Bioresource Technology 128 (2013) 8–13

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Cogeneration of biodiesel and nontoxic rapeseed meal from rapeseed through in-situ alkaline transesterification

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HIGHLIGHTS

- Biodiesel and detoxified rapeseed meal was produced by in-situ transesterification.
- The conversion rate of rapeseed oil into FAME was 98%.
- The glucosinolate content in rapeseed meal was reduced to 0.07%.
- The detoxified rapeseed meal can be used as a source of protein in animal feed.

ARTICLE INFO

Article history:
Received 8 May 2012
Received in revised form 3 September 2012
Accepted 8 October 2012
Available online 17 October 2012

Keywords:
Biodiesel
Glucosinolates
In-situ alkaline transesterification
Rapeseed oil
Nontoxic rapeseed meal

ABSTRACT

In-situ alkaline transesterification of rapeseed oil with methanol for the production of biodiesel and nontoxic rapeseed meal was carried out. Water removal from milled rapeseed by methanol washing was more effective than vacuum drying. The conversion rate of rapeseed oil into FAME was 92%, FAME mass was 8.81 g, glucosinolates content in remaining rapeseed meal was 0.12% by methanol washing, while by vacuum drying the values were 46%, 4.44 g, 0.58%, respectively. In the presence of 0.10 mol/L NaOH in methanol, with methanol/oil molar ratio of 180:1 and a 3 h reaction at 40 °C, a conversion rate of 98% was achieved, and the glucosinolates content was reduce to 0.07%, a value which below the GB/T 22514-2008 standard in China. Thus the rapeseed meal can be used as a source of protein in animal feed. The FAME prepared through in-situ alkaline transesterification met the ASTM specifications for biodiesel.

1. Introduction

Biodiesel (fatty acid methyl esters, FAME) is a clean-burning, renewable fuel which is made from vegetable oils or animal fats with a short-chain alcohol by transesterification in the presence of a catalyst such as acid, alkali or an enzyme (Soares et al., 2012; Li et al., 2012; Azocar et al., 2011). At present, the predominant raw material for biodiesel production is semi-refined or refined vegetable oil. Its relatively high costs render the resulting fuels unable to compete with petroleum-derived fuel.

Contemporary production processes for refined vegetable oil involve extracting triglycerides (TG) from oilseeds by using solvents, degumming and refining. In contrast, in-situ transesterification (Qian et al., 2008; Qian and Yun, 2009; Hass et al., 2004; Carrapiso and Garia, 2000; Lei et al., 2010; Xu and Mi, 2011; Kasim et al., 2010) utilizes the original agricultural products as the source of triglycerides for direct transesterification, eliminates costly solvent extraction and oil refining processes and works with virtually any lipid-bearing material. Thus, this method could reduce biodiesel production time, maximize alkyl ester yield, reduce the use of reagents and solvents and reduce waste.

Rape is cultivated throughout the world for the production of vegetable oil, animal feed and biodiesel (Shin et al., 2012; Aydin and Llkilic, 2011; Tang et al., 2011). The seeds contain about 40% oil, and a meal with about 38–43% protein is obtained after extraction of the oil. Rapeseed oil is the preferred oil stock for biodiesel production because rape produces more oil per unit of land area than other crops. Rapeseeds could also be a significant source of protein if it were not for their content of toxic glucosinolates that can cause thyroid enlargement, liver damage, and even death of animals (Vermorel et al., 1987; Bourdon and Aumaitre, 1990; McMillan et al., 1986). According to GB/T 22514-2008 standard in China, feed grade rapeseed meal should not contain more than 0.34% glucosinolates. Thus, it is necessary for rapeseed meal to

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http://dx.doi.org/10.1016/j.biortech.2012.10.017

be further processed to reduce glucosinolates to permissible levels as animal protein feed resources.

The production of feed-grade cottonseed meal through in-situ alkaline transesterification has already been demonstrated (Qian et al., 2008; Qian and Yun, 2009). The cottonseed oil methyl esters prepared met the ASTM specifications for biodiesel and the free gossysol content in cottonseed meal was reduced to 0.01%, which is below the FAO standard of 0.045%. So the detoxified cottonseed meal could be used as animal protein feed resources. Based on these experiences, it was hypothesized that the toxic glucosinolates would also be extracted from the rapeseed solids by excess methanol during in-situ alkaline transesterification.

2. Methods

2.1. Materials

Rapeseeds were obtained from Jiangsu Zhengda Group (Jiangsu, China) and milled using an electric grinder to a mesh size of 40–60. The oil content of the milled rapeseed was 38.3% (wet basis). The acid value of the rapeseed oil was 0.8 mg KOH/g, the saponification value was 191.4 mg KOH/g, and average molecular weight of rapeseed oil was 883.0 g/mol.

Methanol (>98%) and petroleum ether (60–90 °C) were purchased from Nanjing Huaqingnanfang Chemical Ltd. (Nanjing, China) and distilled before used. All other chemicals, including sodium hydroxide, were of analytical reagent (AR) grade.

2.2. In-situ alkaline transesterification

Milled rapeseeds (25 g) were mixed with 50 mL of methanol for 10 min, the slurry was vacuum-filtered on a Buchner funnel, and the filter cake was mixed with methanol (100–200 mL) in which sodium hydroxide (0.16–1.12 g) had been dissolved (alkaline alcohol). The mixture was preheated to the desired temperatures before starting the reaction in a water bath. Alcoholysis was carried out in a three-necked 500-mL round bottom flask. The flask was immersed in a water bath with a temperature controller and mechanical stirrer. After 1–5 h, the reaction mixture was vacuum-filtered on a Buchner funnel, and the filter cake was washed with petroleum ether. After drying overnight at room temperature, glucosinolates in the rapeseed meal were determined by using official methods ISO9167-1. The filtrate was left to settle to separate into two layers. The lower layer was the methanol phase and was recovered under vacuum (10 ± 1 mmHg) at 50 °C in a water bath. The upper layer, which included the FAME (crude biodiesel), petroleum ether and some unreacted triglycerides, was washed with water until the wash water became neutral. The upper layer was dried over sodium sulfate, filtered and evaporated to remove the petroleum ether, and the remaining liquid was considered as crude biodiesel. The experiments also to be repeated three times at various larger scales (100, 500, 1000 g milled rapeseed) in the laboratory at the optimum conditions obtained according to the above small scale.

2.3. Analytical methods

After each reaction, samples of crude biodiesel were analyzed by a gas chromatograph (GC) equipped with a flame ionization detector using nitrogen as carrier gas. The analysis of biodiesel for each sample was carried out by dissolving 1.0 g of biodiesel sample and 0.2 g of methyl salicylate, added as a Reference, into 8 ml of n-hexane and injecting 1 μl of this solution into the GC (Qian et al., 2008). The injected sample was separated in a stainless steel column (2 m × 4 mm) packed with 8% polydiethylene glycol adipate on Chromosorb G AW-DMCS purchased from Sinopharm Chemical Co., Ltd. (Shanghai, China). The oven temperature of the GC was increased from 150 to 215 °C at a rate of 5 °C min^{-1} and held at 215 °C for 20 min. Both temperatures of injector and detector were heated to 260 °C and the flow rates of nitrogen, hydrogen and air were 19, 40 and 300 ml min^{-1}, respectively. The purity of biodiesel samples was calculated as based on the area of FAME over the reference by the following equation (Qian et al., 2008):

$$\text{Purity}\ (\%) = \frac{(\text{area of FAME})/(\text{area of reference}) \times (\text{weight of reference})}{\text{weight of biodiesel sample}} \times (\text{correction factor}) \times 100$$

The purity of a biodiesel sample corresponds to the conversion rate of rapeseed oil into FAME.

The glucosinolate content in rapeseed meal, oil content in rapeseed flours and meals, free fatty acid content of the rapeseed oil, moisture content, nitrogen content and crude protein content were determined according to ISO 9167-1, ISO 659-1988, ISO 660-1996, ISO 665-1977 and ISO 5983-1979, respectively.

All the experiments were carried out three times in order to determine the variability of the results and to assess the experimental errors. In this way, the arithmetical averages and the standard deviations were calculated for all the results. Through analyses, the standard deviations of these results were lower than 0.5, indicating that the experimental errors were insignificant.

3. Results and discussion

3.1. Comparison of different pretreatment methods

Since the activity of alkali catalysts is affected by water in the reaction system, the rapeseed flour was drying or washed with methanol to decrease the water content before in-situ alkaline transesterification. As shown in Table 1, the conversion rate of rapeseed oil into FAME was approximately only 15%, the FAME mass produced from 25 g of rapeseed was only 1.44 g, and glucosinolates content in rapeseed meal was 0.46% without pretreatment. Vacuum drying of rapeseed flours caused an increase in rapeseed oil conversion rate and FAME mass, but also increased the glucosinolate content in the rapeseed meal. In contrast, with methanol washing before in-situ transesterification, the conversion rate of rapeseed oil into FAME was 92%, the FAME mass was 8.81 g, and the glucosinolates content in the rapeseed meal was reduced to 0.12%. When 25 g of milled rapeseed was washed with 50 mL methanol, about 22.5 g of milled rapeseeds remained and the methanol extracted contained about 1 g (2.5 wt%) water, 0.04 g (0.1 wt%) free fatty acids, 0.18 g glucosinolates (0.45 wt%), and 1.28 g (3.2 wt%) of other substances such as colloids and pigments.

3.2. Effect of NaOH concentration in methanol on oil conversion rate and glucosinolates content

The reaction profile of Fig. 1 indicates that rapeseed oil conversion rate and glucosinolates content in rapeseed meal by in-situ alkaline transesterification were dependent upon the NaOH concentration in methanol. When the NaOH concentration was increased from 0.04 to 0.10 mol/L, the conversion rate of rapeseed oil into methyl ester increased from 36% to 92%, and the glucosinolates content in rapeseed meal decreased from 0.28% to 0.12%. However, NaOH concentration exceeding 0.10 mol/L, had no significant effect on the rapeseed oil conversion rate and glucosinolates content in rapeseed meal.

Compared with in-situ acid-catalyzed transesterification (Harrington and D'Arcy-Evans, 1985; Siler-Marinkovic and Tomasevic, 1998), the in-situ alkali-catalyzed process can produce