of fatty acid alkyl esters and belongs to ecological fuel because of its qualitative composition. As fuel of biological origin, it is recommended by the European Union and classified as a prospective future fuel [1]. The alternative diesel fuels must be technically acceptable, economically competitive, environmentally acceptable and easily available [2]. The biggest obstacle in biodiesel commercialization is production cost [3]. When produced from refined edible vegetable oils or animal fats, feedstock cost contributes more than 70% to the cost of biodiesel [3,4]. Furthermore, the utilization of these types of sources has given rise to certain concerns as some of them are important food chain materials. In other words, the production of biodiesel from human nutrition sources can cause a food crisis [5]. Therefore, the majority of researchers have focused on low cost oils as feedstock for biodiesel production such as non-edible oils [6–8] or waste oils [9–11]. It is reported that the usage of waste oils can reduce biodiesel production cost by 60–90% [4,12].

The production of edible oils generates an intermediate crude oil that contains not only triglycerides but also partially substituted glycerides, phosphoglycerides, free fatty acids and minor components. All these must be removed from the triglyceride fraction to produce acceptable edible oil. One step in the refining process involves the addition of water and alkali, causing precipitation of a semisolid material known as soapstock, which contains not only the free fatty acids but also some residual triglycerides, mono- and diglycerides, phosphoglycerides, pigments, some of the lesser components of the crude oil, and water [13]. Conventional way to utilize soapstock involves the acidulation of soapstock which needs high temperature steam and excess acid. The product is acid oil containing free fatty acids (FFAs) and glyceride, which is typically sold as a feed of livestock. But acidulation of soapstock is one of the least desirable processes in an integrated facility because the process is rather difficult to perform effectively and its cost cannot have significant return [14,15]. With the development of oil industry, the outputs of soapstock exhibit increasing trend in china and in some regions of the world [16]. Soapstock is generated at a rate of about 6% of the volume of the crude oil produced. Compared to refined oils, soapstock represents an

---

* Corresponding author at: Enzyme and Fermentation Technology Laboratory, College of Light Industry Science and Engineering, Nanjing Forestry University, Nanjing 210037, PR China. Tel./fax: +86 25 85428906.

E-mail address: ezhsu@njfu.edu.cn (E. Su).

http://dx.doi.org/10.1016/j.enconman.2014.08.041
0196-8904/© 2014 Elsevier Ltd. All rights reserved.

inexpensive source of fatty acids, with its price being as low as one-tenth that of refined oil [17]. At the same time, the production of soapstock is relatively centralized, eliminating the need for a collection infrastructure [13]. All of the mentioned points make the soapstock be one of the most promising candidates for biodiesel production.

There have been several reports on conversion of soapstock oil to biodiesel [13–18]. From these previous works, it can be found that the soapstock oil containing high FFAs cannot be effectively converted to biodiesel directly. It is required to reduce the FFAs concentration to below the threshold limits prior to being processed by standard biodiesel manufacturing. Therefore, two-stage process was generally adopted for the production of biodiesel from soapstock oil [13–15,17,19]. The traditional base catalysis does not work for reducing FFAs, due to the formation of soap between the base and FFAs. To solve this problem, soapstock oil may be pretreated via acid-catalyzed esterification of FFAs. Homogeneous acid catalysts such as sulfuric acid were used for the esterification of FFAs, but suffering from several problems such as complex neutralization, corrosion, and environmental issues [20]. The use of heterogeneous acid catalysts is a little greener, but their catalytic performance for the esterification has been thus far unsatisfactory [10,21]. In contrast, lipase catalysis is a better choice, which can catalyze both esterification and transesterification to produce biodiesel from soapstock oil. Such an approach can enhance the production efficiency (changing two-stage to one-stage) and provide green and sustainable process due to the mild reaction conditions and the non-toxicity of the lipase catalyst [10,21]. Haas and Scott [13] conducted lipase catalyzed biodiesel production from soapstock oil, and only 81% of conversion was obtained under the optimal conditions. Immobilized *Candida rugosa* lipase catalyzed preparation of biodiesel from rapeseed soapstock oil was optimized by Response surface methodology, conversion of 63.6% was obtained when the optimum conditions were used [18]. The low conversions were mainly resulted from the water byproduct produced by lipase catalyzed esterification of FFAs. Too much water presenting in the reaction system will not only affect the lipase activity and stability, but also the biodiesel yield. In this work, the yield of biodiesel produced from soapstock oil was improved significantly by systematically optimizing the lipase catalyzed reaction system and conditions.

2. Materials and methods

2.1. Materials

Novozym 435 (lipase B from *Candida antarctica*, a nonspecific lipase immobilized on a macroporous acrylic resin with a specific activity of 10,000 propyl laurate unit (PLU) g^{-1}. PLU is based on a reaction between propyl alcohol and lauric acid at 60 °C for 15 min under the alcohol/acid molar ratio of 12:1) was bought from Novo Nordisk Bioindustrials Inc. Methyl esters of myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid and standard test kit for mono-, di- and triglycerides were obtained from Sigma and were chromatographically pure. *t*-Butanol and *t*-pentanol were obtained from commercial supplier (Shanghai Chemical Company, China). All other chemicals and reagents were obtained commercially and were of analytical grade. All the organic solvents were treated with molecular sieve 3 Å for several days before use. Molecular sieve 3 Å was bought from Honeywell International Inc. Macroporous and microporous silica gels were obtained from Changquan Silica Gel Desiccant Co., Ltd. (Shanghai, China). The molecular sieve 3 Å and silica gel were dried at 250 °C for 6 h before use.

2.2. Preparation of the soapstock oil

The soapstock was provided by Zouping Zhengda Oil Factory (Shandong, China). The soapstock was mixed with petroleum ether (boiling range of 30–60 °C) at the ratio of 1:1 (v/v), and extracted at 25 °C and 150 rpm for 2 h. After vacuum filtration with suction flask, the filtrate was pooled and centrifuged at 5000 rpm for 10 min. The supernatant was collected into a round bottom flask and the solvent was evaporated using a rotary evaporator. The obtained product was the crude soapstock oil. After heating the crude soapstock oil to 60 °C, 7% (based on crude oil weight) of distilled water was added in 30 min with stirring at 60–70 rpm, then the temperature was elevated to 70 °C and kept for another 6 h. The oil–water mixture was centrifuged at 5000 rpm for 10 min. The supernatant was collected and the water was removed using a rotary evaporator. The final product was used as soapstock oil in this work.

2.3. Characterization of the soapstock oil

The acid value, moisture and volatile matter, and saponification value of the soapstock oil sample were determined according to the official methods of the American Oil Chemists Society [22]. The average molecular weight of the soapstock oil was calculated according to the saponification value. For determination of the fatty acid composition, the soapstock oil was converted by BF_3-methanol esterification procedure to their corresponding methyl esters [22], which were then analyzed by a capillary gas chromatography method using a capillary column, HP-5 (5% phenyl methyl siloxane capillary, 30.0 m × 320 μm × 0.25 μm nominal), and a flame-ionization detector in an Agilent 6890 gas chromatography. The column temperature was kept at 180 °C for 1 min, heated to 300 °C at 10 °C/min, and then maintained for 2 min. The temperatures of the injector and detector were set at 260 and 280 °C, respectively.

2.4. Lipase-catalyzed methanolysis

In isooctane system: a certain molar ratio of soapstock oil and methanol in isooctane (total 5 mL) was mixed with appropriate amount of immobilized lipase in a 25 mL screw capped vial. The methanol may be added by one-step method (at 0 h) or three-step method (at 0 h, 2 h and 6 h). The reactions were carried out at 45 °C and 150 rpm in a thermostatted shaker. Aliquots of the reaction mixture were taken at intervals and centrifugated at 10,000 rpm for 5 min. Samples (18 μL) were withdrawn and mixed with 500 μL isopropanol/n-hexane mixture (5:4, v/v) for HPLC analysis.

In solvent-free system: a certain molar ratio of soapstock oil and methanol was mixed with appropriate amount of immobilized lipase in a 10 mL screw capped vial. The other operation procedures were the same as the isooctane system. Samples (9 μL) were withdrawn and mixed with 500 μL isopropanol/n-hexane mixture (5:4, v/v) for HPLC analysis.

2.5. HPLC analysis of the reaction product

The composition of fatty acid methyl esters (FAME), monoglycerides (MAG), diglycerides (DAG), triacylglycerols (TAG) and FFAs in the reaction mixture was analyzed by HPLC method [23,24] using an Agilent 1100 High Performance Liquid Chromatograph, equipped with a binary pump, a Zorbax XDB-C18 column (4.6 mm × 250 mm, 5 μm) and an UV/VIS detector. The flow rate of a binary solvent mixture (methanol: solvent A and isopropanol/n-hexane (5:4, v/v): solvent B) was 1 mL/min with a linear gradient from 100% A to 40% A + 60% B in 15 min. The ratio of 40% A + 60% B was kept to 18.60 min, and then changed to 100% A to last to 24.5 min. The