Fuel Processing Technology 131 (2015) 452–457

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Evaluation of Soxhlet extractor for one-step biodiesel production from *Zanthoxylum bungeanum* seeds

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ARTICLE INFO

Article history:
Received 22 May 2014
Received in revised form 15 December 2014
Accepted 15 December 2014
Available online 30 December 2014

Keywords:
Biodiesel
Soxhlet extractor
Zanthoxylum bungeanum seeds
Methanol
Ethanol
Free fatty acids

ABSTRACT

Soxhlet extractor was applied for biodiesel production from *Zanthoxylum bungeanum* seeds containing high amount of free fatty acids (FFA) using methanol and ethanol as both extractants and reactants. The yields, fatty acid concentration and acid values of *Z. bungeanum* seed oil (ZSO) extracted with different solvents were determined. With a solvent-to-seed ratio of 6 (ml/g), extraction time of 4 h and water bath at 95 °C, the yields of ZSO with methanol and ethanol reached above 20%, which was almost as efficient as *n*-hexane, and the acid values of the corresponding ZSO were 56.9 and 41.9 mg KOH/g, respectively. The final acid values of ZSO were reduced to below 10 mg KOH/g when sulfuric acid was used as a catalyst presented in receiver flask in 4 h extraction and reaction. After 12 h of extraction and transesterification in a Soxhlet extractor with methanol and ethanol, the conversion of ZSO from *Z. bungeanum* seeds into ZSO biodiesel was almost complete as confirmed by ^{1}H NMR. Application of the Soxhlet extractor for one-step biodiesel production from *Z. bungeanum* seeds containing high FFA avoided solid–liquid separation process and solvent wash, showing great potential of reducing the production cost of biodiesel.

1. Introduction

At present, the production cost of biodiesel is still high compared to the cost of petroleum-based diesel fuel and exploring ways to reduce the cost of biodiesel attracts much interest in recent decades. The use of inexpensive and non-edible vegetable oils as raw materials may significantly reduce the cost of biodiesel. *Zanthoxylum bungeanum* seed has an estimated annual production potential of one million metric tons in China and most of the seeds are used as muck and solid fuel. Usually, *Z. bungeanum* seed oil (ZSO) contains a high amount of free fatty acids (FFA) and therefore it is unsuitable for human consumption [1]. The high amount of FFA in ZSO is attributed to the presence of lipase and water in the *Z. bungeanum* seeds [2]. Thus, the formation of FFA in the seeds is mainly due to the hydrolysis of lipid by lipase with the presence of water. ZSO with high amount of FFA is a potential cheap feedstock for biodiesel production compared with refined and edible-grade vegetable oils.

Traditional steps for biodiesel production from vegetable oils were: extraction of oil and transesterification with short chain alcohols. Previously, ZSO biodiesel was produced from ZSO by acid-catalyzed esterificaion followed by alkali-catalyzed transesterification and a high yield was obtained [1]. Compared to traditional method, reactive extraction is also a feasible technology to produce biodiesel and has the potential to cut the high cost of biodiesel production. This method differs from conventional biodiesel production in which oil extraction and transesterification take place at the same time, reducing the reaction step. During reactive extraction, the alcohol acts both as an extractant and as a reactant. At present, NaOH [3,4], KOH [5], H_2SO_4 [6,7] and enzyme [8] have been used as catalysts in one-step reactive extraction for biodiesel production. One-step acid-catalyzed reactive extraction can be used for the biodiesel production from the feedstock containing FFA whereas a long reaction time is required [7]. For rice bran oil with FFA, a two-step reactive extraction method was developed, which combined an in situ acid-catalyzed esterification with an in situ alkali-catalyzed transesterification [9,10]. However, a solid–liquid separation process is necessary after reactive extraction, and the solid phase should be washed with solvent to remove residual oil [10]. The application of the Soxhlet extractor for biodiesel production is, to some extent, similar with reactive extraction, which combines the extraction of oil from seeds and the transesterification with extracted oil with the presence of catalysts in the receive flask of the Soxhlet extractor. One of the advantages of biodiesel production from plant seeds in the Soxhlet extractor is avoiding solid–liquid separation process and solvent wash. However, the application of the Soxhlet extractor for biodiesel production was less investigated.

In this work, the production of biodiesel from *Z. bungeanum* seeds in the Soxhlet extractor with methanol and ethanol as both extractants and reactants was evaluated. The effect of different acid catalysts on the esterification of FFA in extracted ZSO was investigated. Biodiesel

Abbreviations: FAEE, fatty acid ethyl esters; FAME, fatty acid methyl esters; FFA, free fatty acids; PE, petroleum ether; ZSO, *Zanthoxylum bungeanum* seed oil.

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http://dx.doi.org/10.1016/j.fuproc.2014.12.025

was produced from *Z. bungeanum* seeds in the Soxhlet extractor and the conversion of ZSO to biodiesel was monitored by ^{1}H NMR. The results of this work will be beneficial to evaluate the potential application of the Soxhlet extractor for biodiesel production from *Z. bungeanum* and other vegetable seeds.

2. Materials and methods

2.1. Materials

Z. bungeanum seeds were obtained from a local company located in Hancheng, Shaanxi Province, China. This is a high yield area for *Z. bungeanum* Maxim. *Z. bungeanum* seeds were dried at 80 °C for 2 h and were ground by a mini-mill. The ground *Z. bungeanum* powder was sieved to less than 1 mm. Methanol, ethanol, petroleum ether (PE, 60–90 °C), *n*-hexane, sulfuric acid, stannic chloride, ferric sulfate, sodium bisulfate monohydrate and other chemical reagents were of analytical reagent grade. The 60–90 °C distillation fraction of PE was used for comparison because it is mostly used as solvent for vegetable oil extraction in the laboratory.

2.2. Oil extraction

Different solvents, including methanol, ethanol, PE and *n*-hexane were utilized for ZSO extraction in the Soxhlet extractor. The 100 g *Z. bungeanum* seeds were weighed into a filter package and placed in a Soxhlet device. The extraction solvent was poured into a round-bottomed receiver flask equipped with a reflux condenser and the water bath was heated to the desired temperature. The volume of solvent was in the range of 400–700 ml with a solvent-to-seed ratio of 4:1 to 7:1. During the extraction, any evaporated solvents were returned to the glass container by the condenser. After 4 h of the extraction, the mixture was allowed to recover under vacuum at 65 °C with a rotational evaporator for removing solvents, and then dried at 105 °C in an oven to remove the remaining impurities until its weight was constant to calculate the weight of ZSO obtained. Two replicate experiments were carried out and average values are presented.

Factors affecting oil extraction including type of solvents (methanol, ethanol, PE and *n*-hexane) and solvent-to-seed ratio (ml/g) were investigated.

2.3. Oil extraction and reaction in the Soxhlet extractor

Oil extraction and reaction for biodiesel production was conducted in the same Soxhlet extractor as described previously. The temperature of water bath was kept at 95 °C to make quicker turnover of the solvent. The solvent in the flask was evaporated and condensed in the condenser at atmospheric pressure. Methanol and ethanol were used as both extraction solvents and reaction reagents, respectively. The acids (sulfuric acid, stannic chloride, sodium bisulfate and ferric sulfate) used as catalysts for esterification and transesterification were added into the round-bottomed receiver flask of the extraction system. After the extraction and reaction, the solvent in the round-bottomed flask was removed under vacuum at 65 °C with a rotational evaporator. Then, the mixture was allowed to settle in a separating funnel to wash at least four times using hot water (80 °C) and dried with anhydrous sodium sulfate. Two replicate experiments were carried out and average values are presented.

2.4. Acid value and oil yield determination

The acid value was determined according to the national standard of China [11]. 2 g of sample was added into a 250 ml flask, after that 100 ml ether/ethanol (2:1, v/v) solution using a solvent was added. Three drops of phenolphthalein as an indicator were added to the solution. Titration was conducted using 0.1 M potassium hydroxide solution. The acid value was calculated in accordance with the following equation:

$$AV = \frac{v \times N \times 56.1}{W}$$

in which AV is the acid value (mg KOH/g), v is the consumption of 0.1 M KOH (ml), N is the true concentration of KOH (mol/l), and W is the weight of the sample (g).

In this work, each oil yield (Y) was calculated according to the masses of extracted ZSO (M_{oil}) and *Z. bungeanum* seed (M_{seed}), i.e.:

$$Y = M_{oil}/M_{seed}.$$

2.5. Fatty acid composition analysis

Fatty acid composition of ZSO was analyzed by the same gas chromatograph system as described in a previous work [12]. Fatty acid composition of crude ZSO was analyzed by a Trace GC Ultra gas chromatograph (Thermo Electron Corporation, USA) equipped with a flame ionization detection system. The column was Agilent DB-WAX (30 m length, 0.25 mm inner diameter, and 0.25 μm film thickness). The temperature program was as follows: 180 °C for 2 min, 8 °C/min up to 240 °C, and holding time of 8 min. Nitrogen was used as a carrier at a flow rate of 1.0 ml/min. A sample volume of 1.0 μl was injected using a split ratio of 1:80.

2.6. ^{1}H NMR spectrum analysis

^{1}H NMR analyses were performed on a Varian INOVA-400 MHz spectrometer (Varian, USA) using $CDCl_3$ as the solvent, and tetramethylsilane as the internal standard. The conversion of ZSO biodiesel with methanol was calculated from the integration values of the glyceridic and methyl ester protons in ^{1}H NMR [13]. In order to monitor the formation of ethyl ester in esterification of FFA with ethanol, the peak areas of A1/A2 in the region of 4.05–4.40 ppm in ^{1}H NMR spectra were calculated, in which the term A_1 corresponds to the area related to glycerol hydrogen atoms and A_2 corresponds to the area of the ethoxy quartet of ethyl esters with glycerol peaks [14].

3. Results and discussion

3.1. Extraction of ZSO by methanol and ethanol

The ZSO extraction experiments were carried out in the Soxhlet extractor with methanol and ethanol at a water bath temperature of 85 and 95 °C (Fig. 1), respectively. Although the boiling point of methanol (64.5 °C) and ethanol (78.4 °C) were much lower, higher temperature could increase the turnover of the solvent and thus potentially increase the extraction yield. PE and *n*-hexane were the most common extracting solvents and were used for comparison. As expected, the highest oil yield (24.7%) was obtained from *n*-hexane (Fig. 1A). Methanol and ethanol were less efficient than PE and *n*-hexane at both 85 and 95 °C. The oil yields reached 19.2 and 18.9% when *Z. bungeanum* seeds were extracted with methanol and ethanol at 95 °C, respectively. Lower oil yields (14.5 and 14.6%) were obtained with methanol and ethanol at 85 °C, respectively. Although methanol and ethanol were not as efficient as *n*-hexane in the extraction of ZSO, most of ZSO could be extracted from the *Z. bungeanum* seeds.

The acid values of ZSO extracted by different solvents were determined and the results showed that the contents of FFA in all ZSO preparations were above 20%, corresponding to acid values of above 40 mg KOH/g (Fig. 1B). The results were in accordance with