Production and characterization of biodiesel from *Annona muricata* seed oil

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**Abstract.** Due to the depletion of available energy resources, the usage of fossil fuel has increased steadily. Additionally, the gas emissions of fossil fuel proved to be harmful to the environment. Therefore, researches now focus on utilizing second-generation biodiesel that do not compete with edible seed oils but still can be of great use as an alternative to commercially-produced diesel. The purpose of this research is to extract the oil from *Annona muricata* (Guyabano) seeds and convert it to biodiesel by esterification using hydrochloric acid and transesterification using potassium hydroxide. The average oil yield was 18.92% while the average crude biodiesel yield was 94.76%. The characterization results of the biodiesel composed of 5% guyabano methyl ester in commercial diesel (B5) were all within the limits set by the Philippine National Standards (PNS). However, the water content for the pure biodiesel (B100) was not within the standard range. The kinematic viscosity of B100 is at the maximum limit of PNS. Nevertheless, it suggests that pure Guyabano biodiesel has the potential to be utilized in diesel engines.

1. Introduction

A common global problem is the continuous decrease of fossil fuels. The global energy supply is heavily dependent on fossil fuel reserves which constitute 88% of the total global energy consumption [1]. Moreover, the inevitable rise of the world population brought about the increase in the use of vehicles and products that are heavily reliant on fuels. These worsen the environmental problems due to high carbon emission. To address these problems, the development of bioenergy prompted to come up with alternative fuels [2].

Biodiesel is one of the alternative fuels that continually receive a special attention because it is easily produced from available and renewable resources such as vegetable oils, animal fats, non-edible oils, and waste cooking oil [3].

Biodiesel is a mixture that constitutes mono-alkyl esters of long chain fatty acids derived from the mentioned renewable resources when reacted with an alcohol and the presence or absence of a catalyst [4]. It is considered one of the best alternative for petroleum-based fuels because of its similar calorific value, low toxic emissions, biodegradability, high flash point, excellent lubricity and environmental compatibility [5]. These characteristics made biodiesel the most common alternative fuel to match the required criteria of a diesel fuel during the last decade. Normally, the use of biodiesel does not require any engine modifications with the exceptions of dated engine design constructions [6].

This paper evaluated the feasibility of using a local fruit seed, *Annona muricata* or Soursop/Guyabano, the seeds of which contain a potentially high percentage of oil, as one of the possible biodiesel feedstocks. Soursop seeds constitute 20% - 25% mass of the fruit and have the potential to produce about 33-34% of oil with nutritional and functional properties highly similar to those of edible oils [7]. A group of Filipinos have investigated the biodiesel yield of this feedstock using base-catalyzed transesterification with NaOH, KOH and Ca(OH)$_2$ as base catalysts and Ca(OH)$_2$ [8]. Most of the
researchers in this field ended up in producing a biodiesel that is comparative to diesel fuel with various techniques but there are still gaps in each study such as maximizing the biodiesel yield by using a different acid catalyst in the esterification process.

This particular study aimed at converting biodiesel by first subjecting the guyabano oil to acid esterification with, HCl as the catalyst, followed by alkali-based transesterification using separately the NaOH and KOH, as base catalysts, to determine the maximum biodiesel yield. The ultimate goal of this study is to establish the fuel characterization of the biodiesel, guyabano methyl ester (GME) with the base catalyst that provided the maximum yield in its pure form (B100) and in blended form (B5).

2. Materials and Methods

2.1. Materials and Reagents

The oil from *Annona muricata* (guyabano) seeds obtained from Tupi, South Cotabato were extracted using separately analytical grade (J.T.Baker) solvents, petroleum ether and n-hexane to determine the higher oil yield. Since the feedstock oil contains high levels of free fatty acid (FFA), it underwent a pre-treatment stage, acid-catalyzed esterification, to reduce the free fatty acid (FFA) content before doing the transesterification process. KOH catalyst was chosen for the actual experimental run because using NaOH produced a solid, chunky layer of glycerin during the dry run compared to KOH which produced a liquid glycerin layer. Anhydrous sodium sulfate (Na2SO4, Merck) was used to remove traces of water from the biodiesel.

2.2. Experimental Set-up

The collected dried seeds were ground until they were crushed into fine particles for better contact between the seeds and solvent. The ground seeds were collected, weighed, and transferred in a clear bottle. The solvent extraction method was applied for the extraction of oil. Petroleum ether and n-hexane were used as solvents to first determine which solvent will result to higher oil yield. The ground seeds were immersed in the solvent in 1:2 volume ratio for 3-5 days to allow longer contact time between the crushed seeds and solvent. The mixture was filtered using the vacuum filtration method. The residue was gathered and properly disposed while the filtrate was treated using the rotary evaporator to separate the oil from the solvent. The mixture was subjected to heating at around 60°C until all the solvent condensed. The temperature was based on the boiling point of n-hexane which is 68°C with the consideration of the vacuum pressure environment. The oil extract was stored in the refrigerator while the solvent was distilled for the following batch of oil extraction.

The FFA content of the guyabano oil was reduced by the addition of hydrochloric acid and methanol as a pre-treatment for the transesterification stage. For every volume of oil, concentrated HCl (1.0% concentration by volume in solution) and 10:1 methanol to oil molar ratio reacting at 65°C for 1.5 hours under constant stirring was done for the pre-treatment stage. The parameters, namely, amount of catalyst, alcohol to oil ratio, reaction time and temperature were obtained from a previous study by Su *et al* (2018) [9]. The mixture was then placed in a separatory funnel to allow the complete separation of the esterified oil from the water by-product for 3-5 days.

The KOH (1.0% concentration by weight in solution) was used as the base catalyst and was reacted with the esterified oil with 8:1 alcohol to oil molar ratio at 65°C for 30 minutes under constant stirring. The parameters for the transesterification process were obtained from previous studies by Kawentar and Budiman (2013) [10] and Su *et al* (2018) [9]. The resulting mixture was placed in a separatory funnel for 3-5 days until the clarity of the two components that indicated complete separation.

Purification was done by washing the biodiesel twice with warm distilled water to remove any excess glycerol, methanol, catalysts, and other impurities. After washing, the biodiesel was dried using anhydrous sodium sulfate (Na2SO4) to remove traces of water. One liter of each samples B100 (pure guyabano methyl ester) and B5 (5% pure guyabano methyl ester in commercial diesel) were brought to the Department of Energy Fuels Testing Laboratory for the determination of their respective fuel
characteristics. The samples were tested for acid number, cloud point, copper strip corrosion, flash point, free and total glycerin, kinematic viscosity, sulfated ash, sulfur content, and water content.

3. Results and Discussion

3.1. Oil Yield

Vacuum filtration was used to separate the oil bearing filtrate from the residue. The crude oil was obtained by subjecting the mixture to rotary evaporation. The average oil yield using petroleum ether and n-hexane was 17.09% and 18.92%, respectively. Therefore, n-hexane was the solvent used in extracting oil for the mass production of biodiesel because it has the highest yield and of low cost.

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\% \text{Yield} = \frac{\text{weight of guyabano oil}}{\text{weight of guyabano seeds}} \times 100
\]  

3.2. Biodiesel Yield

The extracted crude oil was subjected to a two-step catalytic process of esterification and transesterification. The calculated average crude biodiesel yield (w/w) using the parameters gathered from Kawentar and Budiman (2013) [10] and Su et al (2018) [9] was 94.76%. The average yield was lower compared to the optimal yield which was 97.02%. However, one experimental run had a biodiesel yield of 99.94% which was higher than the optimal yield from the previous study by Su et al (2018).

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\% \text{Yield} = \frac{\text{weight of GME produced}}{\text{weight of guyabano oil used}} \times 100
\]

3.3. Fuel Characterization

The physicochemical properties of samples pure GME (B100) and B5 were analyzed at the Department of Energy (DOE).

The acid number of the B100 and B5 samples were 0.21 and 0.02 mg KOH/g, respectively. The obtained acid number for B100 sample falls within the given specification of PNS of 0.50 mg KOH/g, which is lower than the maximum standard. It is also much lower compared to the acid number of Su et al (2018) which was 0.8 mg KOH/g. Thus, the FFA in the solution were efficiently reduced by the esterification process. There was no available acid number standard for B5 samples, but still it falls within the maximum acidity of B100 samples. Since the acid number of both samples are of low values, the fuels may not cause corrosion, poor cold flow properties, fuel system deposits, or filter plugging [11].

| Test/Analysis | Method | B100 PNS Results | B5 PNS Results |
|---------------|--------|-----------------|---------------|
| Acid number, mg KOH/g | ASTM D 664 | 0.50 max | 0.21 | 0.02 |
Cloud point is a measure of fuel’s cold weather characteristics, where in small and solid crystals are formed when the fuel cools. Based on the result, B100 passed the standard specification of PNS. This can be further lowered and enhanced, whereby as based from the previous study of Lee et al (1996), through another processing method called “Winterization”, saturated methyl esters are removed by cooling the fuel to cause crystallization and then separating the high melting components by filtration. B5 has no available cloud point standards. But if it will be compared to the B100 standards, it gave a result of 2°C, which is lower than the maximum allowable limit. The results suggest that both samples may be used at low operating temperatures. Samples B100 and B5 had a result of 1a in the copper strip corrosion test, which is below the limit set by the PNS. The results indicate that both samples have low levels of corrosion. Therefore, both fuels will not corrode the diesel engine. Flash point refers to the lowest temperature at which the vapor of the fuel will ignite. The flash point of biodiesel is higher because it is raw, unlike the commercial diesel which is pre-treated and has additives. Samples B100 and B5 have a flash point of 160°C and 92°C, respectively, which are above the minimum limits. The flash point of B100 is higher compared to the previous study by Su et al (2018) [9] which was 123°C. Having met the specifications, both fuel blends are safe for handling, storage, and transport. Free glycerin is a result of incomplete separation or washing during the biodiesel purification step. The free glycerin content for B100 was 0.02% which is the maximum limit. Despite passing the specifications set by the PNS, further washing should be done during the purification process. Total glycerin is the sum of the free glycerin and bound glycerin. The total glycerin content for B100 was reported at 0.14%.
which is also below the maximum specifications limit set by the PNS. From this result, it can be computed that the bound glycerin content of B100 is 0.12%. This means that there were glycerides that did not undergo complete conversion to methyl esters. The viscosities of both samples are within the PNS limits, with 4.5 and 3.5 mm²/sec, for B100 and B5, respectively. This shows that the samples have enough viscosities for efficient combustion and emissions as the fuel is injected. The sulfated ash in mass % for B100 & B5 are 0.005 & less than 0.001, respectively and are still within their corresponding PNS limits. It appeared that the ash formed from inorganic metallic compounds that were present in the biodiesel was negligible since the sulfated ash for the two biodiesel blends were of low value. Therefore, ash deposition and filter plugging will be avoided. Results have shown that the sulfur content in ppm for B100 and B5 are 5 and 28, respectively and are within their corresponding PNS limits. It can be observed that the sulfur content of the pure biodiesel is lower than the blended one which means that it is safer to use blended biodiesel with higher guyabano biodiesel percentage for it will produce small amount of SOx. On the other hand, the B5 shows that it will provide the best lubrication in engine for it contain the higher amount of sulfur. The sample B100 exceeds the limit set by the PNS with a value of 0.05, as it yielded 0.13 of moisture content. However, the impure sample (B5) adheres to the standard. Since biodiesel is hygroscopic in nature, the results were justified as the pure sample absorbed atmospheric moisture during the production and storage. The high water content of B100 can also be attributed to insufficient drying of the biodiesel. This then shows that aside from the addition of Anhydrous Sodium Sulfate, the final product should be subjected to heating to allow the complete moisture removal in the GME.

4. Conclusion

The *Annona muricata* seed oil was extracted using *n*-hexane as the best solvent with an average oil yield of 18.92%. The two-step process of biodiesel production resulted to an average biodiesel yield of 94.76%, with one trial run producing as high as 99.94%. This indicated that the esterification process using HCl, as catalyst, effectively reduced the acid value of the biodiesel while the KOH proved to be the better base-catalyst for the transesterification process. The fuel properties of B100, except for the water content, were within the specifications limits while all fuel properties of B5 passed the standards set by the PNS. The fuel characterization results of the biodiesel blends suggest that *Annona muricata* seed oil is a potential feedstock and can serve as an alternative for commercial biodiesel diesel fuel feedstock.

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