Bioresource Technology 239 (2017) 17–20

Contents lists available at ScienceDirect

Bioresource Technology

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

Rapid biodiesel synthesis from waste pepper seeds without lipid isolation step

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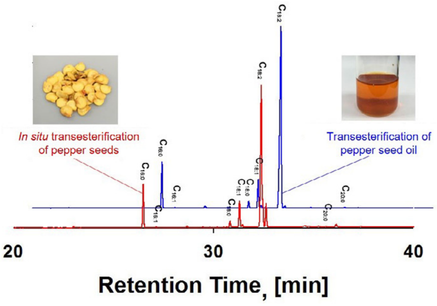
HIGHLIGHTS

- Biodiesel production with high yield from waste pepper seeds without lipid isolation.
- Biodiesel synthesis with high tolerance against impurities contained in the seeds.
- Optimization of reaction temperature for thermally induced *in situ* transmethylation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 April 2017
Received in revised form 1 May 2017
Accepted 2 May 2017
Available online 5 May 2017

Keywords:
Food waste
Biodiesel
Fatty acid methyl esters (FAMEs)
Transmethylation
Waste-to-energy

ABSTRACT

In situ transformation of lipid in waste pepper seeds into biodiesel (*i.e.*, fatty acid methyl esters: FAMEs) via thermally-induced transmethylation on silica was mainly investigated in this study. This study reported that waste pepper seeds contained 26.9 wt% of lipid and that 94.1% of the total lipid in waste pepper seeds could be converted into biodiesel without lipid extraction step for only ~1 min reaction time. This study also suggested that the optimal temperature for *in situ* transmethylation was identified as 390 °C. Moreover, comparison of *in situ* process via the conventional transmethylation catalyzed by H_2SO_4 showed that the introduced biodiesel conversion in this study had a higher tolerance against impurities, thereby being technically feasible. The *in situ* biodiesel production from other oil-bearing food wastes can be studied.

1. Introduction

The cost of fossil fuels has been gradually increasing, and fossil fuel consumption accounts for 80% of the total world energy consumption (Patel et al., 2016). Combustion of fossil fuels emits CO_2 into the atmosphere, which is one of the biggest contributors for climate change. In addition, the uneven geological distribution of fossil fuel reserves leads to energy security issues (Alvira et al., 2010). Thus, many developing countries are trying to find the renewable energy resources and develop sustainable energies to reduce their consumption of fossil fuels. In these respects, biofuels have been one of the most promising substitutes for petro-derived fuels due to their high compatibility with the current energy system (Saber et al., 2016). Utilizing biomass as an initial feedstock for energy recovery is highly desirable since biomass is carbon–neutral, cheap, and ubiquitous (Chen et al., 2015). Current industrialized biofuels use edible biomass such as corn and sugarcane as an initial feedstock. However, the use of edible feedstocks causes an increase in the cost of crops and poses ethical dilemmas (Tran, 2016). In order to avoid these problems, the production of biofuels from non-edible feedstocks has extensively studied (Atabani et al.,

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http://dx.doi.org/10.1016/j.biortech.2017.05.011

2013). Biodiesel synthesized from inedible fats (*e.g.*, animal fats) and vegetable oils (*e.g.*, Jatropha oil) and microalgae is one of the typical biofuels that can be produced from non-edible raw materials (Erkelens et al., 2014).

A huge amount of food waste is generated worldwide. According to a report from Food and Agriculture Organization of the United Nations in 2011, approximately 1.3 billion tonnes of food (around one third of the food produced) is wasted (FAO, 2011). In Republic of Korea, around 17,600 tonnes of pepper seeds are produced annually during producing red pepper powder, a traditional Korean cooking ingredient (Ku et al., 2008). Given that 75% of total biodiesel production cost is associated with raw materials (Vieitez et al., 2014), employing the waste pepper seeds as the feedstock of biodiesel is highly desirable.

Typically, biodiesel production includes lipid isolation step from the feedstocks with organic solvents to prevent any interferences in the synthesis of fatty acid methyl esters (FAMEs). The lipid isolation not only be time-consuming and cumbersome but also needs an extra instrumental setup. For example, Soxhlet extraction, one of the most widely used extraction techniques, needs long extraction times (~1 day) (Yang et al., 2015). Supercritical fluid (mostly CO_2) extraction has been used as an alternative way (Eller and King, 1996), but high water content-samples must be freeze dried prior to the extraction (Dunford et al., 1997). Therefore, the lipid isolation step in biodiesel production should be avoided.

To avoid these concerns, *in situ* FAME synthesis (*i.e.*, simultaneous lipid extraction and transesterification) has been considered. *In situ* conversion of lipids into FAMEs that have been reported use basic catalyst (*e.g.*, $NaOCH_3$ and tetramethylguanidine) (Carrapiso and García, 2000). Although the basic systems give a rapid derivatization, the esters are saponized especially in high water containing samples (Suter et al., 1997). Acid catalyzed *in situ* FAME synthesis (*e.g.*, HCl, H_2SO_4, and BF_3) normally gives high yields of FAMEs from triglycerides, but it takes longer reaction times than base catalyzed one (Carrapiso and García, 2000). Importantly, both base and acid catalyzed *in situ* derivatization techniques requires organic solvents (*e.g.*, hexane, dioxane, benzene, toluene, and tetrahydrofuran) (Carrapiso and García, 2000). Solubility of water in the organic solvents is a critical issue of the conventional *in situ* transesterification, thereby requiring an additional water scavenger (Tserng et al., 1981). Furthermore, the use of homogenous catalysts and organic solvents results not only in producing toxic wastes but also in making the process dangerous. Hence, it is highly desirable to develop an *in situ* transmethylation process for waste oil-bearing seeds (*i.e.*, simultaneous lipid extraction and transmethylation).

In all senses, this study is to develop a new-fashioned way to make biodiesel from waste pepper seeds via *in situ* transmethylation in the presence of a mesoporous material. Reaction time for the *in situ* conversion of the waste pepper seeds into FAMEs was ~1 min with a high yield of biodiesel. In addition, *in situ* transmethylation of solid seeds with the mesoporous material could be applied to characterizing and estimating functional properties of various food compounds beyond the production of biofuels.

2. Materials and methods

2.1. Lipid isolation by Soxhlet extraction

Waste pepper seeds were obtained from a local factory to make Gochugaru in Seoul, Republic of Korea. Lipid was extracted from the waste pepper seeds by Soxhlet extraction method using methylene chloride (≥99.9%, Sigma-Aldrich). 32 ± 0.1 g of the waste pepper seeds was loaded in a Soxhlet extractor, and then extraction was performed at 80 °C for 120 h. After the extraction, methylene chloride was recovered by a rotary evaporator.

2.2. Thermal gravimetric analysis (TGA) of waste pepper seeds

A Mettler Toledo TGA system was employed for TGA test of waste pepper seeds. 10 ± 1.5 mg of sample was loaded and ultra-high purity nitrogen was used for purge gas with the flow rate of 40 mL min^{-1}. Temperature for the TGA was set from 30 °C to 900 °C (heating rate: 10 °C min^{-1}).

2.3. Biodiesel production from waste pepper seeds

Conventional transesterification reaction was conducted over H_2SO_4 (95–98%, Sigma-Aldrich) catalyst, as described elsewhere (Kim et al., 2016). Briefly, waste pepper seeds or oil extracted from the waste pepper seeds, methanol (≥99.9%, Sigma-Aldrich), and H_2SO_4 were placed in a glass vial and stirred at 1000 rpm at 63 °C for 8 h. The amount of H_2SO_4 added was 5 wt% of sample. Esterified products were diluted to 1:14 with methylene chloride before injection into to a GC-FID unit.

For thermally induced transesterification, 8 ± 1.5 mg of sample, 200 μL of methanol, and 170 ± 1.0 mg of silica (Sigma-Aldrich) was loaded in a 2-mL batch reactor. The weight ratio of methanol to the waste pepper seeds was 20. The reactor was placed in a furnace to reach a desired reaction temperature (ramping rate: 20 °C min^{-1}). After reaction, the reactor was cooled down to ambient temperature by quenching in a cold bath. Each experiment was triplicate for verifying its reproducibility.

2.4. Chemical analysis

FAMEs derived from waste pepper seeds and oil extracted from the waste pepper seeds was identified and quantified using a Shimadzu GC-2010 Plus GC-FID equipped with an Agilent DB-Wax column (30 m × 0.25 mm × 0.25 μm) and a Shimadzu auto injector (AOC-20i) was applied for quantification of FAMEs. The GC analysis conditions are provided in Supporting Information (Table S1). For the GC-FID calibration, FAMEs standard mixture (37 FAME MIX, CRM47885, Sigma-Aldrich) was used (Fig. S1).

3. Results and discussion

3.1. Characterization of thermal decomposition of waste pepper seeds

To characterize the thermal decomposition of the waste pepper seeds, the TGA test was performed. Fig. 1 shows the thermogram (TG) and differential thermogram (DTG) of the waste pepper seeds. As shown in Fig. 1, there are three distinctive mass decay zones: 100–160 °C, 160–330 °C, and 370–420 °C. About 21 wt% of char remained after the TGA experiment. These three different zones would be attributed to different chemical compositions of the waste pepper seeds. The first thermal degradation zone indicates vaporization of water contained in the waste pepper seeds. The second zone results from thermal degradation of cellulose and hemicellulose. The third zone between 370 and 420 °C (~27% mass decay) is where lipid in the waste pepper seeds are thermally decomposed (lipids are thermally degraded from 370 to 500 °C (Lee et al., 2016)). The ~27 wt% of lipid in the waste pepper seeds is agreement with previous literature (Jarret et al., 2013). The thermal decomposition of lipid in the waste pepper seeds occurring between 330 and 420 °C mainly comes from direct bond scission of fatty acids from the backbone of triglycerides in the waste pepper seeds (Jung et al., 2016). Generally, boiling point of triglycerides is hard to be measured owing to the thermal scission of