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Sythesis of Biodiesel from Coconut Waste via In-situ Transesterification

M. N. Noorzalila*, M. A. Nurul Asikin

Faculty of Chemical Engineering, Universiti Teknologi MARA Pulau Pinang, 13500 Permatang Pauh, Pulau Pinang, Malaysia

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A B S T R A C T

The increasing number of environmental pollution through carbon emission from combustion of fuels and the unstable fluctuation of global petroleum prices have alarmed a signal that a clean alternative energy is in urgent need. Through the past years, a lot of researches have been focusing in producing biodiesel which can be made from natural elements such as plants and recyclable materials, hence defined its renewable properties as biodegradable, sustainable and non-toxic fuel. The focuses have been varied from the variable of feedstock used, development of catalysts and different kind of methodologies for the production of biodiesel. In this study, the feasibility of biodiesel to be synthesized from a low cost feedstock which is coconut waste has been investigated. The abundance of coconut waste readily obtained from the market, restaurants and hotels were converted to a value-added fuel through an in-situ transesterification. It is found that at ratio of 12.5:1 of methanol to solid coconut waste, with reaction time of 6 hours and 5wt% of catalyst could obtain up to 90% of biodiesel content. This investigation concludes that coconut waste has the potential to be further used for synthesis of biodiesel through in-situ transesterification reaction.

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INTRODUCTION

The world nowadays is facing the worst energy crisis due to the depletion of the fossil fuel and the increasing of environmental concerns. Due to the expanding urbanization, increasing number of population and the demand for a better living standard, the world energy demand is expected to be increased [1]. Fossils fuels can be found in a layer far underneath the ocean which is formed from the remaining plants and animals. Petroleum, crude oil and coal are the examples of non-renewable fossil fuel. Almost all countries in the world are still depending on the petroleum and the major usage of petroleum as transportation fuel are used every day in our daily life and cause the price are increase due to the demand of petroleum [2].

There are other alternative energies to replace petroleum such as alcohol fuel, biodiesel, biofuel, hydrogen, solar energy, wind and electrical vehicle so that the usage of petroleum can be reduced to maintain the source. Biodiesel is one of the renewable energies that can replace the dependence on fossil fuels and it will give a substantial contribution to the future of the world. Biodiesel is an environmentally viable fuel which is also renewable and sustainable [2]. Biodiesel has been produced by varieties of feedstock either from edible or nonedible plants and animal fats. The examples of edible sources include palm, coconut, soybean and sunflower oil. Meanwhile, the non-edible sources include Jatropha, sea-mango and *Croton megalocarpus* oil.

In producing biodiesel, a catalyst is used to initiate the esterification reaction for making biodiesel. The catalyst could enhance the solubility of alcohol and thus increase the reaction rate [3]. The most common type of catalyst used in biodiesel production are base catalyst such as sodium hydroxide and potassium hydroxide [4]. Normally, homogeneous base catalyst is used when free fatty acid (FFA) content of the feedstock is less than 1%. Meanwhile, homogeneous acid catalysts such as

* Corresponding author: M.N. Noorzalila
E-mail: zalila2871@ppinang.uitm.edu.my; Tel: +60043822544

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sulphuric and phosphoric acid are used when there is high amount FFA content of more than 1%. The base-catalyzed process proceeds faster than acid-catalyzed reaction. However, base-catalyzed reaction is affected by water content and free fatty acids of oils or fat to form soaps and water, thus decreasing the yield of biodiesel. On the other hand, the advantage of using acid catalyst is that they can directly produce biodiesel from low-cost lipid feedstock, generally associated with high FFA concentrations [5]. However, reaction with acid catalyst has slow reaction rate and requires high ratio of alcohol to triglyceride [3].

The exploitation of edible oils for biodiesel production may lead to controversial issues of food versus fuel. This is because the supply and demand of oil for fat and food industries may be jeopardize if edible oils are being utilize for fuel as well. On the other hand, the non-edible sources are limited and may require extensive empty land for the plantation of these plants if they are to be utilized for biodiesel feedstock. Due to this factor, it is crucial to search for other alternative oil feedstock for biodiesel production to substitute edible and non-edible oil. Earlier findings on the Soxhlet extraction of the coconut waste oil showed that about 45% of oil content can be obtained from the extraction which is sufficient to be converted to biodiesel. Hence in this study, there is an interest to investigate the feasibility of low cost feedstock which is coconut waste to be used in synthesizing biodiesel. There is abundance of coconut waste that is readily obtainable and only small quantities of them are re-used in agriculture as fertilizers to the plantation and animal feed which is not corresponding with the large amount of coconut waste produce daily. Hence, the objective of this research is to determine the fatty acid methyl ester (FAME) content through in-situ transesterification of coconut waste which combines the extraction and transesterification process at the same time to produce biodiesel.

MATERIALS AND METHODS

Materials

The raw material used in this study is the solid coconut wastes which were obtained at the market and grocery shop around Seberang Jaya, Pulau Pinang. The chemicals used for the in-situ transesterification study includes methanol and n-hexane as the solvent, sulphuric acid as the catalyst, methyl heptadecanoate as the internal standard, and other pure methyl esters such as methyl myristic, methyl oleate, methyl palmitate, methyl stearate, and methyl linoleate. The internal standard and pure methyl esters were used during analysis using gas chromatography to determine the FAME content.

Extraction of oil

The soxhlet extraction of coconut waste was performed to determine the amount of oil content in coconut waste. The experimental conditions of oil extraction were selected and improvised based on procedures reported in literature [6, 7]. The coconut waste was first dried for 48 hours at temperature of 70°C in an oven. The coconut waste was then weighed for 20g and was filled inside a thimble before placed in Soxhlet container. 200 ml of hexane used as solvent was filled in 250 ml round-bottomed flask which was then attached to the Soxhlet container. The flask was heated up until it reaches the boiling point of n-hexane using a heating mantle which is at 68 °C. The n-hexane was allowed to vaporize in the chamber, and continuously diffused through the thimble and the oil was extracted from the coconut waste until the n-hexane reached a level where the siphon effect occurred. The extraction was kept for 8 hours and then the oil was separated from n-hexane using rotary evaporator.

In-situ transesterification process

The experimental conditions of in-situ transestrification were selected and improvised based on procedures reported in literature [8]. 20 g of coconut waste were initially weighed and placed inside a 250ml round-bottomed flask filled up with methanol and sulphuric acid (95-97% purity). A condenser was attached at the top of the flask and the flask was heated in a heating mantle to the boiling point of methanol (65 °C). The effect of 1.5, 2.0 and 5 wt% of catalyst, followed by effect of reaction time of 4-6 hours and methanol to coconut waste ratio at 7.5:1, 10:1, 12.5:1 and 20:1 were investigated in this study. Once reaction was completed, the sample was first washed using methanol followed by washing with distilled water to remove the sulphuric acid. Two layers of samples were obtained at the end of process in which the biodiesel sample was at the top and the glycerin and other by product at the bottom. The biodiesel sample was obtained by filtrating out the glycerol and heated using rotary evaporator to remove excess methanol.

Gas Chromatography

The sample were analyzed by using gas chromatography (PerkinElmer, Clarus 500) with Nukol^{TM} capillary column (15 m x 0.53 mm; 0.5 µm film) and flamed ionized detector (FID) to determine the presence of fatty acid methyl esters (FAME). Methyl heptadecanoate was used as the internal standards as well as the other pure methyl esters such as methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate have been injected prior to sample analysis to determine their standard area and retention time. n–Hexane was used as the solvent while helium was used as the carrier gas. The oven

temperature was set at 110°C and then increased to 220°C at a rate of 10°C/min. Temperature of detector and injector were set at 250 and 220°C, respectively. After all samples have been diluted with internal standard, 1 µl of each sample was injected into the gas chromatography column.

RESULTS AND DISCUSSION

Yield of Extraction

From the Soxhlet extraction of coconut waste, it was determined that the oil extracted using n – hexane as the solvent gives the yield percentage of 45.14 %. This finding agrees with the amount found in the literature which stated that the seed kernel oil of Jatropha contained 40-60% oil [9]. The n-hexane would increase the extractability of oil because of its non-polar solvent and able to penetrate into matrix of raw materials during extraction process [10]. In addition, it has also been claimed that coconut waste can be extracted by solid liquid extraction using solvent because it gives a higher yield and less turbid oil [11, 12]. The oil has been extracted at the optimum extraction time of 8 hours, hence with the yield of more than 40%, this would be sufficient to convert into biodiesel, a value-added alternative fuel and make the coconut waste as one of the potential low cost feedstock for biodiesel production.

Effect of weight percent of catalyst

In general, the presence of catalyst could increase up the transesterification reaction for making biodiesel. In this experiment, sulphuric acid is used for acid catalyzed in situ transesterification with different weight percentages (%). Sulphuric acid is chosen because it has the advantage to directly produced biodiesel from low-cost lipid feedstock which associated with high free fatty acid concentrations used in this study which is coconut waste. For this study, 1, 1.5, 2.0 and 5 wt% of catalyst were investigated for its effect on FAME content at constant reaction time of 6 hours and 12.5: 1 alcohol to solid coconut waste ratio. From the result, it is shown that the FAME content increases with the increasing of wt% of catalyst. The 5.0 wt% gives the higher percentage of FAME content compared to other weight percentage. The addition of sulphuric acid enhances the solubility of alcohol hence increase the reaction rate [4]. Consequently, this contributes to the high conversion of FAME towards the end of reaction.

Effect of reaction time

Another variable that has been investigated in this study is the effect of reaction time on the FAME content. It can be clearly seen in Figure 2 that the FAME content begins to increase when reaction time proceed from 4 to 6 hours of reaction.

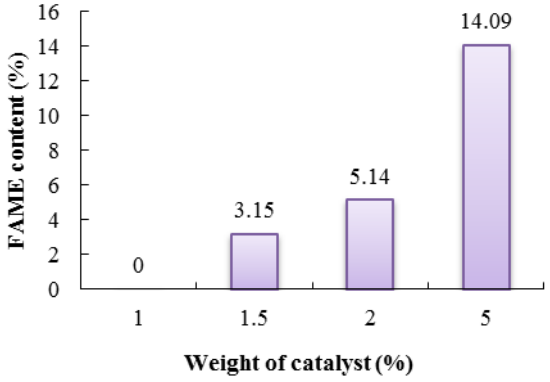

Figure 1. Weight percent of catalyst vs. FAME content

This is because longer reaction time will allow the trasnesterification reaction to proceed towards complete conversion, resulting in increasing of FAME content [13,14]. This result reported a similar finding by [15] who have also claimed a reaction time of 6 hours for complete conversion of Jatropha curcas oil to methyl ester to obtain 90% yield of biodiesel. However prolonged reaction time up to 10 hours has resulted in significant drop in the FAME content. Possible reason for this phenomenon is may be because of the reversible reaction in the transesterification, in which causing the biodiesel to go back to the right side of equilibrium when the reaction is extended up to 10 hours. Consequently, this reduces the overall content of FAME.

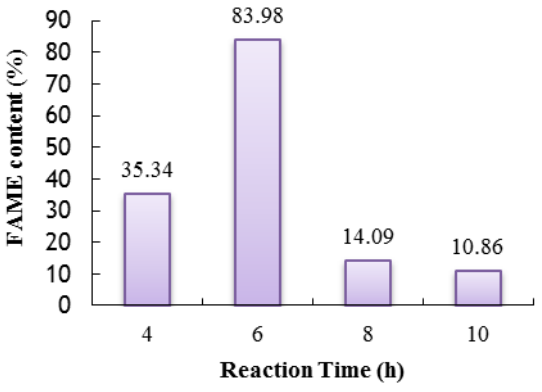

Figure 2. Reaction time (hours) vs FAME content

Effect of ratio of coconut waste to alcohol

The solvent to coconut waste ratio can be considered to be another variable which could affect the transesterification. The study on the effect of ratio of alcohol to solid coconut waste has been performed at 7.5:1, 10:1, 12.5:1 and 20:1, at heating temperature of 65 °C with optimized 5 wt% of catalyst and reaction time of 6 hours as obtained from the previous study. 20 grams of coconut waste was constantly tested with different amount of methanol. The result reported a significant finding as more than 90% of FAME content can be obtained at ratio of 12.5:1 of alcohol to solid coconut waste. Initially, about 31% of FAME can be obtained at ratio of 7.5:1 methanol to solid coconut waste. However, increasing of methanol added in the reaction did not help to increase the FAME content. This might be due to insufficient amount methanol for the reaction to achieve equilibrium. At 12.5:1 ratio, the FAME content exceeded more than 90% of yield, hence reported the highest percentage of FAME obtained in the study. Excess amount of alcohol of ratio of 20:1 however reduced the FAME content significantly to 12%. This is because with a fixed reaction time of 6 hours, the excess amount of alcohol added did not help to push the reaction forward or to the product side, hence a significant drop in FAME content was obtained. Unless, if the reaction time is prolonged to more than 6 hours, this may help increase the FAME content at the molar ratio of 20:1.

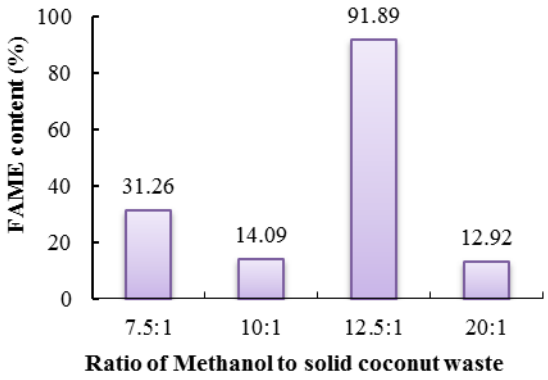

Figure 3. Ratio of methanol to solid coconut waste vs. FAME content (%)

CONCLUSIONS

The current research work has utilized the coconut waste as the low cost feedstock for synthesis of biodiesel. It was determined that the combination of both extraction and reaction through in-situ transesterification of coconut waste and alcohol could produce more than 90% of FAME content. The highest FAME content was obtained at reaction time of 6 hours, with 5wt% of sulphuric acid as catalyst and solvent to solid coconut waste ratio of 12.5:1. Consequently, this conclude the aim of the research that coconut waste is feasible to be utilized further for producing value-added alternative fuel which is biodiesel and the in-situ transesterification shows an effective method in reducing the required cost and processing time of biodiesel production.

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Persian Abstract

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چکیده

افزایش تعداد منابع آلاینده محیط زیست از طریق انتشار کربن ازاحتراق سوخت ها و نوسان ناپایدار قیمت جهانی نفت، نیاز فوری به یک انرژی جایگزین پاک را هشدار می‌دهد.طی سال‌های گذشته، بسیاری از تحقیقات روی تولید بیودیزل که می‌تواند از مواد طبیعی مانند گیاهان و مواد قابل بازیافت تولید شود، متمرکز شده‌اند. از این رو، خواص تجدیدپذیر آن به عنوان سوخت زیست تخریب‌پذیر، پایدار و غیر سمی تعریف شده‌اند. تمرکز روی موارد مختلف می‌تواند از استفاده‌ی خوراک متغیر، گسترش کاتالیست‌ها و انواع روش‌ها برای تولید بیودیزل متغیر باشد. در این مطالعه، امکان تولید بیودیزل از یک خوراک کم هزینه که ضایعات نارگیل بوده، بررسی شده است. ضایعات نارگیل به آسانی از بازار، رستوران‌ها و هتل‌ها تهیه شد و از طریق یک تبادل استری در جا به یک سوخت ارزش افزوده تبدیل شد. این سوخت با نسبت دوازده و نیم به یک متانول به زباله جامد نارگیل، با زمان واکنش شش ساعت و پنج درصد وزنی کاتالیست تا نود درصد محتوای بیودیزل به دست آمد. این تحقیق نتیجه می‌گیرد که زباله نارگیل این پتانسیل را دارد که با توان بیشتری برای سنتز بیودیزل از طریق واکنش تبادل استری درجا استفاده شود.