



Conversion of lipid from food waste to biodiesel



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ARTICLE INFO

Article history:

Received 17 December 2014

Accepted 18 March 2015

Available online 3 April 2015

Keywords:

Food waste

Hydrolysis

Lipid

Base

Lipase

Biodiesel

ABSTRACT

Depletion of fossil fuels and environmental problems are encouraging research on alternative fuels of renewable sources. Biodiesel is a promising alternative fuel to be used as a substitute to the petroleum based diesel fuels. However, the cost of biodiesel production is high and is attributed mainly to the feedstock used which leads to the investigation of low cost feedstocks that are economically feasible. In this paper, we report on the utilization of lipid obtained from food waste as a low-cost feedstock for biodiesel production. Lipid from food waste was transesterified with methanol using base and lipase as catalysts. The maximum biodiesel yield was 100% for the base (KOH) catalyzed transesterification at 1:10 M ratio of lipid to methanol in 2 h at 60 °C. Novozyme-435 yielded a 90% FAME conversion at 40 °C and 1:5 lipid to methanol molar ratio in 24 h. Lipid obtained from fungal hydrolysis of food waste is found to be a suitable feedstock for biodiesel production.

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1. Introduction

Depletion of fossil fuels, increasing demand for fuels and environmental pollution have intensified the need for alternative fuels. Biodiesel is an alternative fuel obtained from fats and oils. It is used as a substitute for the conventional diesel fuel without requiring any major modifications in existing engines (Ma and Hanna, 1999; Demirbas, 2007, 2009). Although biodiesel is considered a green fuel, it is expensive to produce due to the high cost of the feedstocks (Demirbas, 2007, 2009; Machetti et al., 2008). Alternatively, the feasibility of using low-cost feedstocks such as waste cooking oil, nonedible oils and lipid rich microalgae have been investigated to lower the cost of biodiesel (Karmee et al., 2004, 2006; Karmee and Chadha, 2005; Chen et al., 2009; Enweremadu et al., 2009; Gnanaprakasam et al., 2013; Yaakob et al., 2013; Atabani et al., 2013; Khan et al., 2014; Renzi et al., 2013; Shin et al., 2014). Furthermore, edible feedstocks are generally used for biofuel production. In this context, increasing fuel demand will increase the food shortage (Mathews, 2008). This underlines the importance to use resources that do not compete with food products and rather make use of waste materials for bio-fuel production.

In the above context, lipid obtained from food waste can be used as a potential source for biodiesel preparation. However, isolation of lipid is required since food waste contains other

substances such as carbohydrates, protein, phosphate and minerals (Pleissner et al., 2014a,b; Yang et al., 2014a,b). Food waste contains 5–30% of lipids (Fig. 1). Lipid from food waste can be separated by solvent extraction (Pleissner et al., 2014a,b). Even though solvent extraction methods are effective for isolating the lipid, separation and recycling of the organic solvents will increase the cost of the biodiesel production. Furthermore, volatile organic solvents such as hexane are harmful to the environment. In this study, lipid is isolated from food waste after fungal hydrolysis (Pleissner et al., 2014a,b). Lipid is easily separated by centrifugation from the resultant hydrolysate (Pleissner et al., 2014a,b). The hydrolysate is used as a nutritional medium for microorganism cultivation and the separated lipid can be used for biodiesel production (Karmee and Lin, 2014a,b). After hydrolysis, the fungal biomass containing lipid mixture is heated to 100 °C to remove the water and the water free lipid is isolated (Karmee and Lin, 2014a). This lipid obtained from food waste is used as a potential source for biodiesel production.

Biodiesel or fatty acid methyl esters (FAME) are produced by the transesterification reaction (Leung et al., 2010). This reaction can be catalyzed by acids, bases, or enzymes. In addition, biodiesel can be synthesized under supercritical conditions without using any catalysts. Yield of biodiesel is generally affected by temperature, molar ratio of lipid to methanol, reaction time and the type of catalyst used (Ma and Hanna, 1999; Karmee and Chadha, 2005).

Commercially, bases are used as a catalyst for the large scale biodiesel production due to high biodiesel yield and short reaction time. However, the base catalyzed process is sensitive to moisture and free fatty acid (FFA) content (Ma and Hanna, 1999; Darnoko

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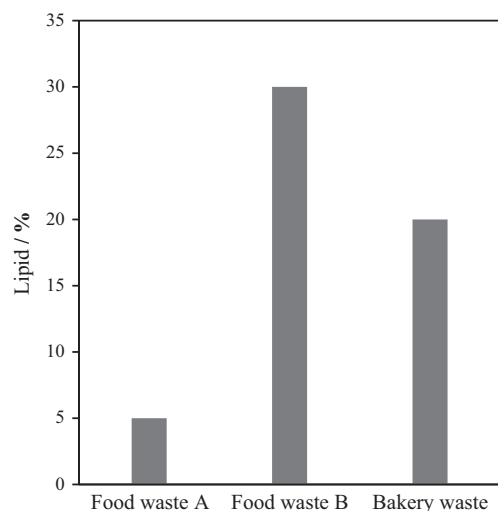


Fig. 1. Amount of lipids in different types of food wastes (Pleissner et al., 2014a,b); food waste samples A and B were obtained from same restaurant in separate days.

and Cheryan, 2000; Demirbas, 2007, 2009). Acid catalysts are not affected by FFA content but requires longer reaction time and higher reaction temperature (Ma and Hanna, 1999; Yaakob et al., 2013; Khan et al., 2014). Furthermore, there is an increase in capital cost of the biodiesel production due to the corrosive nature of acids and bases.

As an alternative to the chemical methods, lipases are used for biodiesel production (Parawira, 2009; Fukuda et al., 2008; Ranganathan et al., 2008). Lipase catalyzed biodiesel production is moisture and FFA tolerant. Additionally, biocatalysts are sustainable and require mild reaction conditions (Karmee, 2008, 2009). Also, the use of lipase allows for an easy separation of glycerol and catalyst (Parawira, 2009; Fukuda et al., 2008; Ranganathan et al., 2008). Recent study conducted in our group estimated the biodiesel production cost in Hong Kong from waste cooking oil as a feedstock (Karmee et al., 2015). The use of acid (H_2SO_4) and base (KOH) catalysts for the biodiesel production are found to be less expensive (US\$0.80 and US\$0.90) than the average biodiesel price in Hong Kong (US\$1.01). Whereas the use of lipase as a biocatalyst is found to be expensive (US\$1.15).

According to government reports, approximately 9,278 tonnes of municipal solid waste were thrown away at landfills in Hong Kong every day (Environment Bureau, Hong Kong, 2014; Environmental Protection Department, Hong Kong, 2012). Municipal solid waste contains 41.7% food waste or putrescible (Environment Bureau, Hong Kong, 2014; Environmental Protection Department, Hong Kong, 2012) which contains up to 30% of lipids that are discarded without any further use (Pleissner et al., 2014a,b) which can be utilized to help increase Hong Kong's energy security as well as alleviate waste disposal issues.

In the current study, lipid obtained from food waste was used for the preparation of biodiesel to make the process cost-effective as well as to test its feasibility as a low-cost feedstock (Scheme 1). Novozyme-435 was used as a catalyst for biodiesel production and various reaction conditions were optimized to get high yield of biodiesel. Furthermore, base (KOH) was used for the high yield biodiesel production from lipid obtained from food waste. Both enzymatic and chemical catalysts were utilized for the biodiesel production from lipid isolated from food waste. The methods described here demonstrate sustainable utilization of food waste as a low-cost resource for biodiesel synthesis.

2. Materials and methods

2.1. Materials and apparatus

Methanol was purchased from Anaoua Chemical Supplies, USA and distilled before use. Lipid was prepared by fungal hydrolysis of bakery waste collected from the local Starbucks Coffee (Pleissner et al., 2014a,b). The obtained waste lipid was heated to 100 °C for 8 h to remove moisture. *Candida antarctica* lipase-B (Novozyme-435), standard fatty acid methyl esters and CDCl_3 -TMS were purchased from Sigma-Aldrich, St. Louis, Missouri, USA. Potassium hydroxide and anhydrous sodium sulfate were purchased from ACROS Organics, Geel, Belgium. Ethyl acetate was purchased from HK Labware, Hong Kong. The conversion of lipid to FAME produced in each reaction was calculated using ^1H NMR (Knothe, 2000; Karmee and Chadha, 2005). A Bruker 400 MHz instrument was used for recording of ^1H NMR spectra. The reaction was monitored qualitatively by thin layer chromatography (TLC). The TLC plates were purchased from Macherey–Nagel, Düren, Germany. All reactions were performed in 50 mL round bottomed flasks. Each reaction was carried out in duplicate and the results presented here were averaged.

2.2. Transesterification of waste lipid using potassium hydroxide

To a mixture of waste lipid (1 g) and KOH (0.05 g, 5 wt.%), different amounts of methanol (147 μL and 457 μL) were added. Reactions were carried out at 1:3 and 1:10 M ratio of lipid to methanol and the reaction temperatures were 40 °C and 60 °C. After 2 h of reaction the obtained mixture was neutralized with dilute sulfuric acid and extracted using ethyl acetate. The resulting mixture was filtered through anhydrous sodium sulfate to remove the water phase. The obtained organic phase was dried under vacuum at 60 °C. Subsequently, the obtained sample was used for ^1H NMR analysis.

2.3. Kinetics of base catalyzed transesterification

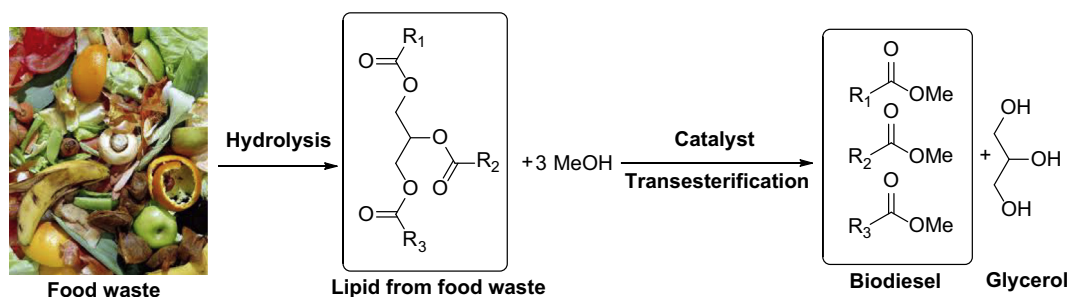
Methanol (457 μL) was added to a mixture of waste lipid (1 g) and KOH (0.05 g, 5 wt.%). The temperature was kept constant at 60 °C and the reaction was monitored for 2 h. Samples were taken at 10, 30, 60, 90 and 120 min. The work-up of the samples was carried out as described above. The obtained samples were analyzed by ^1H NMR.

2.4. Temperature optimization of lipase catalyzed reaction

Methanol (162 μL) was added to a mixture of waste lipid (1 g) and lipase (0.1 g, 10 wt.%). The reactions were carried at different temperatures (30 °C, 40 °C, 50 °C and 60 °C). After 6 h of reaction the sample and enzyme was separated by filtration. The resulting samples were then dried and analyzed by ^1H NMR.

2.5. Molar ratio optimization of lipase catalyzed reaction

Different amounts of methanol (1:3, 137 μL ; 1:4, 162 μL ; 1:5, 227 μL ; 1:6, 274 μL ; and 1:10, 457 μL) were added to the mixture consisting of waste lipid (1 g) and lipase (0.1 g, 10 wt.%). The temperature was kept constant at 40 °C. After 6 h of reaction, the samples were separated from the enzyme by filtration. The resulting samples were then dried and analyzed by ^1H NMR afterwards.



Scheme 1. Transesterification of lipid from food waste with methanol in the presence of chemical and enzymatic catalysts.

2.6. Reaction time optimization of lipase catalyzed reaction

To a mixture of waste lipid (1 g) and lipase (0.1 g, 10 wt.%), methanol (227 μL , 1:5) was added. The reaction was carried out for 36 h and the temperature was kept constant at 40 $^{\circ}\text{C}$ during the reaction. Samples were taken at 6, 12, 24 and 36 h from the reaction. All the samples were filtered to separate the enzyme. The samples were then dried under vacuum and analyzed by ^1H NMR.

3. Results and discussions

The transesterification reaction using KOH as a catalyst gave an excellent 100% FAME yield at 60 $^{\circ}\text{C}$ and 1:10 M ratio of lipid to methanol (Fig. 2). Further decrease in temperature to 40 $^{\circ}\text{C}$ reduced the yield of FAME (Fig. 2). Changing the molar ratio from 1:3 to 1:10 greatly influenced the yield of FAME (Fig. 2). This indicates that a high amount of methanol increases the yield of the biodiesel. Lipid to methanol molar ratio 1:10 and 60 $^{\circ}\text{C}$ were found to give the highest FAME conversion for the base catalyzed reaction.

Kinetics of the base catalyzed transesterification was studied at 1:10 M ratio of lipid to methanol and at 60 $^{\circ}\text{C}$ temperature. Rapid conversion of lipid to FAME was observed during the base catalyzed transesterification of lipid to methanol (Fig. 3). At 10 min, 89% of FAME was formed; and after two hours of reaction 100% FAME yield was achieved (Fig. 3). Using KOH as a catalyst, high FAME conversion within short reaction times (10 min to 2 h) was previously reported (Ma and Hanna, 1999; Darnoko and Cheryan, 2000; Karmee and Chadha, 2005). Recently, Yang et al. (2014a)

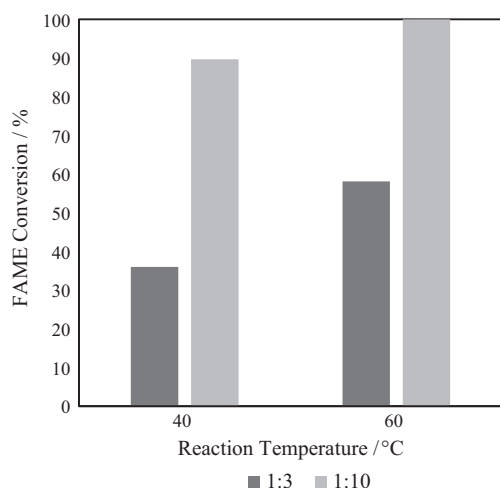


Fig. 2. Base catalyzed transesterification at different molar ratio of lipid to methanol.

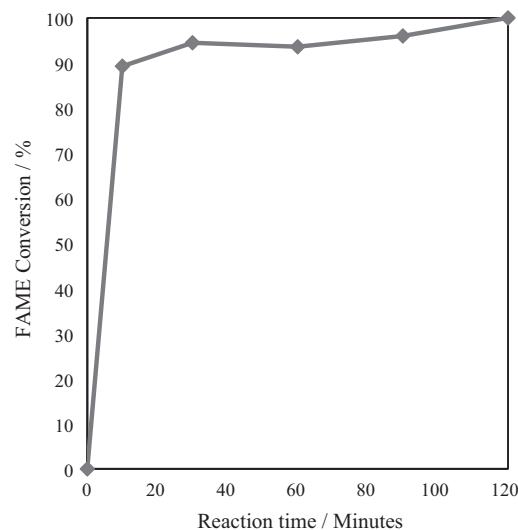


Fig. 3. Kinetics of the base catalyzed transesterification of lipid from food waste.

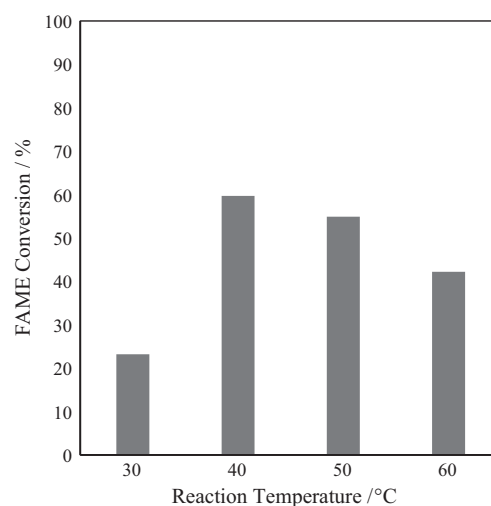


Fig. 4. Temperature optimization of the Novozyme-435 catalyzed transesterification reaction.

reported the use of KOH as a catalyst and converted lipid from instant noodle waste to biodiesel in 2 h with 98.5% FAME conversion. Similarly, Alptekin et al. (2014) utilized waste animal fat as a biodiesel feedstock and achieved 90% FAME conversion although the feedstock required multiple pretreatments with the harmful sulfuric acid.

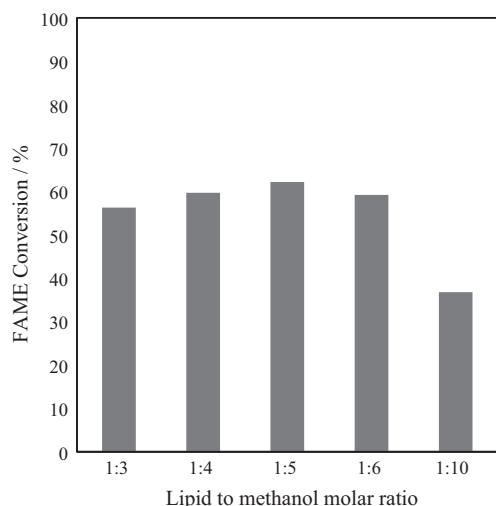


Fig. 5. Lipid to methanol molar ratio optimization for the Novozyme-435 catalyzed transesterification.

Novozyme-435 is known to be an efficient biocatalyst for biodiesel preparation (Parawira, 2009; Fukuda et al., 2008; Ranganathan et al., 2008). Optimization of reaction temperature for Novozyme-435 catalyzed transesterification reaction was performed and a FAME conversion of 60% was obtained at 40 °C (Fig. 4). At 60 °C, the FAME yield decreased to 42% which can be attributed to the evaporation of methanol; whereas, at 30 °C the lipid remained mostly solid throughout the reaction which is likely the main cause of the low yield (23%) of FAME (Fig. 4). For Novozyme-435 catalyzed reaction, 40 °C was found to be the optimum temperature. While the optimum molar ratio of lipid to methanol was found to be 1:5 with a FAME yield of 62% (Fig. 5). At molar ratio of lipid to methanol 1:10, a decrease in FAME yield was observed. This can be attributed to the deactivation of the lipase in the presence of high amounts of methanol.

The progress of the Novozyme-435 catalyzed transesterification was studied. Reaction was carried out for 36 h at 1:5 M ratio and 40 °C reaction temperature. Samples were taken at 6, 12, 24 and 36 h. After 24 h of reaction, 90% of FAME yield was achieved (Fig. 6). Further increase in reaction time did not affect the yield

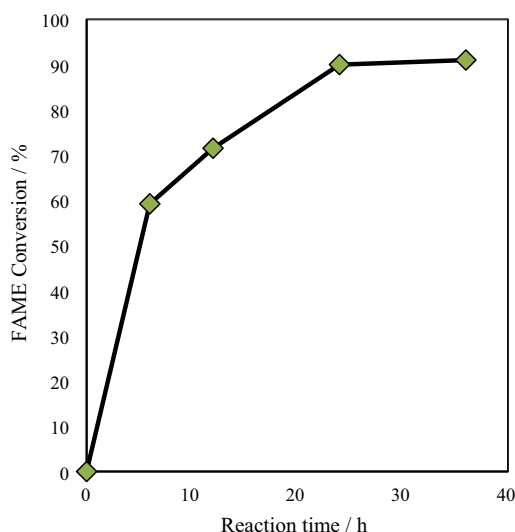


Fig. 6. Kinetics of the Novozyme-435 catalyzed transesterification of lipid from food waste with methanol.

of FAME and only 91% of FAME yield was obtained after 36 h. Yang et al. (2014a,b) have also reported the production of biodiesel from lipid from noodle waste using Novozyme-435 as a catalyst, observing a 95.4% FAME conversion in 36 h reaction time.

Although the conversion of the base-catalyzed transesterification provides a higher FAME conversion in a shorter time, the use of KOH hinders the separation of FAME, glycerol, a valuable by-product, and the catalyst (Parawira, 2009; Fukuda et al., 2008; Ranganathan et al., 2008). However, the slower reaction time and higher cost of lipase have a negative impact on its economic feasibility. To fully test the economic feasibility of utilising lipase in industrial processes, more studies have to be conducted to test the reusability of the lipase.

4. Conclusions

In this paper, the utilization of lipid from food waste as a non-edible and low-cost resource for biodiesel preparation is successfully demonstrated. Lipid obtained from food waste was used as a potential feedstock for biodiesel production using both a chemical catalyst and a biocatalyst. Base (KOH) catalyzed transesterification of the lipid allowed a 100% conversion of biodiesel in 2 h; whereas, Novozyme-435 yielded 90% biodiesel in 24 h. The processes presented in this study has the potential to provide a solution to the municipal food waste disposal problem of Hong Kong by sustainable conversion of food waste to biofuel.

Acknowledgement

SKK is grateful to the School of Energy and Environment, City University of Hong Kong for a postdoctoral fellowship under the Graduate Teaching Assistant (GTA) scheme.

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