Metal Additives Influence in the Storing Stability Degradation of Biodiesel

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Abstract. Recently, biodiesel is used as an alternative fuel to reduce the air pollution. However, storage stability comes as it reduces the biodiesel properties after it been stored for a long period. This study was conducted to investigate the effect of storage duration on the stability degradation of biodiesel and the influence of metal additives nanoparticles blend to retard the deterioration of biodiesel. Biodiesel was synthesized using transesterification of waste cooking oil Gas Chromatography was performed to characterized the elements of biodiesel. Silver, manganese and iron nanoparticles were synthesized following sol-gel method. Nanoparticles were blended with biodiesel in concentration of 100 and 500 ppm using the ultrasonicator bath. Storage stability observation was performed according to ASTM4625 method which is 43 °C for one week. Gas Chromatography peaks shows similar components as standard biodiesel such as methyl palmitate, methyl stearate and methyl linoleate. Density and acid value were sis results proved that nanoparticles can help to retard the stability degradation of biodiesel.

1. Introduction

Biodiesel is a fuel derives from animal fat and vegetable oil and it is usually produced by pyrolysis, micro-emulsification, dilution and transesterification of triglycerides. Biodiesel can be run in a normal diesel engine without having modifications of engine parts [1], and it is a type of sustainable and environmental friendly fuel, nontoxic and does not contribute to the global warming as much as fossil fuel due to it releases less emission [2]. Therefore, recently the research on biodiesel has taken great attention.

However, biodiesel has its own stability degradation that can affect its effectiveness and functionality. Stability degradation is the changes to physical and chemical characteristics by interactions with environments [3]. Concerns have risen in term of stability degradation if the biodiesel is stored for a longer period. Compositional changes can occurs in biodiesel as the effect of increasing storage time which is possibly among the main concerns for the biodiesel storage stability. It is reported that after 6-months storing of biodiesel, it cannot be utilized as fuel because of losing stability, while as reported by Du Plessis et al. [4], after 90 days storing, the stability of biodiesel degrades due to the fix motions of acids, aldehydes, peroxides and the viscosity will increase. The biodiesel also experiences an increase in density when the storage time is long [5].

Improvements of the biodiesel can be achieved through the process of purifying during production, adding of additives and modifications of storage conditions. Addition of additives is becoming a field of knowledge nowadays. Nanoparticles such as silver can be used as a stabilizing agent in biological
and chemical sciences [6]. The high surface area of nanoparticles shows better properties over micron size. These nanoparticles have been studied for the stability in biodiesel. Some of the fuel properties such as flash point and viscosity have proven to be increased with the addition of nanoparticles [7].

2. Methodology

2.1. Materials and Equipments
Waste cooking oils (WCO) were used as the feedstock for biodiesel. Silver nitrate (AgNO) (Sigma Aldrich, ≥99.5%), iron sulphate (FeSO4) (Sigma Aldrich, ≥98.0%), manganese sulphate (MnSO4) (Sigma Aldrich, ≥98.0%) were used as the precursors for metal additives. Sodium hydroxide (NaOH) (Sigma Aldrich, ≥99.5%) was used as reduction agent, methanol (CH3OH) (Sigma Aldrich, ≥99.8%) and ethanol (C2H5OH) (Sigma Aldrich, ≥96.0%) were used in transesterification reaction, while phenolphthalein as indicator and potassium hydrogen (KOH) as catalyst.

Gas Chromatography (GC) was used in characterization of biodiesel elements and pycnometer for density measurement.

2.2. Synthesis of Biodiesel
Biodiesel was prepared following Shaila Siddiqua et al. [8]. Briefly, sodium hydroxide and methanol were mixed properly. Then, waste cooking oil was added to the alcohol-catalyst mixture and heated at 55 °C for three hours. The waste cooking oil was heated at 45 °C before added to the alcohol-catalyst mixture. Separation of biodiesel and glycerin was performed by gravity settling for twenty-four hours. The biodiesel was then washed and dry in an oven for ten minutes at 100 °C to remove residual water, glycerin and methanol. Biodiesel produced was then analysing by using GCMS.

2.3. Synthesis of Metal Additives Nanoparticles
Three types of nanoparticles, silver, manganese and iron were synthesized following sol-gel method by Ningsih et al. [9]. Silver nitrate was dissolved in methanol solution and stirred for 1 hour respectively. NaOH was then added dropwise to the mixtures and mix vigorously at room temperature for 2 hours. It was then dried 1 hour at 110 °C and further calcined at 450 °C for 1 hour. Silver nanoparticles were produced. Similar procedure was performed for manganese and iron nanoparticles synthesis.

2.4. Storage Stability Study
Two concentrations of nanoparticles were prepared for blending biodiesel which is 100 and 500 ppm to observe the effect of concentration on the properties of biodiesel. Nanoparticles were dispersed in 100 ml of biodiesel produced separately using ultrasonicator. Samples with nanoparticles blend was then be stored at 43 °C for one week. According to ASTM D4625 method, a week of 43 °C storage is considered to one month of 21 °C of actual underground storage. Analysis of the samples was carried out by using pycnometer and acid value analysis.

3. Results and Discussions

3.1. Biodiesel Characteristics
GCMS was used to quantify and identify individual components of Fatty Acid Methyl Ester (FAME) in the biodiesel sample. After transesterification process, biodiesel is prepared in sample vial and analyzed. Peak graph obtained is compared with the standard peak of biodiesel.
Figure 1 shows the graph of produced biodiesel. The peak obtained was compared with standard biodiesel peaks. Peaks at retention time 25.78, 27.99 and 28.31 min are similar to the standard of biodiesel peaks. Main components identified are methyl palmitate, methyl stearate and methyl linoleate. These components are the main components of methyl ester that make up the biodiesel. Different components appear at different time because of these three methyl esters have different boiling point. The higher the boiling point, the more polar its molecule. Thus, the longer the retention time for the components in the column. Besides, it is observed that the longer the methyl ester chain, the longer it takes to obtain the peak. From the figure, it is clear that the larger peak area shows the FAME components in biodiesel is dominant compared to other components exist.

3.2. Storage Stability Degradation

3.2.1. Density.
Density of biodiesel after a week was tested by using AccuPyc II 1340 type of pycnometer. EN3675 method and limit is used to quantify the density of the sample.

Figure 2 shows simplified data of density after storage duration of one week. It can be seen from the graph that the higher the storage time, the density will increase. However, the increasing of density does not exceed the standard limit of biodiesel which is from 860 – 900 kg/m³. A previous study stated that the density will increase as the storage time increase. However, the increasing is high to exceed the standard limit. Therefore, blending of biodiesel with nanoparticles help to maintain the density in the range of this limit. This is because nanoparticles themselves help to hold the particles and components of the biodiesel due to their small surface area. This result is similar with theory that indicated various significant of density from blending of nanoparticles at different concentration [10].
3.2.2. Acid Value.

Acid value is crucial to determine the quality of biodiesel. Acid value is obtained by using EN 14104 method of titration with potassium hydroxide (KOH) and phenolphthalein as a colour indicator. Data for acid value is shown in the following graph.

Acid value represents the acidity of biodiesel. Acidity happens when the fatty acid methyl ester components are broken down. Limit standard for biodiesel is 0.5. From figure 3, all blended samples show over limit of acid value. This means that nanoparticles in biodiesel cannot hold the fatty acid methyl ester components strong enough causing the components to break down and become fatty acid. However, it can be observed that higher concentration of nanoparticles in biodiesel have lower acid value compared to lower concentration due to its fatty acid chain. Acid value increase shows increasing of the acidity. Therefore, it is not suitable to be used as an alternative fuel. The methyl ester components may have strong bond if the concentration of nanoparticles is increased. Based on the theory, as the storage time increase, the acid value is increased thus increasing the stability degradation of biodiesel. Therefore, the result is in line with the theory stated and the blended nanoparticles with biodiesel can help to slow down its degradation.
4. Conclusions
The influence of metal additives in biodiesel storage stability has been studied. It is found that the nanoparticles can retard the storage stability of biodiesel. Increased concentration of nanoparticles in the biodiesel resulting in higher density of biodiesel. However, these values are not exceeding the standard limit of biodiesel. In contrary, acid value after the storage duration exceeds the standard limit, indicating the ineffectiveness of additives in the blending. Therefore, the use of such metal addives at study parameters needs to re-evaluate.

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