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TRANSESTERIFICATION BY POST-HEATING AND PRE-HEATING OF FEEDSTOCK WITH METHANOL AND CATALYST

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ABSTRACT

The conventional method of biodiesel production is by preheating the feedstock to the reaction temperature before adding a mixture of alcohol and catalyst. In this study, transesterification of *Jatrophacurcas*oil was carried out by mixing the feed with methanol and super base calcium oxide catalyst and the mixture heated to reaction temperature of 60ºC for 60 and 90 minutes. Other reactions were carried out by introducing the mixture of alcohol and the catalyst after preheating the feedstock to 60 ºC reaction temperature for 60 and 90 minutes respectively. The products obtained were analyzed with GC-MS and the ester contents were calculated. The viscosities and cetane numbers of each sample were estimated from pure individual esters. Ester content, viscosities and cetane numbers of post-heating were 100 %, 4.93 and 68.82 and 98.68 %, 4.52 and 61.15 respectively. While that of pre-heating were 99.99 %, 4.85 and 63.93 and 100 %, 4.85 and 71.76 respectively. With these results, it is a waste of energy to preheat the feedstock before introducing alcohol and catalyst.

Keywords: alcohol**,** catalyst**,** post-heating feedstock, pre-heating feedstock, transesterification.

INTRODUCTION

The progressive depletion of oil resources in combination with increasing energy consumption and the environmental degradation impact of fossil fuel use have caused a shift towards alternative sources of energy that are renewable, sustainable, efficient, cost-effective and generate reduced emissions[1]. Emissions of air contaminants such as CO_2, sulfur dioxide, nitrogen oxides, unburned hydrocarbons and aerosols of vehicles [2] are increasing due to increasing automobile and stationary engines that use hydrocarbon fuels. These emissions have resulted in intense air pollution, identified to be one of the reasons for climatic changes that result infrequent heavy rains, hurricanes and floods, threatening lives and properties [3].

It is reported by Pilot *et al*, [4] that most of the physical properties of biodiesel depend on the constituent fatty alkyl esters which include viscosity, cetane number and energy content. Biodiesel is made up of several components. The main components of biodiesel fuel depend on the raw materials used, and consequently, a wide range of esters can be present [5]. For example, palmitate ester is the major component of biodiesel made from palm oil and oleate ester in *Jatropha* oil as the triglycerides of palmitate and oleate esters are the major component of the two sources respectively.

In this investigation, post heating and preheating of *Jatrophacurcas* seed oil feedstock before transesterifications were carried out to compare their products in terms of esters yields, viscosity, cetane number, specific gravity, heating value, saponification value and iodine value. The transesterifications were carried out at 60ºC for 60 and 90 minutes with 20% and 1.5% methanol and super base calcium oxide catalyst respectively.

EXPERIMENTAL

The materials used for this study include *Jatrophacurcas* oil obtained from NARICT *Jatropha* farm, laboratory grade methanol, super base calcium oxide catalyst, sulphuric acid, propan-2-ol, phenolphthalein, 250 and 2000 ml conical flasks, 500 and 1000 ml separating funnels, filter paper, Gallykamp hot plate magnetic stirrer,n-hexane and GC-MS machine (QP2010 Plus Shimadzu/Japan).

The feedstock, *Jatrophacurcas* oil was purified by esterification to 0.5 mgKOH/g of Free Fatty Acid (FFA). This was done by adding 25 ml propan-2-ol to 2 g of *Jatrophacurcas* oil and three drops of phenolphthalein after thorough mixing. The mixture was well shaken and was titrated against 0.1 molar potassium hydroxide to pink. The FFA of the oil was calculated from the titre value. About 1000 g of the raw oil was heated to 60ºC on a GallyKamp hot plate magnetic stirrer and the mixture of 22.5 g methanol and 0.5g sulphuric acid was added and was maintained at this temperature for 60 min. The product was transferred into the flask and left for about an hour. The lower part of the product was tapped off from the flask and tested for FFA.

Post heating transesterifications were carried out as follows: 100 g of the esterified feedstock was mixed with 20 g of methanol and 1.5 g of super base calcium oxide catalyst in 250 ml conical flask. Another mixture of same constituents in another 250 ml conical flask was prepared. The two were transesterified at 60ºC for 60 and 90 minutes respectively.

Pre-heating transesterifications were carried out by heating 100 g oil to 60^{o}C in two conical flasks after which the mixture of 22.5 g and 0.5 g of methanol and sulphuric acid were added. One was transesterified for 60 min and the second for 90 min at 60°C. The products of the two processes were filtered. About 2 ml of each sample was diluted with n-hexane filled into samples bottles and inserted into the GC-MS for esters content analysis. The results were interpreted and their esters contents were calculated. Using the viscosities and cetane numbers of the pure sample obtained from Barabás and Todoruţ [6] and other literatures, the products viscosities, cetane numbers, saponification values, iodine values and energy values were estimated. Viscosity of methyl arachide (eicosanoate) was obtained from Fratas *et al.* [5]. Viscosity of methyl caprate (octanoate) was obtained from Gopinath *et al*. [7]. The cetane numbers of methyl laurate and methyl myristate were obtained from Bamgboye and Hansen [2]. Viscosities of ethyl sterate and ethyl arachidate were obtained from Fratas *et al.* [8]. Viscosity of methyl ricinoleate was obtained from Knothe and Steidly [9] and its cetane number from Knothe [10].

The correlation equation developed by Klopfenstei [7] was used to estimate the cetane number of some other fatty acid esters whose viscosities were not found in literature. The correlation is expressed as in Equation 1.

$$CN = 58.1 + 2.8(No\ of\ carbons/2) - 15.9 \times No\ of\ double\ bonds \quad (1)$$

The expression provided by Gopinath *et al* [7] as expressed in Equation 2 was used to estimate the iodine values of the samples.

$$IV = 100 \times \frac{253.82 \times db}{MW} \quad (2)$$

Where IV is iodine value, db is number of double bond and MW is molecular weight.

Saponification values of pure fatty acid esters were estimated with Equation 3 as expressed by Gopinath *et al.* [7].

$$SV = \frac{56106}{MW} \quad (3)$$

Where SV is the saponification of pure individual fatty acid esters and MW is the molecular weight.

Gopinath *et al.* [7] provided expression for specific gravity, SG, as in Equation 4 and it was used to estimate the specific gravity of the samples.

$$SG(15^{o}C) = 0.8475 + 0.0003IV + 0.00014SV \quad (4)$$

Where SG is the specific gravity of individual fatty acid ester, IV is the iodine value and SV the saponification of individual esters respectively.

Equation 5 [7] expresses the upper heating value of biodiesel

$$HV = 49.43 - (0.041SV + 0.015IV) \quad (5)$$

Where HV is high heating value, SV is saponification and IV is iodine value of individual esters.

RESULTS AND DISCUSSION

All the products met the satisfactory ester content requirement for use in compression ignition engine. The minimum esters content for compression ignition engine is 96.5% [11]. The post heating transesterified for 60 min yielded 100% methyl esters and same with the two preheating. The post heating for 90 min yielded 98.68% methyl esters as shown in Figure 1. With these results, preheating may be required when the temperature is low such that the oil freezes otherwise it might lead to extra production cost.

Viscosity is one of the most critical fuel properties, which is closely related to the molecular structure and length of the hydrocarbon chain [7]. It is one of the reasons why straight vegetable oil (SVO) is not used in diesel engine. Viscosities of the post heated products were 4.92 and 4.52 mm^2/s respectively and that of preheated products were 4.85 mm^2/s as depicted Fig. 2. Their viscosity fall within the range of standard set for biodiesel for use in compression ignition engines. The EN standard is 3.5-5.0 and ASTM is 1.6-6.0 [11].

The cetane number is the property which specifies the ignition quality of a diesel engine fuel [7]. It is the measure of the ignition delay of a diesel engine. Ignition delay is the period between the start of injection and the start of combustion [1]. The higher the cetane number, the shorter is the ignition delay time, and vice versa. The cetane number of biodiesel increases with increase in chain length but decreases with increase in the number of double bonds. All the four products have satisfactory cetane value. They met the minimum standard set by EN and ASTM of 51 and 47 as shown in Fig. 4. The preheating product for 90 min transesterification reaction time had the highest cetane number of 71.76 followed by post heating for 60 min with 68.82. This indicates

that preheating is not necessary except in cold weather when the oil freezes due to low temperature. The esters yields of the two products are equal at 100% for 60 min. The esters yield of post heating for 90 min was 98.74% which is the lowest, yet, still higher than the minimum ester content for biodiesel of 96.5% [11].

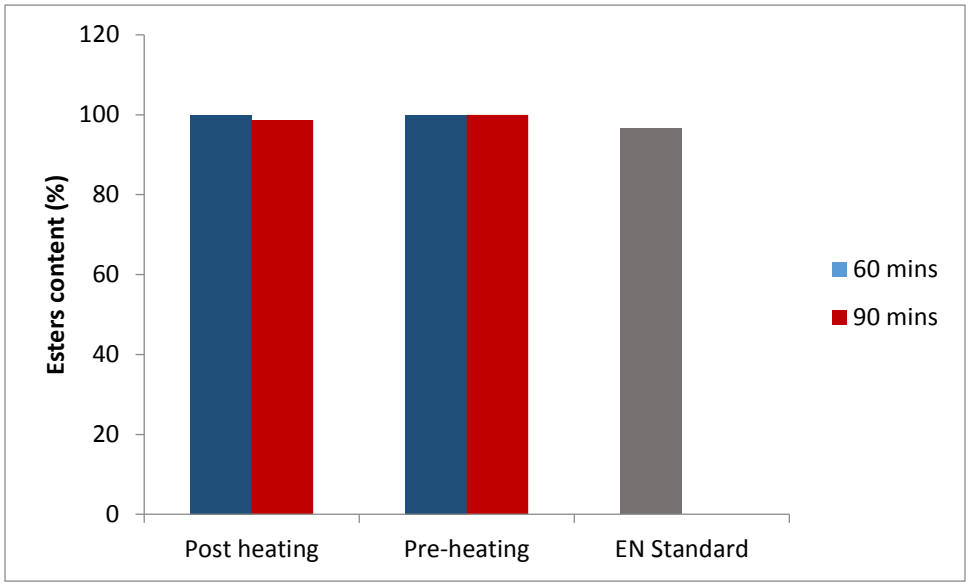

Fig. 1: Esters contents of sample compare with Standard

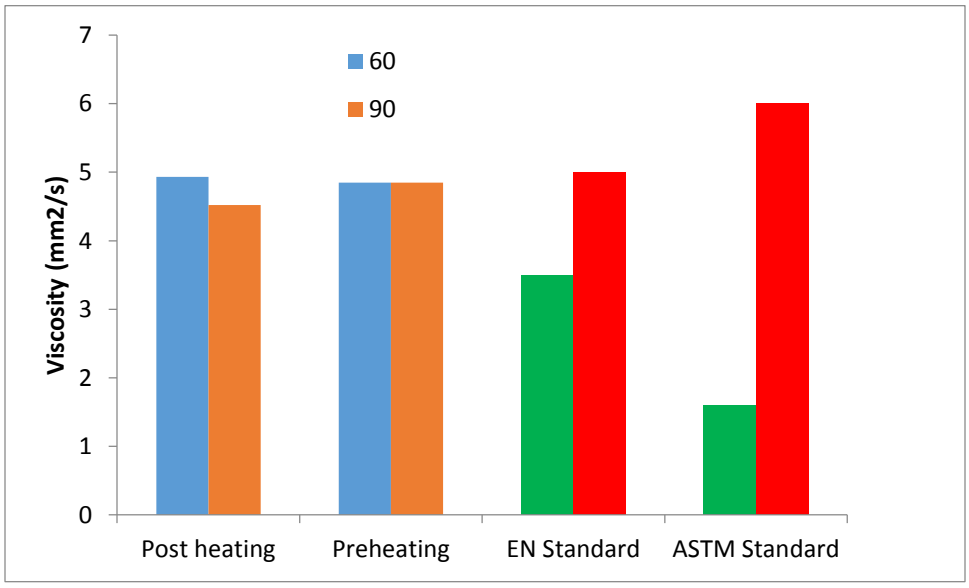

Fig.2: Viscosity of samples and standards

The physical properties of fatty acid alkyl esters in biodiesel are of great importance as they affect the engines in which the fuel is used. The fuel density influences the amount of fuel that

may enter the injection systems, pumps, and injectors [8]. Except the post heated product for 60 min whose specific gravity is 0.862, others have specific gravity below 0.86 which is the maximum set standard by EN. Even with this value 0.862, it is still acceptable for diesel engine as the difference is insignificant. They all have specific gravity below ASTM maximum standard of 0.9 [11] as shown in Fig. 4.

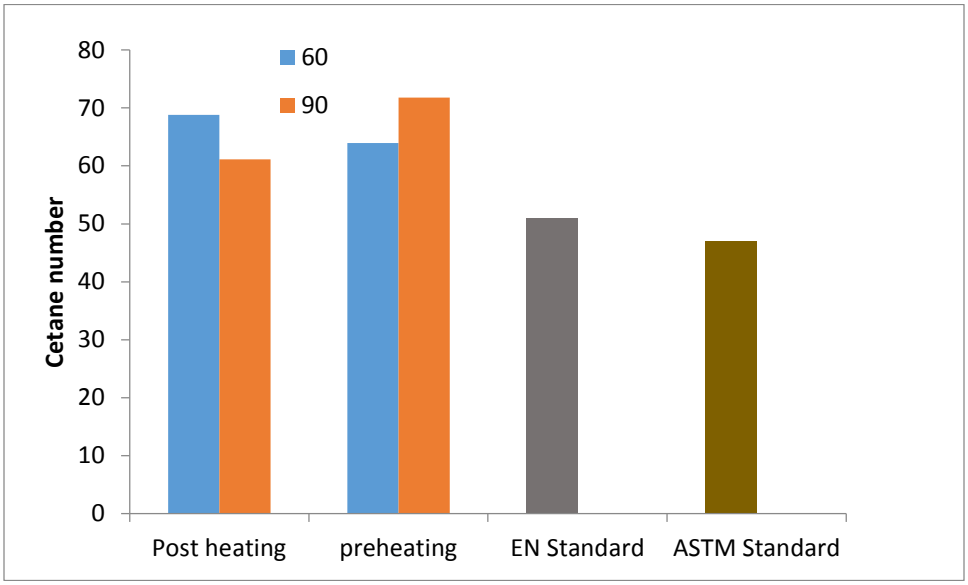

Fig. 3: Cetane numbers of sample with that of Standards

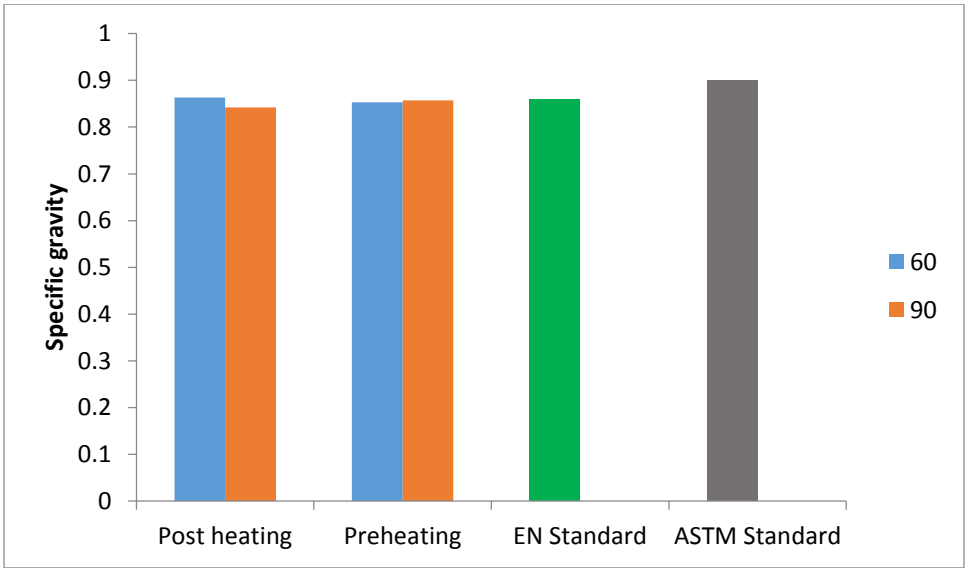

Fig. 4: Specific gravity of samples and Standards

All the products have iodine value less than the EN and ASTM minimum standards of 130 and 120 [11] respectively as shown in Fig. 5 indicating that they have low quantity of unsaturated

esters and hence, they have long shelf life. Equation 2 indicates that biodiesel without unsaturated esters have zero iodine value. Such biodiesel have long shelf life but its viscosity may be too high for compression ignition engine. The presence of unsaturated esters reduces the viscosity as they have lower viscosity than saturated one [7].

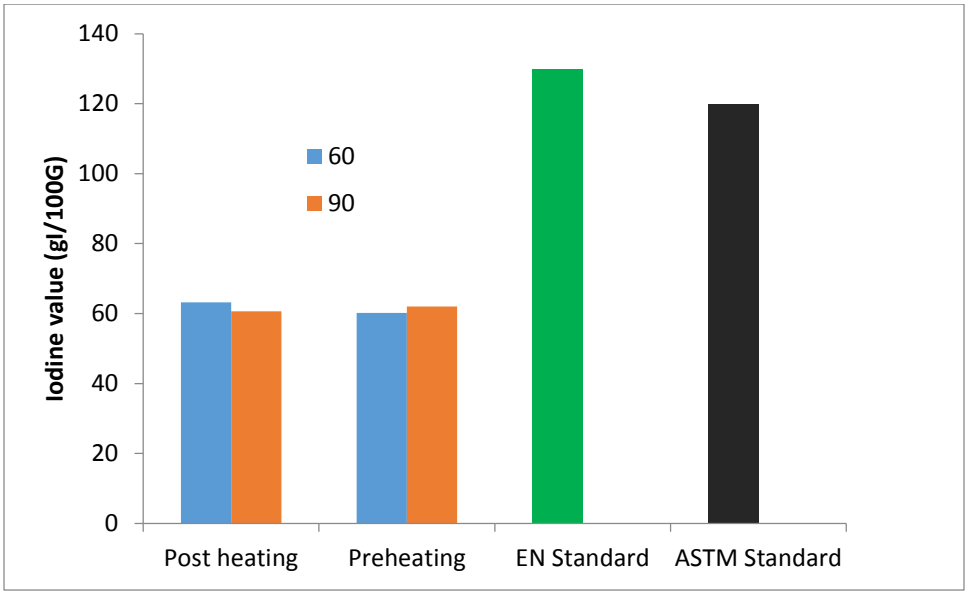

Fig. 5: Iodine value of samples and Standards

The heat of combustion or heating value (or energy content) of a fuel is defined as the number of heat units (kJ or MJ) liberated by the complete combustion of 1 kg or 1 L of fuel [7]. All the products have heating value greater that the EN minimum set standard for biodiesel 37.5 MJ/kg [11]. The heating value of post heated for 60 and 90 min were 48.16 and 47.77 MJ/kg respectively while those of preheated products for 60 and 90 min were 48.44 and 48.19 MJ/kg respectively.

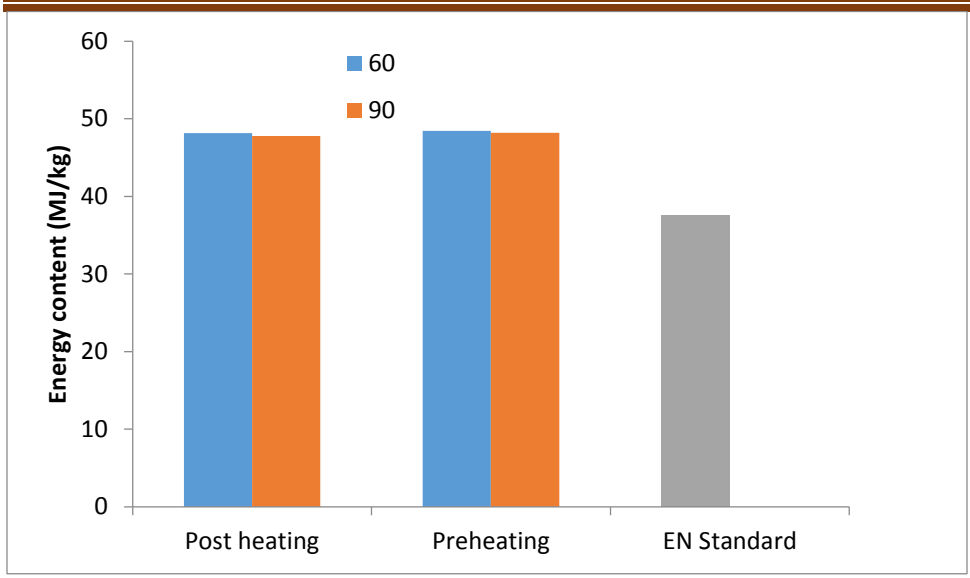

Fig. 6: Heating value (Energy content) of samples and Standard

However, not all the fatty acids of the post heated 90 min transesterification were converted to fatty acid alkyl esters. About 1.26% was not converted to fatty acid ester; hence the estimated properties of its biodiesel may not be as accurate as those of other three. These estimated properties are more accurate for complete (100%) conversion of the feedstock to fatty acid esters.

CONCLUSION

The physical properties of the biodiesel samples produced by post heating and preheating of the feedstock were closely equal in value. Their ester contents were 100% except one that is 98.74% which is still higher than the minimum set standard of 96.5% [11]. Their viscosity, cetane number, specific gravity, energy value and iodine value were all within the range for use in compression ignition engines. If the weather condition is not too cold to freeze the oil feedstock during transesterification, it is not required to preheat as the exercise can increase the production cost.

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