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Title: Production of biodiesel from Sterculia foetida and its process optimization

Article Type: Original Research Paper

Keywords: Biodiesel; Sterculia feotida; esterification; transesterification; physical chemical property; alternative energy

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Abstract: The diminishing supply of fossil fuels reserves and the environmental concerns have made renewable energy an alternative energy source for the future. Sterculia foetida is one of the possible non-edible feedstocks for biodiesel production. This paper explores and examines the potential biodiesel production from sterculia foetida. Besides, this study also aimed to optimize the biodiesel production parameters by using design of experiment (DOE). The parameters involved in the optimization process were the amount of catalyst, reaction temperature, agitation speed and reaction time. Crude sterculia foetida oil has high acid value which is 5.11 mg KOH/g. Thus, two stage acid catalyst esterification and base transesterification methods are used to produce biodiesel from sterculia foetida. The optimum biodiesel conversion efficiency obtained was 93.55% by 1 %vol. of sulphuric acid with 12:1 of methanol to oil ratio at 60oC and 1200 rpm agitation rate for 3 hours. On the other hand, the transesterification process condition is 1 %wt. sodium hydroxide catalyst with 12:1 methanol to oil at 55oC for 2.5 hours. The high viscosity (63.90 mm2/s) of crude sterculia foetida oil was reduced to 3.96 mm2/s after the transesterification process. Moreover, the properties of the produced sterculia foetida methyl esters and all the measured properties are within the limits of ASTM D 6751 and EN 14214 specifications. Therefore, sterculia foetida oil is one of the non-edible feedstocks for biodiesel production.

July 3, 2012

Professor B. Li
Editor
FUEL

Sub: Submission of Article

I am pleased to submit an article entitled "Production of biodiesel from *Sterculia feotida* and its process optimization" for your consideration.

This paper has not been published previously, it is not under consideration for publication elsewhere, and if accepted it will not be published elsewhere in substantially the same form, in English or in any other language, without the written consent of the Publisher.

It would be highly appreciated if you kindly acknowledge the receipt of my article.

Thank you,

Sincerely yours

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March 19, 2013

Ref. JFUE-D-12-01092
Title: Production of biodiesel from Sterculia foetida and its process optimization

Fuel

Dear,

Prof. Dr, Baoqing Li,

Principal Editor (Fuel)

Sub: Re-submission of REVISED Article (JFUE-D-12-01092)

I am pleased to re-submit a revised article entitled "Production of biodiesel from Sterculia foetida and its process optimization (Ref: JFUE-D-12-01092)" for your reconsideration for publication in **FUEL**.

We would like to thank the reviewer and the editor for their insightful and thoughtful comments. We have carefully taken their comments into consideration in preparing our revision. In responding to reviewer comments, we believe that this paper is clearer, more compelling and broader.

The authors' response for reviewers' comments are in the following page.

Sincerely yours,

Ong Hwai Chyuan

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Production of biodiesel from Sterculia foetida and its process optimization (JFUE-D-12-01092)

Reviewer #1:

Reviewer's comment:

Journal of fuel is suitable for this research. Clearly defined scope and purpose for this the study. The scope and applied research methods and materials for the production of biodiesel are selected. Be clearly grounded in standards and statements of the results is very good. Fuel is editor of the journal of the notes have been sent before. Fuel suitable for publication in the Journal.

Author's response:

The authors are very grateful with the comments and recommendations to accept for publication in Fuel journal.

Reviewer #3:

Reviewer's comment:

The manuscript is original and reports mainly on the optimization of the conversion process for making biodiesel from non-edible sterculia foetida seed oil. The oil had a relatively high free fatty acid content requiring a two-step process for conversion. The first step, acid-catalyzed esterification of the free fatty acids with methanol, was apparently not optimized in this work. The second step, the more traditional alkali-catalyzed transesterification with methanol, was optimized to maximize yields with respect to oil/methanol molar ratio, catalyst concentration, reaction time, temperature, and speed of mixing of the reactants. Results showed that a 93.5% conversion rate could be achieved within 2-3 hours. Fuel properties of the product were compared with those for biodiesel made from other feedstocks as well as conventional diesel fuel. The manuscript is generally well written and organized. However, there are at least three issues that need to be resolved before this paper will be suitable for publication.

Author's response:

The authors are very grateful with the comments and recommendations in order to improve the quality of this paper. We agreed and accepted the reviewer's suggestion. The manuscript is revised carefully according to the reviewer's comments and detailed corrections are listed below point by point.

Reviewer's comment #1:

First, Section 2.5.2 (pp. 6-7) gives defined reaction conditions for the alkali-catalyzed transesterification of sterculia foetida seed oil and methanol into biodiesel. It is understood that the main objective of this work was to optimize the reaction conditions. This paragraph should be generalized with respect to conditions that are optimized in this study. This might be resolved by replacing specified conditions with ranges over which the conditions will be tested for optimization.

Author's response #1:

The authors agreed with the reviewer's suggestion that the paragraph should be generalized with respect to optimize conditions. Thus, the revised paragraph is shown below:

Section 2.5.2:

"In this process, the low free fatty acid content oil was mixed with 6:1-15:1 methanol to oil ratio while stirring at a speed of 800-1500 rpm. Then, 0.5-1.5 %wt. of NaOH was diluted in 25 ml of methanol and added into the oil at 40-60°C for 2-4 hours."

Reviewer's comment #2:

Second, important details are omitted with respect to results summarized in Tables 2 and 3. Where did the data for the jatropha curcas, ceiba pentandra, calophyllum inophyllum, and pangium edule oils and their methyl esters come from? Are these properties from the literature or were they reference from earlier studies? If new results were measured for this work, who supplied the oils and what were the apparatuses used and methods applied? Finally, with respect to the properties of the sterculia foetida oil methyl esters, were they measured for the biodiesel produced using the optimized reaction conditions?

Author's response #2:

The data for the jatropha curcas, ceiba pentandra, calophyllum inophyllum, and pangium edule oils are adopted from literature results. And, the sources for the crude oil are added and cited. However, the methyl esters are purchase from Medan, North Sumentera, Indonesia and they were added and mentioned clearly in the manuscript at section 2.1 as shown below:

"However, jatropha curcas methyl ester (JCME), ceiba pentandra methyl ester (CPME), calophyllum inophyllum methyl ester (CIME), pangium edule methyl ester (PEME) were purchased from Medan, North Sumatera, Indonesia."

Besides, the reviewer is correct that the properties of the sterculia foetida oil methyl esters were measured for the biodiesel produced using the optimized reaction conditions

Reviewer's comment #3:

Third, the data in Table 3 present an in-depth analysis of the fuel properties of sterculia foetida seed oil biodiesel. Why are results for so many properties presented yet not discussed aside from one sentence in the Conclusions (Section 4)? If these properties are meant to demonstrate the quality of the biodiesel, then the number of properties could be shortened. For example, just the data for density, viscosity, flash point, cloud point, acid value, oxidative stability, and free and total glycerol would suffice in this case

Author's response #3:

The reviewer is correct with the biodiesel properties of sterculia foetida as shown in Table 3 are meant to demonstrate the quality of the biodiesel. Thus, we have revised and shortened the number of properties. Besides, a short paragraph is added to discuss briefly the properties results obtained at section 3.1 in the manuscript.

"The physical and chemical properties of SFME are compared with JCME, CPME, CIME, and PEME which are listed in Table 3. It is found that all properties fulfilled the ASTM D 6751 and EN 14214 biodiesel specifications. The obtained viscosity was 3.96 mm^2/s, 3.01 mm^2/s, 3.15 mm^2/s, 3.75 mm^2/s and 3.07 mm^2/s for SFME, JCME, CPME, CIME and PEME respectively. According to Devan and Mahalakshmi [15] and Bindhu et al. [13], the viscosity sterculia foetida was observed at 6.0 mm^2/s and 4.72 mm^2/s respectively. Moreover, the density range was 860–880 kg/m3 at 15°C which is an acceptable result. The observed flash point was 160.5°C, 155.5°C, 163.5°C, 161.5°C and 135.5°C for SFME, JCME, CPME, CIME and PEME respectively which satisfies ASTM and EN biodiesel standards. Besides, the calorific values for all biodiesel are lower than petrol diesel fuel (45.825 MJ/kg). The calorific values were 40.427 MJ/kg, 40.179 MJ/kg, 40.490 MJ/kg, 40.254 MJ/kg and 40.079 MJ/kg for SFME, JCME, CPME, CIME and PEME respectively. Furthermore, the acid value of those biodiesel was also in line within the ASTM and EN biodiesel standards which is less than 0.5%. Moreover, CIME possesses the highest oxidation stability (13.05 hours) followed by JCME with 10.42 hours and 5.50 hours for PEME. However, CPME and SFME possess the lowest oxidation stability of 4.42 hours and 3.44 hours respectively. Sterculia foetida and ceiba pentandra contains cyclopropene chain carbon (sterculoyl acid and malvaloyl acid) which leads to increased oxidation rate and caused poor quality of biodiesel [13, 16]. On the other hand, the cetane number of SFME, JCME, CPME, CIME and PEME are 57.9, 56.8, 57.5, 56.2 and 55.2, which is higher than the standard limit. According to Keera et al. [17], the cetane number of biodiesel increases with the increase of the fatty acid proportion. Typically, the cetane number increases with the increasing chain length and decreases with the increasing unsaturation fatty acids. Thus, longer fatty acids chain and more saturated fatty acid will lead to higher cetane number and shows that SFME have highest cetane compared to JCME, CPME, CIME and PEME."

General comments and suggestion

Reviewer's comment 1:

Abstract, next-to-last sentence: Change "ASTM 6751" to "ASTM D 6751".

Author's response 1:

We agreed and revised the "ASTM 6751" to "ASTM D 6751".

Reviewer's comment 2:

Figs. 1-5 are photographs that could be omitted to reduce the length of the paper. Their omission would not affect the overall quality of this work.

Author's response 2:

We agreed and reduced the photographs figures. Thus, the length of the paper is reduced without affecting the overall quality of this work.

Reviewer's comment 3:

Section 2.5: The term "esterified oil" is misleading since triglycerides themselves are esters. Suggest changing to "low free fatty acid content oil

Author's response 3:

We agreed and changed all the term of "esterified oil" to "low free fatty acid content oil" in the manuscript.

Reviewer's comment 4:

Table 3 is not directly referred to in the text of the paper.

Author's response 4:

We revised and referred the Table 3 in the manuscript. Besides, a short description is also included in the manuscript at section 3.1.

Reviewer's comment 5:

Section 3.1.1: Increasing the methanol/oil molar ratio has no effect on solubility or interfacial contact between methanol and triglyceride molecules. Heating and stirring the reactants does enhance solubility and interfacial contact.

Author's response 5:

The reviewer is correct and we revised the sentence in section 3.1.1 as below:

"However, transesterification is an equilibrium reaction in which a high molar ratio is used to drive the reaction to the right. Besides, heating and stirring need to set at optimum to enhance the solubility and increase the contact between the triglycerides and alcohol molecules."

Reviewer's comment 6:

Section 3.1.3, second sentence: Why was 1 % sulfuric acid put into the reaction mixture being optimized?

Author's response 6:

In this study, the optimization is focused on alkaline catalyst transesterification process. Therefore, the acid catalyst (sulfuric acid) is fitted using generalized volume which is 1%. Perhaps, we can carry out the optimization process for acid catalyst esterification process in the future study.

Reviewer's comment 7:

Reference [18] is missing the journal volume number (88).

Author's response 7:

The journal volume number for the reference mentioned above is added as shown below:

"Bindhu Ch, Reddy JRC, Rao BVSK, Ravinder T, Chakrabarti PP, Karuna MSL, Prasad RBN. Preparation and Evaluation of Biodiesel from Sterculia foetida Seed Oil. J AM Oil Chem Soc 2011;89:891–6."

Reviewer's comment 8:

Figs. 6–9: Suggest including the reaction conditions held constant in the figure captions. For example, in Fig. 4, what were the catalyst concentration, reaction time, and stirring speed? Also, the temperature of the reactions conducted for Fig. 9 was not specified anywhere in the paper.

Author's response 8:

We agreed and added the constant parameters such as catalyst concentration, reaction time, stirring speed, molar ratio and temperature accordingly in the Figs 6–9 (new figure number are Figs 4–7). Besides, the molar ratio, temperature and catalyst concentration were also added and included in Fig 9 (new figure number is Fig. 7).

Lastly, I would like to thank the editor and reviewers who have given very valuable comments and suggestions to improve the quality of this article.

Thank you
Ong Hwai Chyuan

Highlight:

1. *Sterculia feotida* is one of non-edible feedstocks for biodiesel production.
2. The fatty acid composition of s*terculia feotida* was found to be 17.7% (palmitic), 35.1% (sterculoyl) and 1.7% (Malvaloyl).
3. The optimum biodiesel conversion obtained was 93.55% by two stage acid-alkaline transesterification process.
4. The properties of the produced *Sterculia feotida* methyl esters such as viscosity, density, flash point, acid value etc have been determined and within the limits of ASTM 6751 and EN 14214 specifications.

Production of biodiesel from Sterculia foetida and its process optimization

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Abstract

The diminishing supply of fossil fuels reserves and the environmental concerns have made renewable energy an alternative energy source for the future. *Sterculia foetida* is one of the possible non-edible feedstocks for biodiesel production. This paper explores and examines the potential biodiesel production from *sterculia foetida*. Besides, this study also aimed to optimize the biodiesel production parameters by using design of experiment (DOE). The parameters involved in the optimization process were the amount of catalyst, reaction temperature, agitation speed and reaction time. Crude *sterculia foetida* oil has high acid value which is 5.11 mg KOH/g. Thus, two stage acid catalyst esterification and base transesterification methods are used to produce biodiesel from *sterculia foetida*. The optimum biodiesel conversion efficiency obtained was 93.55% by 1 %vol. of sulphuric acid with 12:1

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of methanol to oil ratio at 60^{o}C and 1200 rpm agitation rate for 3 hours. On the other hand, the transesterification process condition is 1 %wt. sodium hydroxide catalyst with 12:1 methanol to oil at 55^{o}C for 2.5 hours. The high viscosity (63.90 mm^2/s) of crude *sterculia foetida* oil was reduced to 3.96 mm^2/s after the transesterification process. Moreover, the properties of the produced *sterculia foetida* methyl esters and all the measured properties are within the limits of ASTM D 6751 and EN 14214 specifications. Therefore, *sterculia foetida* oil is one of the non-edible feedstocks for biodiesel production.

Keyword: Biodiesel; *sterculia feotida*; esterification; transesterification; physical chemical property; alternative energy.

Abbreviation

CCIO	Crude *calophyllum inophyllum* oil
CCPO	Crude *ceiba pentandra* oil
CIME	*Calophyllum inophyllum* methyl ester
CJCO	Crude *jatropha curcas* oil
CPME	*Ceiba pentandra* methyl ester
CPEO	Crude *pangium edule* oil
CSFO	Crude *sterculia foetida oil*
DOE	Design of experiment
JCME	*Jatropha curcas* methyl ester
PEME	*Pangium edule* methyl ester

1. Introduction

The diminishing supply of fossil fuels reserves and the growing environmental concerns have made renewable energy an attractive alternative energy source for the future [1, 2]. Biodiesel is a promising alternative fuel for diesel fuel and is produced by chemical reaction of a fat or oil with an alcohol in the presence of a catalyst. The renewable fuel has a lot of technical advantages over fossil fuels such as lower overall exhaust emission and toxicity, biodegradability, derivation from a renewable and domestic feedstock, negligible sulphur content, superior flash point and eco-friendly fuel [3-5].

Sterculia foetida plant belongs to *Sterculiaceae* family which has 2000 type of species and classified as non-drying oils. It is a wild plant and well adapted to tropical and sub-tropical area (30^{o} North Latitude to 35^{o} South Latitude). The plant has an average life span of more than 100 years [6-8]. *Sterculia foetida* is a large, straight, deciduous tree which can grow up to 40 m in height and 3 m in girth [9, 10]. The diameter of trees is around 100–120 cm and ideal planting pitch has been found to be 3×3 m. The fruit is large, woody, red, nearly smooth and about 10 cm long. It contains 10–15 seeds in each fruit which are initially white in color and later turns black when ripe. The single large seed is surrounded by a shell and a thin 1–2 mm layer of pulp. *Sterculia foetida* gives about 200–350 kg of seed annually [7, 8]. **Fig. 1** shows *sterculia foetida* tree, fruit, seeds and kernels.

[Fig.1]

Sterculia foetida has been planted in many parts of the world such as Australia, Bangladesh, Djibouti, Eritrea, Ethiopia, India, Indonesia, Kenya, Malaysia, Myanmar, Oman, Pakistan, Philippines, Somalia, Sri Lanka, Tanzania, Thailand, Uganda and Republic of Zanzibar shown in **Fig. 2** [9, 10]. In Indonesia, *sterculia foetida* is mainly distributed in West

Java, East Java, Madura and other small islands in Java [11]. The main compositions of *sterculia foetida* seeds are fats and protein which are 51.78% and 21.61% respectively. **Table 1** shows the composition of *sterculia foetida* dry shelled seeds [12].

[Fig. 2]

[Table 1]

This paper introduces new non-edible oil which is *sterculia foetida* (poon) as a biodiesel feedstock. *Sterculia foetida* seeds have been collected from Cilacap forest, West Java, Indonesia. The physical and chemical properties of *sterculia foetida* have been studied and compared with other biodiesel feedstocks as well as international biodiesel standards. Besides, the optimization condition of transesterification process for *sterculia foetida* methyl ester (SFME) production was investigated.

2. Material and Methods

2.1 Materials

Sterculia foetida oil was obtained from Cilacap, West Java, Indonesia. However, *jatropha curcas* methyl ester (JCME), *ceiba pentandra* methyl ester (CPME), *calophyllum inophyllum* methyl ester (CIME), *pangium edule* methyl ester (PEME) were purchased from Medan, North Sumatera, Indonesia. Before the extraction of oil, the seeds have been washed by hot water and dried under the sun. The extraction of crude *sterculia foetida* oil was done by a cutting machine and mechanical pressing machine. It was found that kernel of the seeds yields is around 50–60% oil.

2.2 Reagents

All reagents such as methanol (99.9% purity), H_2SO_4 (purity >98.9%), Phosphoric acid (20% of H_3PO_4), sodium hydroxide pellet (NaOH) (purity 99%), $CaCl_2$ and Na_2SO_4 anhydrous (purity 98%) used in this study were purchased from CV. Rudang Jaya (Medan, Indonesia). Qualitative filter paper (filter fioroni, France) of 150 mm size was supplied from Metta Karuna Enterprise (Kuala Lumpur, Malaysia).

2.3 Apparatus

The experiments were conducted using 1 litre of three necked boiling flask with reflux condenser. The reaction boiling three necked flask was placed on hot plate magnetic stirrer (Model: IKA C-MAG HS7). A thermometer was immersed in the boiling necked flask by using a rubber stand. **Fig. 3** shows the experimental apparatus for esterification and transesterification process of crude *sterculia foetida* oil.

[Fig. 3]

2.4 Refining *sterculia foetida* crude oil

After the extraction process, crude oil contains some of the impurities such as uncrushed seed cake and the oil was refined to reduce acid value and moisture content. The crude *sterculia foetida* oil was refined in the laboratory through simple filtration methods. In this process, 0.5 %vol. of H_3PO_4 (20% concentration) was added with crude *sterculia foetida* oil at 60^oC for 30 minutes. Gums were then separated from the oil and the oil was washed twice with warm water at 40°C. After washing, crude oil was filtered using conical glassware with filter paper for three times. After that, these filtered oils were dried in a vacuum pump drier at a constant temperature of 70^oC for 1 hour to remove the traces of moisture. The

refined crude *sterculia foetida* oil was found to have 3.28 mg KOH/g of acid value. The refined oil resulted from this process was reported to be light yellow.

2.5 Esterification and transesterification process

Sterculia foetida oil has high viscosity, low volatility and polyunsaturated fatty acids. Therefore, it cannot be used directly in compression ignition (CI) engines. Thus, acid catalyst is used to reduce the free fatty acids contents before alkaline transesterification process.

2.5.1 Acid catalysed esterification process

In this process, 400 ml or 374.8 g of CSFO was entered into a three-necked boiling flask equipped with a magnetic stirrer, reflux condenser and thermometer. The sample of CSFO was mixed with 12:1 molar ratio of methanol. Then, 1 %vol. sulphuric acid anhydrous (H_2SO_4) was added to the sample drop by drop using a connected pipe to the flask. During the reaction, the mixture was stirred constantly using a magnetic stirrer at a speed of 1200 rpm for 3 hours at 60°C. After that, the low free fatty acid content oil was entered into a separation funnel and left for 15 minutes to remove the upper layer which is extra methanol and the lower layer was low free fatty acid content oil. The oil sample was entered into rotary evaporator for 20 minutes at 65–70°C to remove extra methanol from the low free fatty acid content oil. The low free fatty acid content oil was washed with distilled water in a separation funnel for two times. Then, the low free fatty acid content oil was dried using 100 g $CaCl_2$ anhydrous in a glass beaker for 1 day and then filtered by a paper filter. The oil was further dried with 100 g Na_2SO_4 anhydrous for 3 hours and filtered by a paper filter.

2.5.2 Alkaline catalysed transesterification

In this process, the low free fatty acid content oil was mixed with 6:1–15:1 methanol to oil ratio while stirring at a speed of 800–1500 rpm. Then, 0.5–1.5 %wt. of NaOH was diluted in 25 ml of methanol and added into the oil at 40–60°C for 2–4 hours. After that, the oil was entered into a separation funnel and left for 15 minutes to separate the upper layer of SFME and the lower layer which is extra methanol and glycerol. The SFME was entered into a rotary evaporator for 20 minutes at 65–70°C to remove extra methanol. Then, the produced biodiesel was washed with distilled water for two times in a separation funnel. The SFME was dried using 100 g $CaCl_2$ anhydrous in glass beaker for 1 day and filtered with paper filter. The oil was further dried with 100 g Na_2SO_4 anhydrous for 2–3 hours and filtered by a paper filter again.

3. Results and discussion

3.1 Crude oil and biodiesel *sterculia foetida* properties

The fatty acid composition and physicochemical properties of *crude sterculia foetida* oil such as viscosity at 40^{o}C, density at 15^{o}C, flash point and acid value were analysed and compared to other non-edible oils from the literature study as shown in **Table 2.** The fatty acid composition showed that the primarily composition were oleic acid which is 44.7%, 46.1% and 46.7% for CJCO, CCIO and CPEO respectively. CSFO consists 25% of saturated fatty acid, 15.3% of unsaturated fatty acid, 1.7% of malvaloyl acid and 35.1% of sterculoyl acid. These results matched with the results obtained by Bindhu [13] who reported that *sterculia foetida* oil contains cyclopropene fatty acids namely sterculoyl acid (44.3%) and malvaloyl acid (10.2%). Moreover, *ceiba pentandra* contains a pair of unique cyclopropene

fatty acids (malvaloyl acid) which are more reactive than the double bond carbon (polyunsaturated) in the reaction with radical formation by atmospheric oxygen. Thus, this hydrocarbon chain reduces oxidation stability in vegetable oil [14]. The physical and chemical properties of the *sterculia foetida* methyl ester produced and other methyl ester were tested using ASTM D 6751 or EN 14214 standards.

The physical and chemical properties of SFME are compared with JCME, CPME, CIME, and PEME which are listed in **Table 3**. It is found that all properties fulfilled the ASTM D 6751 and EN 14214 biodiesel specifications. The obtained viscosity was 3.96 mm^2/s, 3.01 mm^2/s, 3.15 mm^2/s, 3.75 mm^2/s and 3.07 mm^2/s for SFME, JCME, CPME, CIME and PEME respectively. According to Devan and Mahalakshmi [15] and Bindhu *et al*. [13], the viscosity *sterculia foetida* was observed at 6.0 mm^2/s and 4.72 mm^2/s respectively. Moreover, the density range was 860–880 kg/m^3 at 15°C which is an acceptable result. The observed flash point was 160.5°C, 155.5°C, 163.5°C, 161.5°C and 135.5°C for SFME, JCME, CPME, CIME and PEME respectively which satisfies ASTM and EN biodiesel standards. Besides, the calorific values for all biodiesel are lower than petrol diesel fuel (45.825 MJ/kg). The calorific values were 40.427 MJ/kg, 40.179 MJ/kg, 40.490 MJ/kg, 40.254 MJ/kg and 40.079 MJ/kg for SFME, JCME, CPME, CIME and PEME respectively. Furthermore, the acid value of those biodiesel was also in line within the ASTM and EN biodiesel standards which is less than 0.5%. Moreover, CIME possesses the highest oxidation stability (13.05 hours) followed by JCME with 10.42 hours and 5.50 hours for PEME. However, CPME and SFME possess the lowest oxidation stability of 4.42 hours and 3.44 hours respectively. *Sterculia foetida* and *ceiba pentandra* contains cyclopropene chain carbon (sterculoyl acid and malvaloyl acid) which leads to increased oxidation rate and caused poor quality of biodiesel [13, 16]. On the other hand, the cetane number of SFME, JCME, CPME, CIME and PEME are 57.9, 56.8, 57.5, 56.2 and 55.2, which is higher than the standard limit.

According to Keera *et al*. [17], the cetane number of biodiesel increases with the increase of the fatty acid proportion. Typically, the cetane number increases with the increasing chain length and decreases with the increasing unsaturation fatty acids. Thus, longer fatty acids chain and more saturated fatty acid will lead to higher cetane number and shows that SFME have highest cetane compared to JCME, CPME, CIME and PEME.

[Table 2]

[Table 3]

3.1 Effect of optimization process

The design of experiment (DOE) is used to determine the optimization condition of transesterification process. This method was conducted to determine the optimum condition for methanol to oil molar ratio, catalyst concentration, reaction temperature and time as well as agitation intensity speed.

3.1.1 Effect of methanol to oil molar ratio and temperature

One of the most important variables affecting the yield of ester is the molar ratio of methanol to oil. The stoichiometric ratio for transesterification requires three moles of methanol and one mole of triglyceride to produce three moles of fatty acid methyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a high molar ratio is used to drive the reaction to the right. Besides, heating and stirring need to set at optimum to enhance the solubility and increase the contact between the triglycerides and alcohol molecules [18, 19]. In the present work, the transesterification reaction was carried out at various ratios of 6:1, 8:1, 10:1, 12:1 and 15:1 and temperature varies from 40–60^{o}C. Besides, other factors were kept unchanged such as agitation speed at 1200 rpm and 1 %wt. of alkali catalyst. Therefore, a numeric optimization of the transesterification yield as a

function of the molar ratio and temperature was carried out using the software design of experiment (DOE). **Fig. 4** shows that the maximum conversion yield methyl ester is 93.55% which can be obtained at methanol to oil molar ratio of 12:1 and temperature of 55^{o}C.

[Fig. 4]

3.1.2 Effect of catalyst concentration and reaction time

Typically, alkali, acid, enzyme or heterogeneous catalysts were used in transesterification process for the conversion of crude oil to methyl ester. In this study, the alkaline catalyst used was sodium hydroxide pellet and the alkaline catalyst concentration ranges from 0.5–1.5 %wt. with reaction time varies from 2–4 hours. Furthermore, other process conditions were fixed at 12:1 methanol molar ratios to oil, at 1200 rpm agitation rate and reaction temperature at 55^{o}C. The effect of this catalyst's concentration on the conversion of methyl esters is depicted in **Fig. 5**. It was observed that using a lower concentration led to an incomplete reaction and resulted in a lower yield of methyl esters. The yield increased with the increase of the catalyst concentration and reached optimum at 1 %wt. of catalyst amount. However, more soap will be produced owing to the excess catalyst at 1.5 %wt. and favouring the saponification process.

[Fig. 5]

3.1.3 Effect of reaction temperature and reaction time

In order to study the effect of reaction temperature, methanolysis of vegetable oil is normally performed near to the boiling point of the alcohol at 65–70^{o}C [20]. In this study, a methanol to oil ratio of 12:1, 1 %wt. sulphuric acid anhydrous and 1 %wt. sodium hydroxide pellet catalyst at speed agitation of 1200 rpm were used. However, the time was varied from

2–4 hours and the reaction temperature was varied from 40–60^{o}C. The conversion of crude *sterculia foetida* oil will be higher as the time increases; but after 3 hours, the yield decreases as shown in **Fig. 6**. From this process, it is proven that the shorter time and temperature will produce less yield methyl ester. On the other hand, with longer time (more than 3 hours) and the higher temperature (above 60^{o}C) will decrease the yield of methyl ester and cause more soap. Thus, the optimal conversion yield was observed at the reaction time of 2.5 hours and reaction temperature of 55^{o}C. Besides, Kafuku and Mbrawa [21] also showed that an increase in the optimum methyl esters yield was observed at 50^{o}C. On the other hand, the yield declined slightly after 60^{o}C and it caused the saponification in the transesterification process.

[Fig. 6]

3.1.4 Effect of agitation stirring and reaction time

In this experiment, the stirring speed was varied from 800–1500 rpm and reaction time 2–4 hours while other parameters were kept at their original values as shown in previous section. The appearance of two layers between methanol and oil was shown clearly when intensity and time reaction were higher and longer. Otherwise, the separation of those layers would not appear due to the lower intensity of stirring and slower reaction time. This occurred as a result of the hydrolysis from alkyl esters which tends to produce more fatty acids and caused the soap formation [21]. The optimal methyl ester yield at the stirring speed of 1200 rpm and reaction time around 2.5 hours was shown in **Fig. 7**.

[Fig. 7]

4. Conclusion

This paper introduces new non-edible oil extracted from *sterculia foetida* oil to be used as a biodiesel feedstock. The summary of the experimental results are described as follows:

- The biodiesel production from crude *sterculia foetida* oil is via two stage acid (H_2SO_4) catalyst esterification and alkaline (NaOH) catalyst transesterification. The conversion yield of *sterculia foetida* biodiesel was obtained up to 93.55%.
- The optimum condition was 12:1 methanol to oil ratio of with 1%.wt alkali catalyst at 55^oC for 2.5 hours. The fuel properties of SFME fulfilled the ASTM D 6751 and EN 14214. Finally, further research and study need to be carried out before *sterculia foetida* can become an alternative fuel in the future.

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Table 1: Composition of dry shelled seeds [12]

Property	Percentage (%)
Fat	51.78
Protein	21.61
Starch	12.1
Sugar	5.00
Cellulose	5.51
Ash	3.90

Table 2: The properties and fatty acid composition of *sterculia foetida* compared with other non-edible vegetable oils

Properties	CSFO[a]	CSFO [13]	CSFO [15]	CJCO[22]	CCPO[16]	CCIO[19]	CPEO[23]
Kinematic viscosity at 40^{o}C (mm^2/s)	63.90	54.0	926.4	35.40	34.45	71.98	35.16
Density at 15^{o}C (kg/m^3)	937.0	920.0	49.7	918.0	905.2	896.0	922.3
Acid value (mg KOH/g)	5.11	–	0.36	11.00	16.80	44.0	6.03
Flash point (^{o}C)	198.5	–	158.0	186.0	170.5	221.0	–
Fatty acid composition							
C12:0 (Lauric acid)	0.1	–	–	–	0.1	0.1	0.1
C14:0 (Myristic acid)	0.2	–	–	0.1	0.1	0.1	0.1
C16:0 (Palmitic acid)	17.7	23.0	22.4	14.2	19.2	14.7	7.7
C16:1 (Palmitoleic acid)	0.2	–	–	0.7	0.3	0.3	0.1
C18:0 (Stearic acid)	4.7	8.2	7.3	7.0	2.6	13.2	5.25
C18:1 (Oleic acid)	6.0	1.0	16.4	44.7	17.4	46.1	46.7
C18:2 (Linoleic acid)	9.1	11.0	45.9	32.8	39.7	24.7	35.9
C18:3 (Linolenic acid)	0.7	2.3	–	0.2	1.5	0.2	2.1
C20:0 (Arachidic acid)	2.3	–	6.46	0.2	0.56	0.8	0.23
18:*CE (Malvaloyl acid)	1.7	10.2	–	–	18.5	–	–
19:*CE (Sterculoyl acid)	35.1	44.3	–	–	–	–	–

*cyclopropene ester

[a]Analysis result

Table 3: Fuel properties of SFME, JCME, CPME, CIME and PEME with comparison to ASTM and EN standard

Property	Unit	Test limit		Non-edible methyl ester						
		ASTM D 6751	EN 14214	SFME[a]	SFME[13]	SFME[15]	JCME[a]	CPME[a]	CIME[a]	PEME[a]
Viscosity at 40 °C	mm^2/s	1.9–6.0	3.5–5.0	3.96	4.72	6.0	3.01	3.15	3.75	3.07
Density at 15°C	kg/m^3	880	860–900	879.1	850.0	875.0	860.1	864.9	869.6	862.2
Acid value	mg KOH/g	Max. 0.50	Max. 0.5	0.14		0.14	0.18	0.18	0.5	0.11
Flash point	°C	100–170	>120	160.5	179.0	162	160.5	163	161.5	135.5
Pour point	°C	–15 – 16	–	−3.0	3.0	1.0	−1.0	0.0	0.0	−1.0
Cloud point	°C	–3 – 12	–	−3.0	3.0	–	−2.0	0.8	−1.0	−1.4
Cold filter plugging point	°C	19	Max. 5	–5.0	–	–	0.0	1.0	−1.0	−2.0
Calorific value	MJ/kg	–	35	40.427	–	–	40.179	40.490	40.254	40.079
Oxidation stability at 110°C	hours	3 min.	6 min.	3.44	3.42	–	3.42	4.22	13.05	5.50
Cetane number	–	47 min.	51 min.	57.9	–	–	56.8	57.5	56.2	55.2

[a][Analysis result]

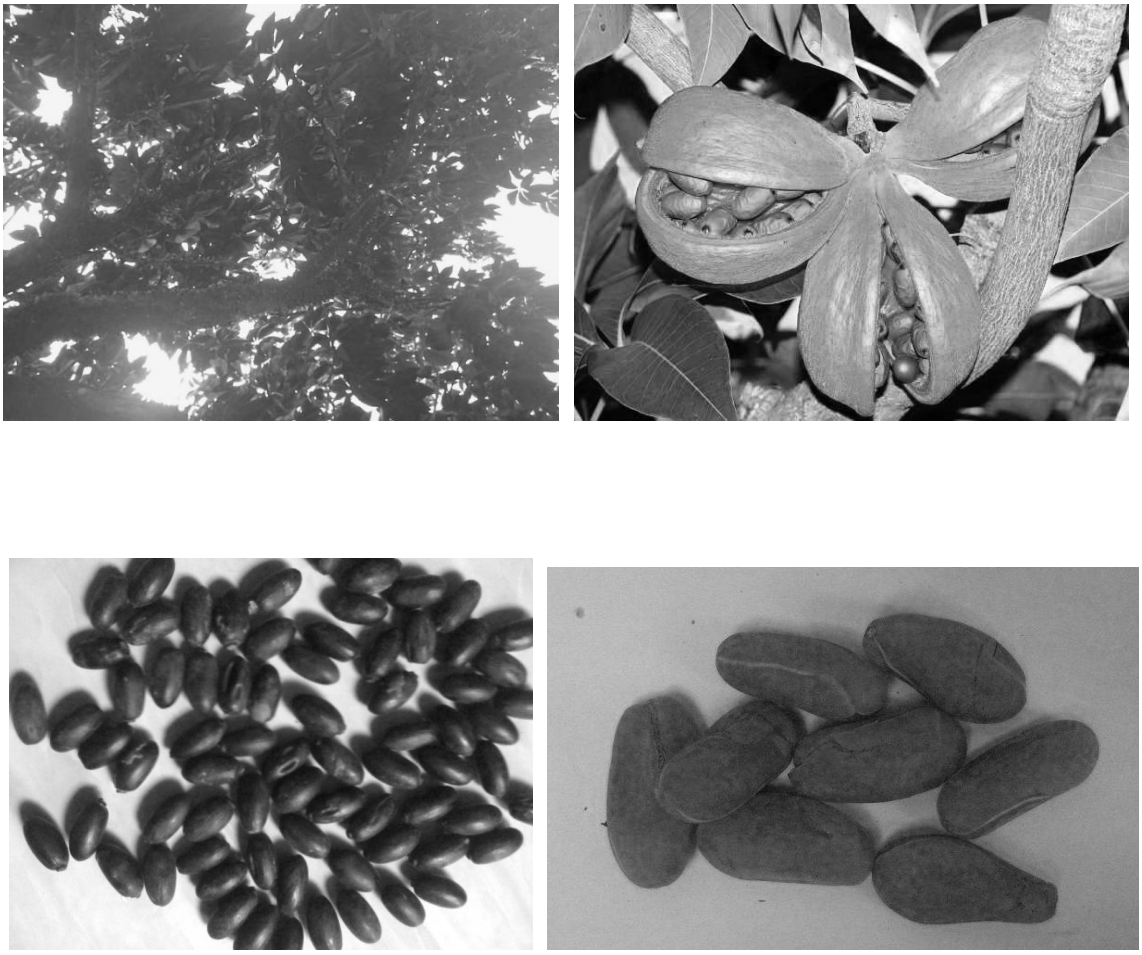

Fig. 1 *Sterculia foetida* tree, fruit, seeds and kernels

Fig. 2 The plantations area of *sterculia foetida* around the world [12]

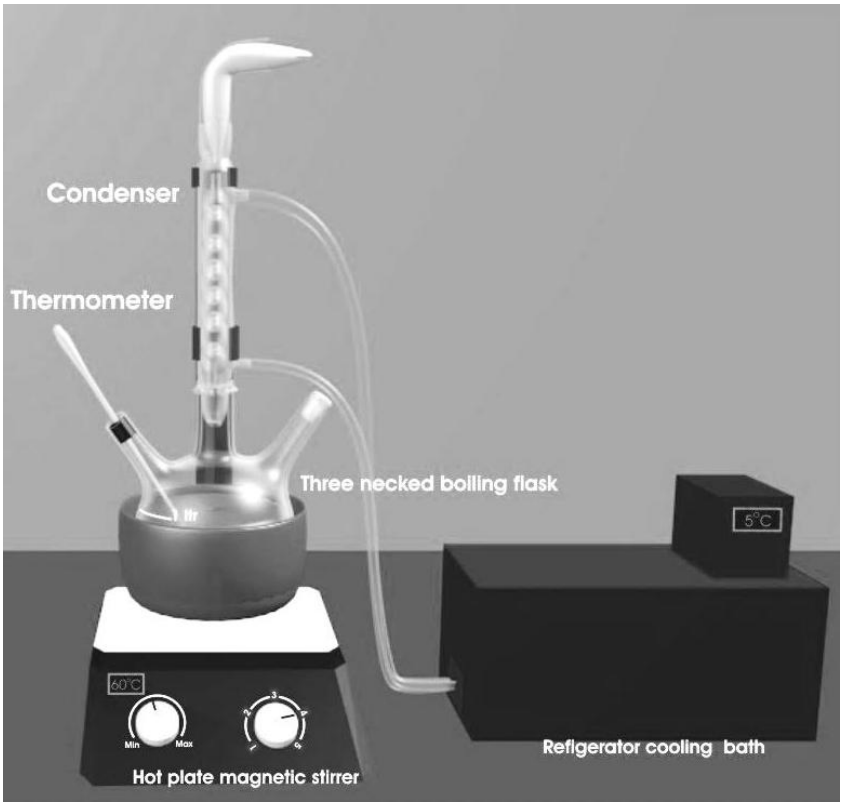

Fig. 3 Apparatus experimental for esterification and transesterification of crude *Sterculia foetida* oil to methyl ester

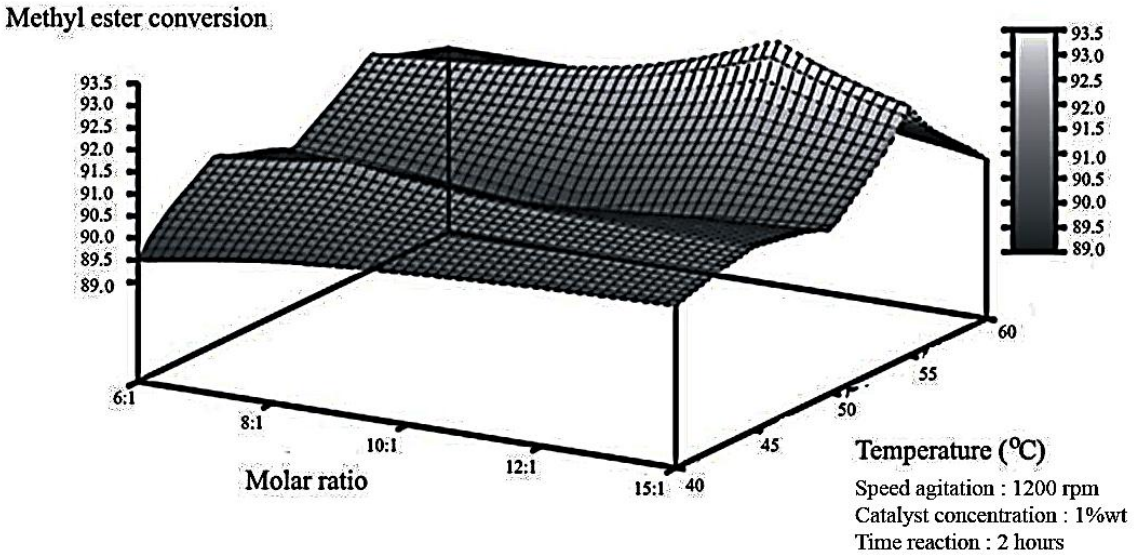

Fig. 4 Effect of methanol to oil molar ratio and temperature

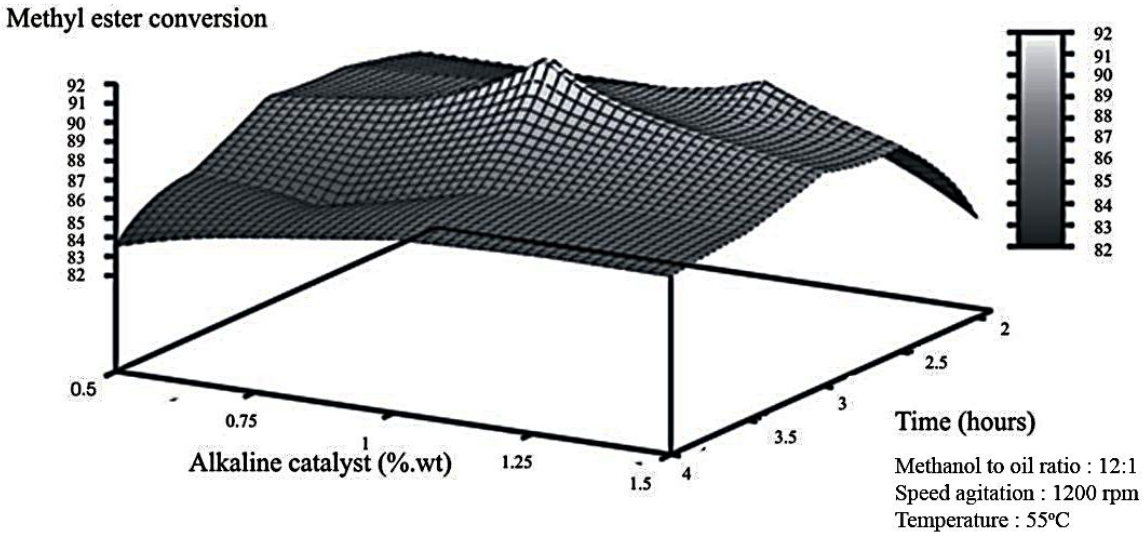

Fig. 5 Effect of catalyst concentration and reaction time

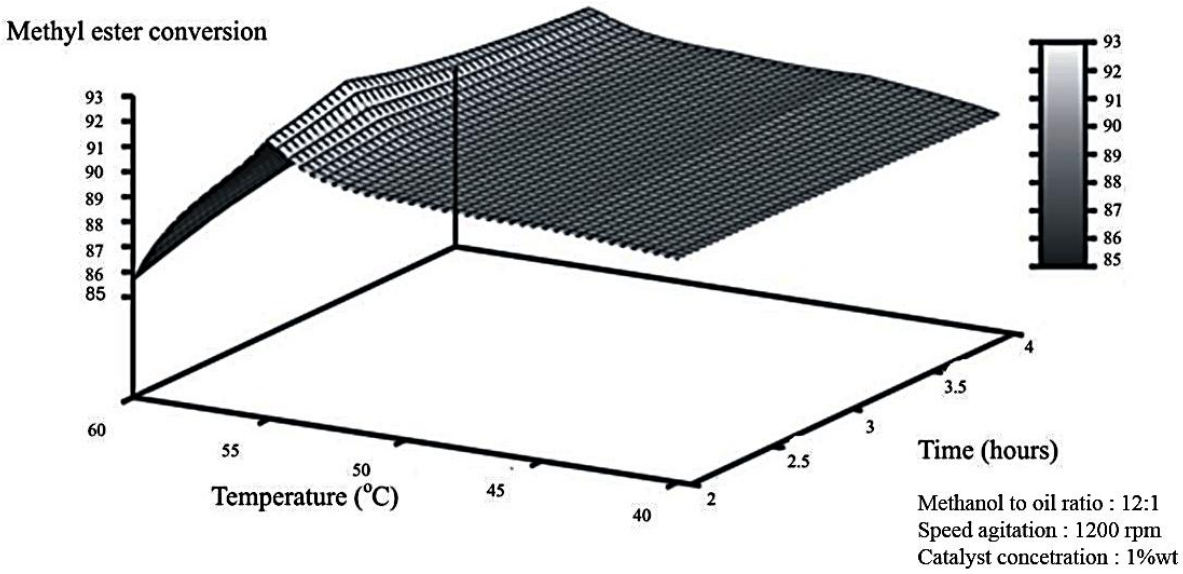

Fig. 6 Effect of reaction temperature and reaction time

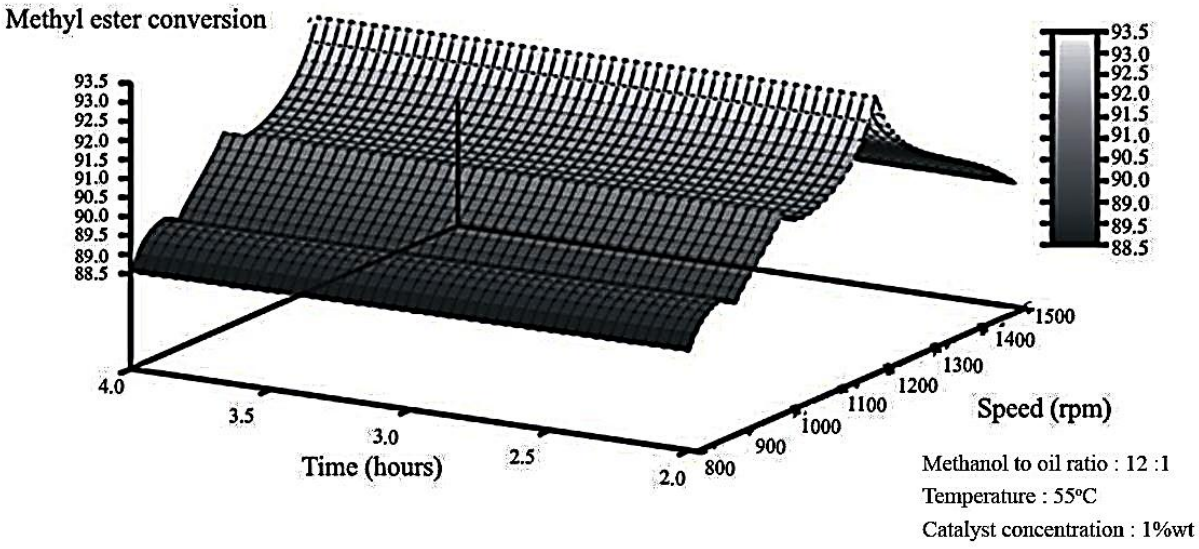

Fig. 7 Effect of agitation stirring and reaction time

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