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Research Article

The Effects of Transesterification and Blending on the Fatty Acid Profiles of Vegetable Oils

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Abstract: Vegetable oils are basically of fatty acids and the amount present can affect the properties of the resulting biodiesel. The aim of this study is to investigate how the transesterification affects the fatty acid profile of the resulting biodiesel produced. Seven vegetable oil types were selected for the study. They were transesterified and blended with diesel and the fatty acid profiles determined by method of gas chromatography. The results obtained shows that fatty acid profile of vegetable oils changes slightly after transesterification and mostly constant with blending.
Keywords: Vegetable oils, fatty acids, transesterification, blending, biodiesel, chromatography.

INTRODUCTION

Vegetable oils are made up of triglycerides, which consist of three fatty acid chains that are attached to one glycerol as shown in Fig.1. They generally have high viscosity which makes them unsuitable for use in diesel engines and needs to be transesterified to methyl ester (biodiesel) before use. Transesterification is the process of reacting vegetable oils with an alkaline in the presence of a catalyst to produce an ester of the vegetable oil. It has also been defined as the displacement of ester by another ester [1]. During transesterification, the fatty acids on the triglyceride are broken and attached to the alkaline, in this case methanol molecules to form the methyl ester or biodiesel while the hydroxyl group from the catalyst stabilizes the glycerol as shown in Fig-2 [2].

Transesterification involves structural rearrangement of molecules and lead to reduction in the molecular weight, viscosity, and most exhaust emissions, while also increasing the volatility, cetane number but maintains heating value. It also improves biodegradability; confer inherent lubricity, gives higher flash point [2-7]. Biodiesel is the mono alkyl ester of vegetable oil or animal fats [8, 9]. It is chemically simple, consisting of between nine and twelve fatty acid esters in the mixture.

The chemical composition and properties of biodiesel usually depends on the length and degree of saturation or unsaturation of the fatty acid alkyl chains and the various structures of fatty acids impart different effects on physical properties on biodiesel. For example, as the amount of unsaturation increases, the relative rate of oxidation will also increases[5]. Fatty acid composition and chain length affect properties such as cloud and pour points, cetane number, kinematic viscosity, oxidation, and NO_x emissions. Thus the final properties of biodiesel always depend on the properties of the component free fatty acids present [10], and this allows biodiesel to be formulated and selected to have predetermined properties. For example, saturated acids exhibit higher freezing points than the unsaturated acids.

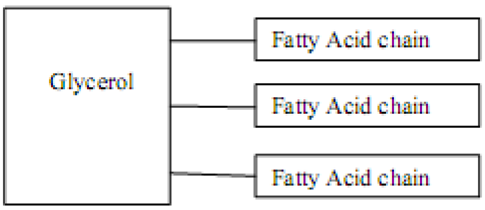

Fig-1: Structure of Vegetable oil

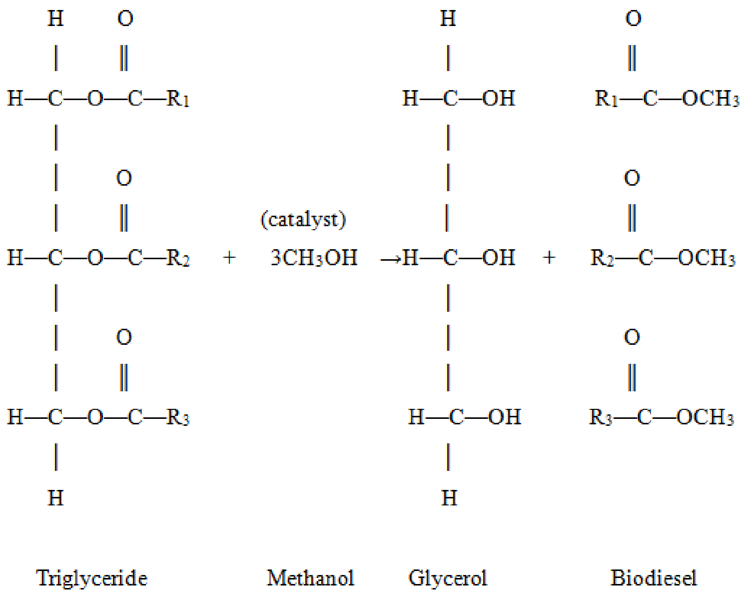

Fig-2: Transesterification Process

The properties of the various individual fatty acid esters that made up the biodiesel determine the overall fuel properties of the biodiesel fuel. The main properties of the various fatty esters are determined by the structural features of the fatty acid and the alcohol moieties present in the esters. Knothe [8] reported that structural features that influence the physical and fuel properties of a fatty ester molecules are chain length, degree of saturation, and branching of the chain. The important fuel properties that are influenced by the fatty acid profile are cetane number, exhaust emissions, heating value, cloud point, pour point, oxidative stability, viscosity and lubricity. It has also been reported that methyl esters of saturated acids have a higher cloud point, cetane number and better stability [11].

Many properties vary with chain length, number of bonds and degree of unsaturation [12]. It was reported that methyl estersof saturated acids have higher cloud point, cetane number and better stability than saturated acids [8].

Fatty Acids Structures

Fatty acids consists of carbon, hydrogen and oxygen atoms that are arranged as a carbon chain skeleton with a carboxyl group (-COOH) at right hand end as follows;

$CH_3(CH_2)_2COOH$

The double bond holds the carbon atoms tightly thereby preventing the rotation of the carbon atoms along the bond axis and no rearrangement of atoms can be done unless the bonds are broken. The bonds can be broken thermally or by transesterification via a catalyst. Thermal cracking occurs between 300 and 350 °C and the fatty acids product can be transesterified under supercritical conditions while the alkyl ester content will be decreased. During transesterification, the triglycerides are decomposed to fatty acids and some gaseous products within the temperature range of 350 - 450 °C [13-16].

Transesterification Mechanism

Transesterification is the process of converting vegetable oil to esters and uses alcohol in the presence of a catalyst to chemically crack the molecules of the vegetable oil during which the glycerol from the triglycerides are removed and replaced with radicals from the alcohol used. The reaction transforms the complex branched molecular structure of vegetable oil into a smaller straight chain molecular structure, identical to but much longer than that of diesel fuel [17]. The small hydrocarbon molecules of the cracking products impart improvement properties on the biodiesel, such as viscosity, density and cold flow properties.

Transesterification can use either a base or an acid as catalyst. For acid catalyst, the mechanism is that the acid active sites make contact with the triglyceride molecules and protonate the carboxyl oxygen in the molecular structure so that the electrophilicity of the adjoining carbon atoms can be enhanced, thereby easing acceptance of the nucleophilic alcohol attack [18].

Vegetable oil have different degrees of unsaturation and saturation, during transesterification the fatty acids detached from the glycerol would be attached to radicals from the methanol reagent and the vacant link created would be occupied by oxygen molecules thus reducing the degree of unsaturation. If for example the oleic fatty acid has its vacant site occupied, it would become saturated and turn to stearic acid. Similarly the linolenic acid can have one vacant link occupied and would turn to linoleic acid.

Enzymatic transesterification has the ability to change the fatty acid composition of vegetable oils and immobilized *Bhizomucarmeiehei* lipase has been reported to replace palmitic acid in palm oil with stearic acid. Pabai *et al*., [19] described a lipase catalyzed interesterification of butter fat that resulted in a considerable decrease in the long chain saturated fatty acids and a corresponding increase in C18:0 and C18:1 acids at position 2 of the selected triacylglycerol. Enzymes transesterification act on the ester bonds of carboxylic acids and results in the conversion of triglyceride, diglyceride, monoglyceride, free fatty acid to fatty acid alkylic esters [20-24].

During the transesterification of algae, Wagenen, *et al*., [25] reported a sharp increase in total fatty acid containing elevated palmitic and palmitoleic during exponential growth at high light intensity but with low light intensity, an increase in the relative abundance of unsaturated fatty acid was noted. They also noted that fatty acid increased inversely with temperature.

The aim of this study therefore is to determine the changes that occur in the different proportions of the fatty acids of vegetable oils after transesterification. The study will allow for more precise prediction of fatty acid characteristic and yield.

MATERIALS AND METHODS

Seven vegetable oil types with a wide range of properties and degree of saturation were selected as follows: Rice bran oil (RBO), cashew nut oil (CNO), castor seed oil (CSO), egunsi melon seed oil (EMO), ground nut oil (GNO), pumpkin nut oil (PNO) and rubber seed oil (RNO). CNO, CSO and RSO are inedible while others are edible to some degree.

The oils were transesterified using methanol as reagent at a molar ratio of 4:1 and 1% (wt.) sodium hydroxide as catalyst. The mixture was stirred at300 rev/min and a temperature of 60^{o}C for 3 hours. It was allowed to settle for five hours so that the biodiesel and glycerol could separate. The biodiesel was separated in a separatory funnel and washed with distilled water and dried. The fatty acid profile of the oil, biodiesel, 10% and 20% blends with diesel were determined using HP 6890 Gas Chromatography analyzer powered by HP Chem Station Rev A 09.11 [1206] equipped with a flame Ionization Detector (FID). The procedure was as reported by Bello and Otu [26]. Nitrogen used as the carrier gas and the initial oven temperature of 60^{o}C.

RESULTS AND DISCUSSION

Changes in the fatty acid profiles are shown in Figs-3 to 7. Gabroski and McCormick [27] reported that since different vegetable oils and animal fats may contain different types of fatty acids, the fuel related biodiesel properties are generally affected by the choice of raw materials, they also found that the cetane index of biodiesel produced from soybean oil ranges between 45.7 and 56.4, and that the cetane index of mixed marine fish-oil biodiesel of 50.9 was larger than the cetane index of the commercial biodiesel from waste cooking oil, which was 48.1. He attributed this to the fact that marine fish-oil biodiesel contained as high as 37.06 wt.% saturated fatty acids, whereas the commercial biodiesel from waste cooking oil contained only 19.77 wt.% saturated fatty acids they hence concluded that the cetane index of the biodiesel increased with the proportion of saturated fatty acids.

Palmitic acid C16:0 is saturated. No significant changes were noted in the values except CNO that reduced slightly. This is shown in Fig. 3.

Stearic acid C18:0 is a saturated acid. The trend for the vegetable oils investigated as can be seen in Fig. 4; new acids are formed after transesterification. The effect of blending with diesel fuel is just detectable and almost linear.

Fig. 5 shows that oleic acid is monounsaturated and decreased slightly for all the vegetable oils investigated. The decrease is most pronounced for castor oil for which ricinoleic acid constituted 89% of the total mass.

Linoleic acid is polyunsaturated C18:2. Oil with low linoleic acid tends to increase total mass while mass of between 20 and 40% tend to decrease in total mass. It was however observed as shown in Fig. 6 that, transesterification and blending remains constant for oil having a mass of above 40%.

Linolenic acid C18:3 is polyunsaturated. Low values tend to remain constant while values above 15% tend to decrease in total value as shown on Fig-7.

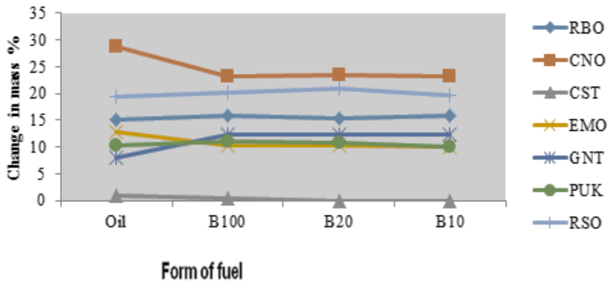

Fig-3: Changes in Palmitic acid

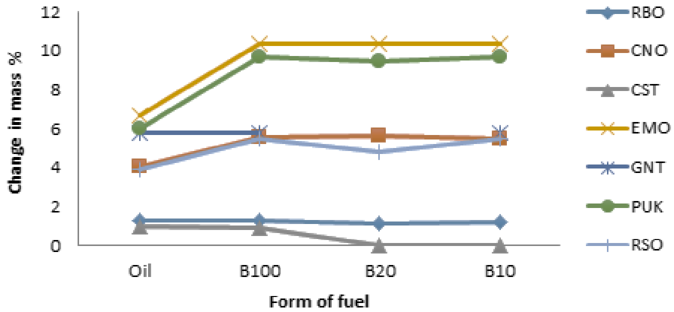

Fig-4: Changes in stearic acid

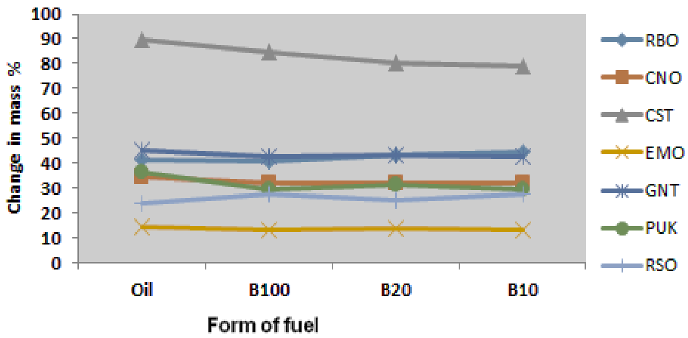

Fig-5: Changes in oleic acid

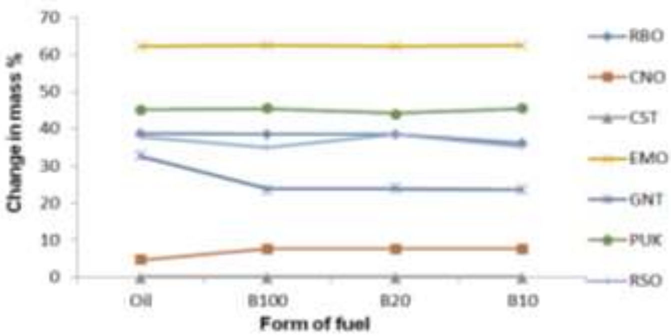

Fig-6: Changes in linoleic acid

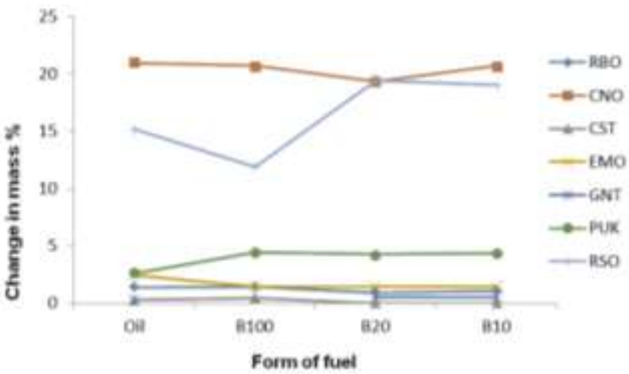

Fig-7: Changes in linolenic acid

CONCLUSION

Transesterification can alter the fatty acid composition of vegetable oils. Blending has very little effect on the fatty acid composition.

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