

INVESTIGATIONS ON EFFECTS OF ALCOHOL TYPES ON ESTERIFICATION OF PYROLYSIS USING GREEN CO-SOLVENTS: PRELIMINARY RESULTS

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ABSTRACT: Esterification of carboxylic acids present in pyrolysis oil is one of the technologies used in upgrading the fuel properties of the oil. This is affected by the nature of alcohol used as solvent, activity of the catalyst used or both. In this preliminary research, supercritical esterification of waste tyre pyrolysis oil was used as an upgrading technique for improving fuel properties of this oil. In addition, green solvents are introduced as both co-solvents and catalysts in the process. The effects of alcohol type (methanol and ethanol) as co-solvents in green solvents had been investigated. Results indicated that density and viscosity of deep eutectic solvents (DESs), reduced with increasing temperature with viscosity been affected much especially beyond 60°C. Methanol-DESs co-solvents systems reduced total acid number (TAN) with lowest value of 6.29% while ethanol-DESs counterparts varied. Density was not affected by alcohol type or co-solvent system but its volume. Although calorific values of the final products were improved significantly up to 37.46 (MJ/kg), they were still below the standard limit generally. Carbon residue values of all samples were higher than the maximum limit of ASTM D6751-08. Finally, it was found that, although supercritical esterification of pyrolysis improved some of the fuel properties, however, it could not improve some important properties of the oil.

KEYWORDS: Esterification, Co-solvents, Fuel properties, FAMES

1. INTRODUCTION

Biodiesel from vegetable oils is increasingly becoming a sustainable future fuel, in spite of its numerous drawbacks such as low heating value and poor oxidation stability. In addition, policy and political issues are also associated with this rising renewable and energy which include large land requirement, waste water generation during processing and low marketability of the fuels compared to fossil diesel. On the other side, in many rural areas in Africa and other developing countries, biodiesel development programs have become major poverty alleviation programs providing income to poor rural populace and ensuring energy security to them as well [1]. Feedstock availability has posed a big question on sustainability of biodiesel, especially, during large scale biodiesel production. In addressing this challenge, other sources of biomass materials such as algae oil, sludge waste, waste cooking oils and pyrolysis oils are also been explored to compliment vegetable oils [2–5].

However, pyrolysis oil has received little attention as potential feedstock for biodiesel production due to number of problems associated with its quality. High acid content,

low calorific value and high viscosity are some of the challenges that have to be overcome for pyrolysis oil to see the light of the day as feedstock for biodiesel production. As such pretreatment is required to upgrade this oil before it can be used in biodiesel production. Esterification is one of such upgrading techniques, owing to its high acid content notable, formic and acetic acids. Other upgrading technologies reported in the literature include hydrotreatment, molecular distillation and catalytic upgrading [6–7].

Organic acids present in pyrolysis oil can undergo esterification reaction in the presence of catalyst. During this reaction, carboxylic acids component of the oil are converted into esters with improved heating value, reduces its acidity and improve lots of fuel properties thereby making it suitable for application on diesel engines.

Methanol and ethanol are the popular primary alcohols used as solvents in esterification of organic acids in oils into corresponding Fatty Acids Methyl Esters (FAMES). Higher alcohols such as propanol, butanol and other branch-chained alcohols have also been used as solvents in transesterification of different vegetable oils into

FAMES [8]. The equation for this reaction proposed that three moles of alcohol are required to react with a mole the oil to convert it into three moles of FAMES and glycerol as products. Figure 1 shows schematic reaction stoichiometry as shown in the following:

The reactivity of solvent (methanol, ethanol or other primary alcohols) can be improved by when such solvents are reacted under supercritical conditions. At the supercritical temperature and pressure of fluids, reactivity is at its highest because the fluids exhibit high dielectric constant and lowest density [9]. Supercritical (trans)esterification of vegetable oils into corresponding FAMES is becoming increasingly attractive to both researchers and entrepreneurs. Using different solvents mixture during supercritical esterification was reported to increase the yield, reduce reaction time and lower temperature. This is because, mass transfer resistance which is the major barrier that has to be overcome between oil and reacting solvent is reduced with the introduction of co-solvents system.

Ionic liquids are new generation solvents that are becoming increasingly popular as laboratory and industrial solvents. However, (trans)esterification of vegetable oils using ionic liquids has not been widely investigated. In spite of their unique solvating and dissolution properties, room temperature ionic liquids (RTIL) otherwise referred to as DESs have not been explore with regards to esterification.

In this research work, supercritical esterification of waste tyre pyrolysis oil using RTIL had been conducted based on choline chloride and three urea, PTSA and glycerol as hydrogen bond donors to for DES 1, 2 and 3, respectively. In addition, characterization of viscosity and density of the DESs was conducted to help in understanding their temperature behaviours. Afterwards,

optimization of TAN reduction was evaluated as the progress of reaction. Finally, the effects of increasing DESs co-solvents was evaluated with methanol and ethanol on fuel properties of FAMES produced.

2. METHODOLOGY

All chemicals used in this research were analytical grade except otherwise stated. DESs were prepared according to the procedure reported by Hayyan *et al.* [10]. The supercritical reactor used in this research is a 100 ml capacity auto-cleave reactor. Figure 2 presents schematic diagram of the supercritical reactor unit used showing its various components. Same reactor was used in producing DESs under nitrogen atmosphere at 120°C, 750 rpm and varying hydrogen bond donor ratio in a fixed molar weight equivalent of choline chloride. Optimization of mixing ratio was conducted earlier; as such only optimal mixing ratios of the hydrogen bond donors are reported in this work. The optimal ChCl-Urea was 1:2, that of ChCl-PTSA was 1:4 and ChCl-Glycerol was 1:4 as well. In conducting supercritical esterification, both methanol and ethanol were mixed with different volumes of DES and used as co-solvents in a non-catalytic supercritical esterification of the oil. Other reaction conditions for esterification include, solvent to oil molar ratio of 1:40, and fixed reaction time of 20 minutes. However, depending on the experiment, reaction temperature was set to correspond to supercritical temperature and pressure of either methanol or ethanol as the case may be. Thereafter, separated of FAMES were tested for fuel properties according to standard methods of analyses using equipment and procedure reported by Atabani [11].

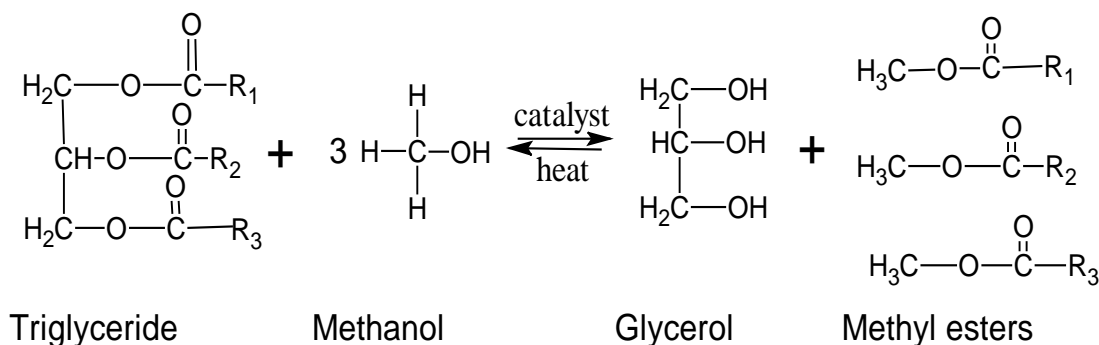


Fig. 1. Schematic diagram of transesterification reaction

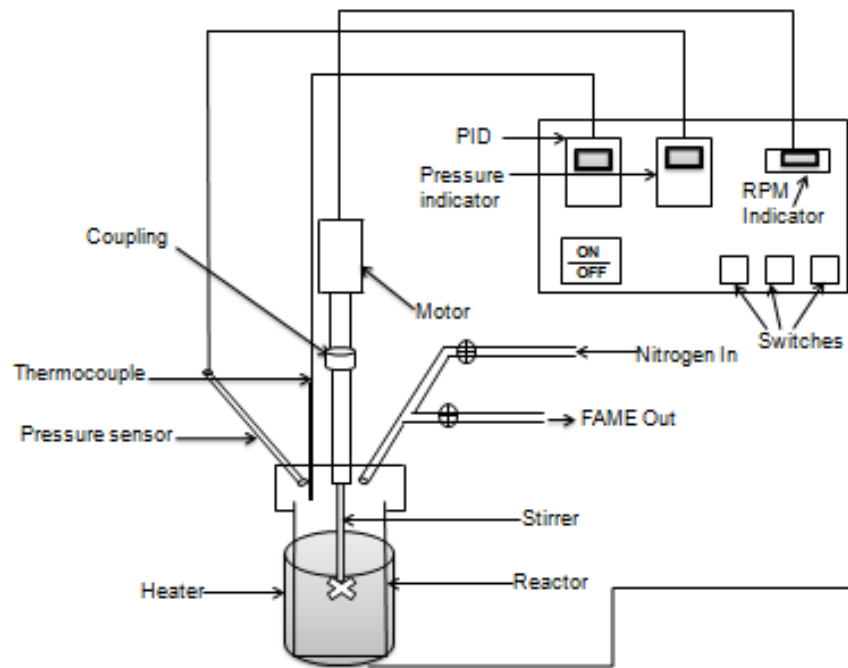


Fig. 2. Schematic diagram of supercritical reactor unit used in this study

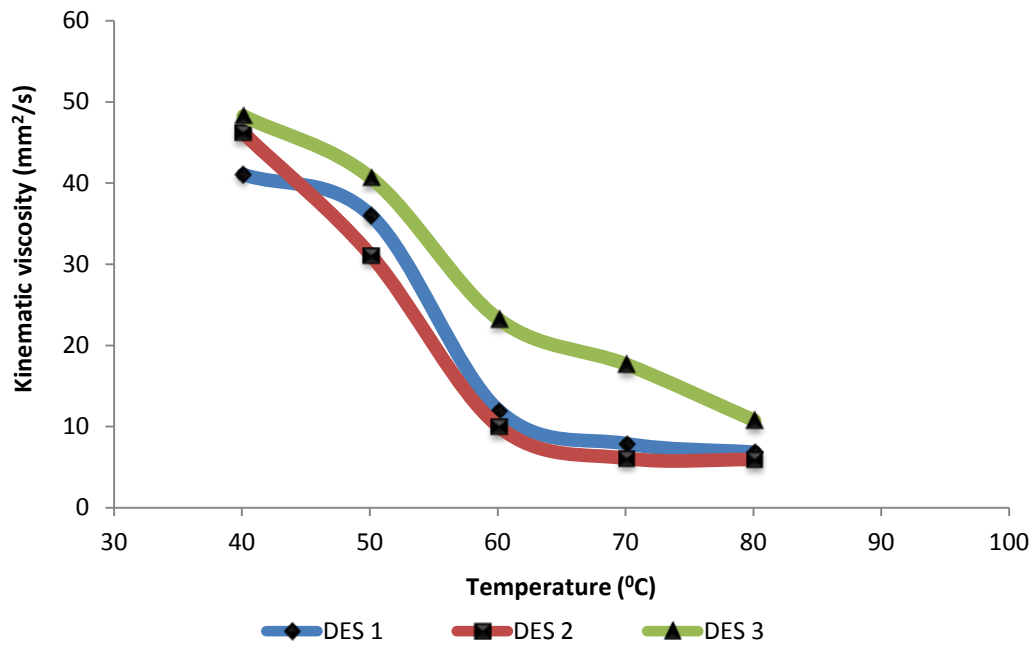


Fig. 3. Effect of increasing temperature on kinematic viscosity of DES

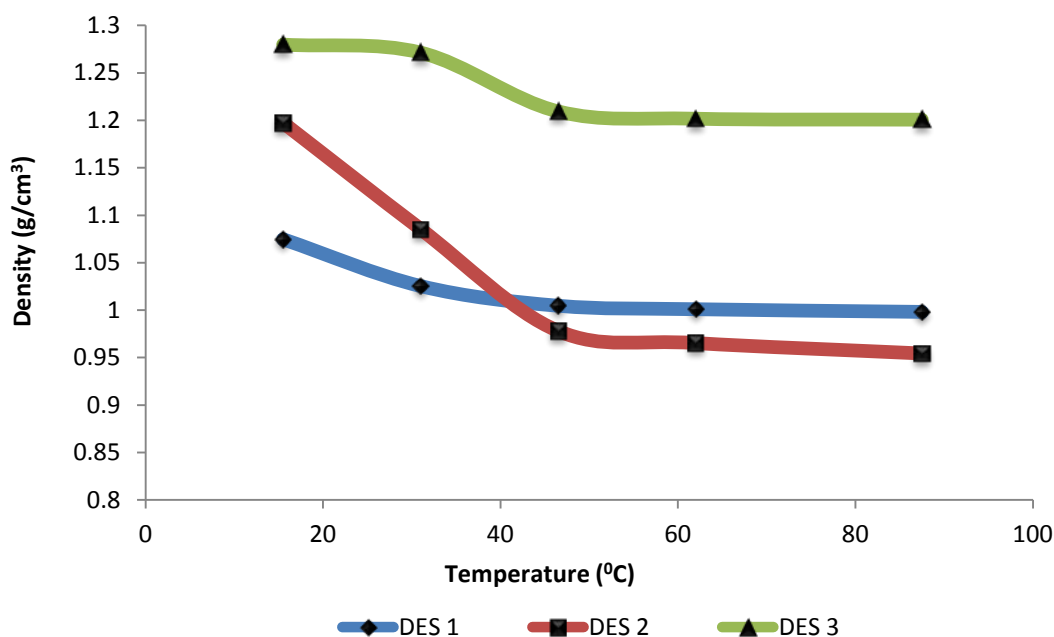


Fig. 4. Influence of temperature on density of DES investigated

3. RESULTS

3.1 Influence of temperature on properties of dess

This section discusses the result of supercritical esterification of waste tyre pyrolysis oil using methanol-DES or ethanol-DES as co-solvents as the case may be. Initially, the temperature dependent properties of DES were tested so that their behaviour during high temperature reactions can be understood. Figure 3 presents the effect of increasing temperature on kinematic viscosity of DESs.

Viscosity decreases with increasing temperature. Notable viscosity decrease was observed beyond 50°C in all DESs samples prepared. This is because the temperature range used in preparing DES is within 60°C to 80°C as such; DES becomes more liquid due to increasing free ionic composition losing its hydrogen bonding. Generally, the trend in decreasing viscosity with increasing temperature of DES revealed that the order is DES 1 > DES 2 > DES 3.

Similar to the viscosity, the density of all DESs decreases with increasing temperature. However, unlike in viscosity, where was no much difference in the density especially that of DES 1 and 3, Figure 4 shows the influence of temperature on density of DES investigated. In DES 2, density was decreased markedly with

increasing temperature. The reason for the behaviour of DES 2 is unconnected to the high dissociation constant of PTSA in ChCl. In addition, density marginally increases with increasing temperature above 50°C in most cases assuming that lowest density could have been attained.

3.2 Effects o alcohol tyoe on fuel properties of esterified pyrolysis oil

3.2.1 Effect on total acid number Figure 5 presents the effect of alcohol type on supercritical TAN reduction of WTPO using DESs co-solvents, showing how TAN reduction was significantly affected by the type of alcohol as well as catalytic activity of DESs. Methanol presents the best TAN reduction probably due to its excellent miscibility with all DESs herein studied. Consequently, effective catalytic activities of all DESs were obvious in methanol, which results in significant TAN reduction. The optimal reduction was as low as 5% when 50% (v/v) of DES 2 was used as co-solvent with methanol. Authors reported that methanol was more polar solvent than ethanol [11–12], although we expected ethanol would have better miscibility with the oil due to improved phase equilibrium that could be easily established.

In all cases, DES 2 which was made up of ChCl-PTSA shows highest TAN reduction compared to the other DESs formed with glycerol or urea as hydrogen bond donors.

DES formed using glycerol showed the highest TAN content either in methanol or ethanol. However, the behaviour of DESs under supercritical conditions could not be established in this work, it is expected that our future works will exploring this area. It is concluded that DES initial addition of DES greatly increases the catalytic activity, while further addition beyond 20% (v/v) did not reduces TAN further. It was believed that equilibrium could have been attained. Ezeanyanaso *et al.* [13] reported an increase in acid number of three biodiesels from neem and rubber seed oils. It was discovered that the increase in acid number was higher after 8 months of storage as the rate of deterioration of the biodiesels became faster after that period.

3.2.2 Effect on kinematic viscosity One of the reasons why pyrolysis cannot be directly used in diesel engines is associated with its high viscosity. Figure 6 presents the effect of alcohol type on supercritical esterification of WTPO on kinematic viscosity. We plotted the values of viscosity of esterified pyrolysis oil in-between the maximum and minimum values of viscosity of biodiesel as stated in ASTM D6751-08. It could be seen that esterification using all DES except when ethanol was used with DES 3 as co-solvent reduces

viscosity of pyrolysis oil. However, the effect of alcohol chain length could increase the miscibility of the final products which separation difficult. This increases the viscosity of the FAMES. In general, all samples esterified using DESs prepared were within the limit of ASTM except when ethanol-DES 3 co-solvent was used. DES 2 was still the best co-solvent for the esterification as expected from its properties stated earlier.

3.2.3 Effect on density Density is an important fuel property of any potential fuel substance. The density of vegetable oils and biodiesels is the mass of unit fuels per volume required. Change in the density of vegetable oils and methyl esters are related to the increase in the acid number of the oils or biodiesels, this is also related to the change in the viscosity of the vegetable oils. In a simpler term, if the acid number increases the viscosity also increases and the density increase as well. Figure 7 presents the effect of alcohol type on supercritical esterification of WTPO on density, showing the changes in density of FAMES. When we plotted against ASTM D6751-08, it was evident that there was improvement in density of FAMES.

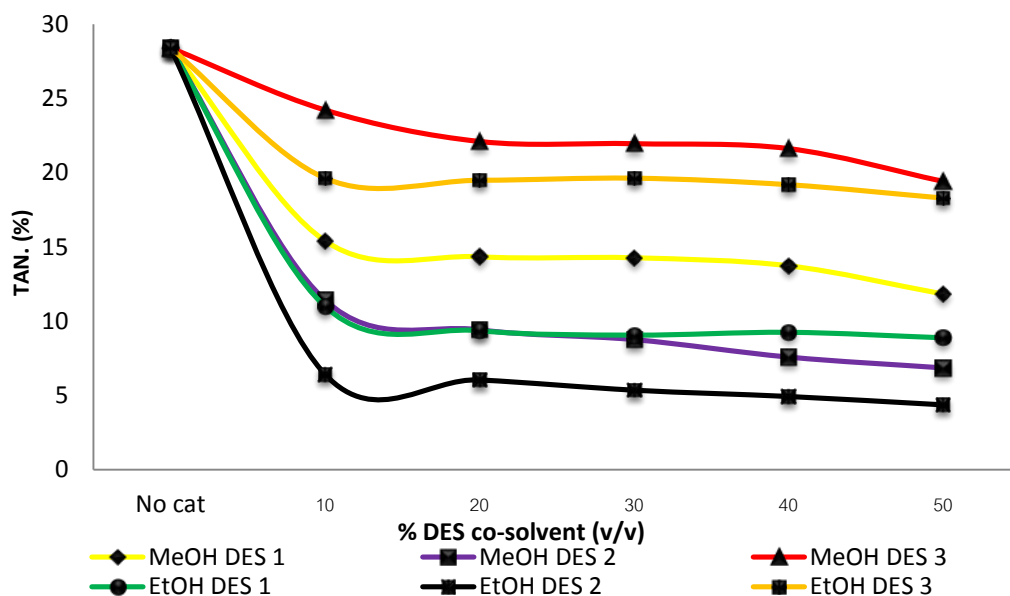


Fig. 5. Effect of alcohol type on supercritical TAN reduction of WTPO using DESs co-solvents

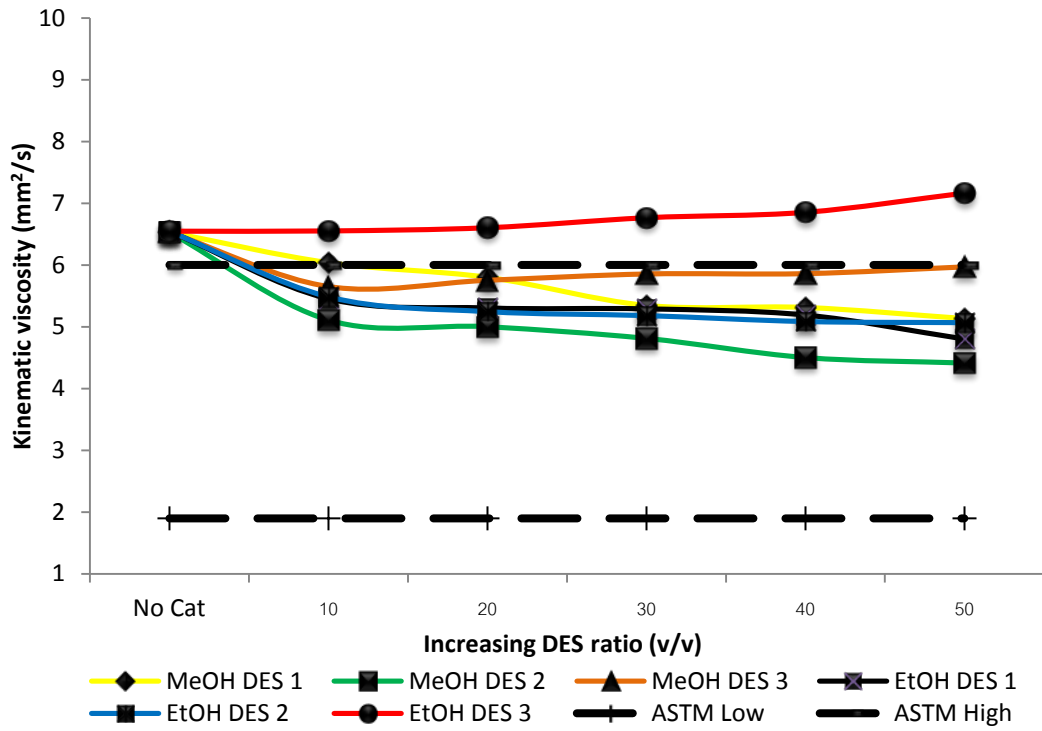


Fig. 6. Effect of alcohol type on supercritical esterification of WTPO on kinematic viscosity

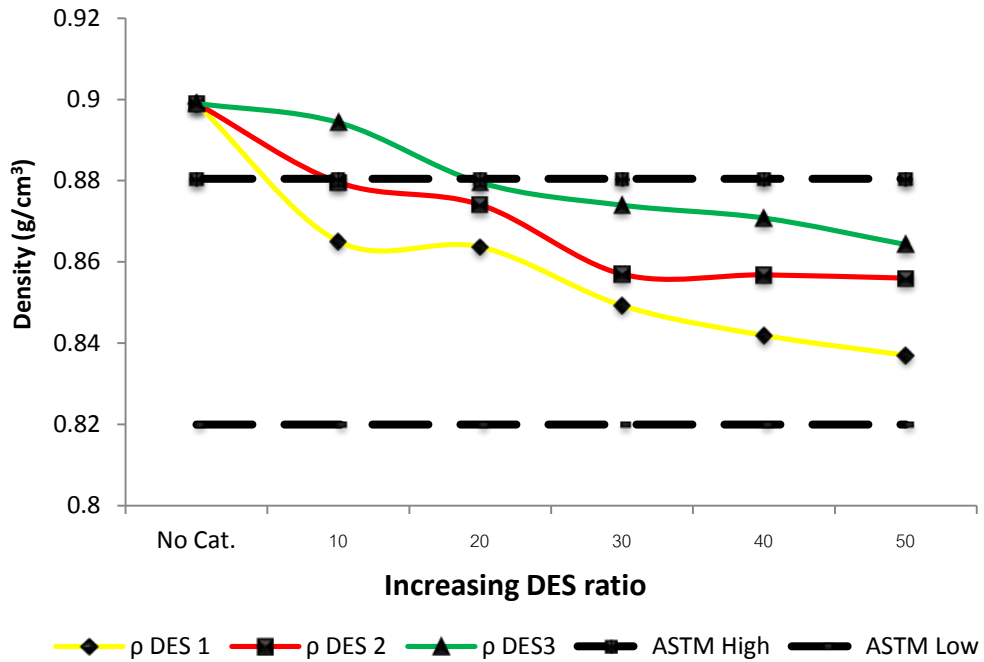


Fig. 7. Effect of alcohol type on supercritical esterification of WTPO on density

3.2.4 Effect on calorific value The calorific value of a fuel is important in determining the application of a biodiesel substance on an ignition engine since the final product is aimed at using it power engine [11]. Figure 8 presents the effect of alcohol type on supercritical esterification of WTPO on calorific values plotted in-between the maximum and minimum calorific values according to ASTM D6751-08. It could be deduced that, all the samples tested except in some few cases were lower than minimum limit as stated. Low calorific value of pyrolysis oil is attributed to its high water content, high oxygen content, high acid content and presence of impurities [12–14]. The type of alcohol used as co-solvent did not significantly improve the calorific value above the minimum values of ASTM. Although the calorific value had improved, blending the final product with diesel is highly recommended.

3.2.5 Effect on carbon residue During combustion in diesel engines, carbonaceous materials present in fuels which do not burn at the ignition temperature of fuel are converted into ash or residue. Fuels with high carbon residue content cause deposition in engine parts that could lead to overheating and finally results in engine knocking. Determination of carbon residue in fuels therefore becomes an important parameter that needs to be determined. Figure 9 shows the effect of alcohol type on supercritical esterification of WTPO on carbon residue. Unfortunately, all FAMES samples herein studied were higher than the maximum limit of ASTM D6751-08. This means that it has a very high tendency of deposition of carbonaceous materials in engines. Irrespective of the type of alcohol and the volume of co-solvent used, the carbon residue is high.

4. CONCLUSION

In this research work, the effects of using green solvents based on deep eutectic solvents in supercritical esterification of pyrolysis oil have been studied. The aim was to improve the fuel properties of the oil for possible application on diesel engines. The result obtained revealed the fact that alcohol type (methanol or ethanol) affected the density and viscosity of final products. Although the only few fuel properties of the final product (TAN, density and viscosity) were affected by the type of alcohol used in esterification. On the other hand, properties like calorific values were improved yet the final products were far below the acceptable limit, whereas the carbon residue is neither affected by type of alcohol nor the co-solvent system used. It was concluded that esterification of

pyrolysis oil was effective technique in improving some fuel properties, yet additional pretreatment of the final product might be required.

5. ACKNOWLEDGEMENT

The principal author wishes to sincerely thank the support of all the staff and students members of the Centre for Advanced Studies & Research in Automotive Engineering (CASRAE) of Delhi Technological University, India. In addition, the continuous support of the management of the National Research Institute for Chemical Technology, Zaria-Nigeria is equally appreciated.

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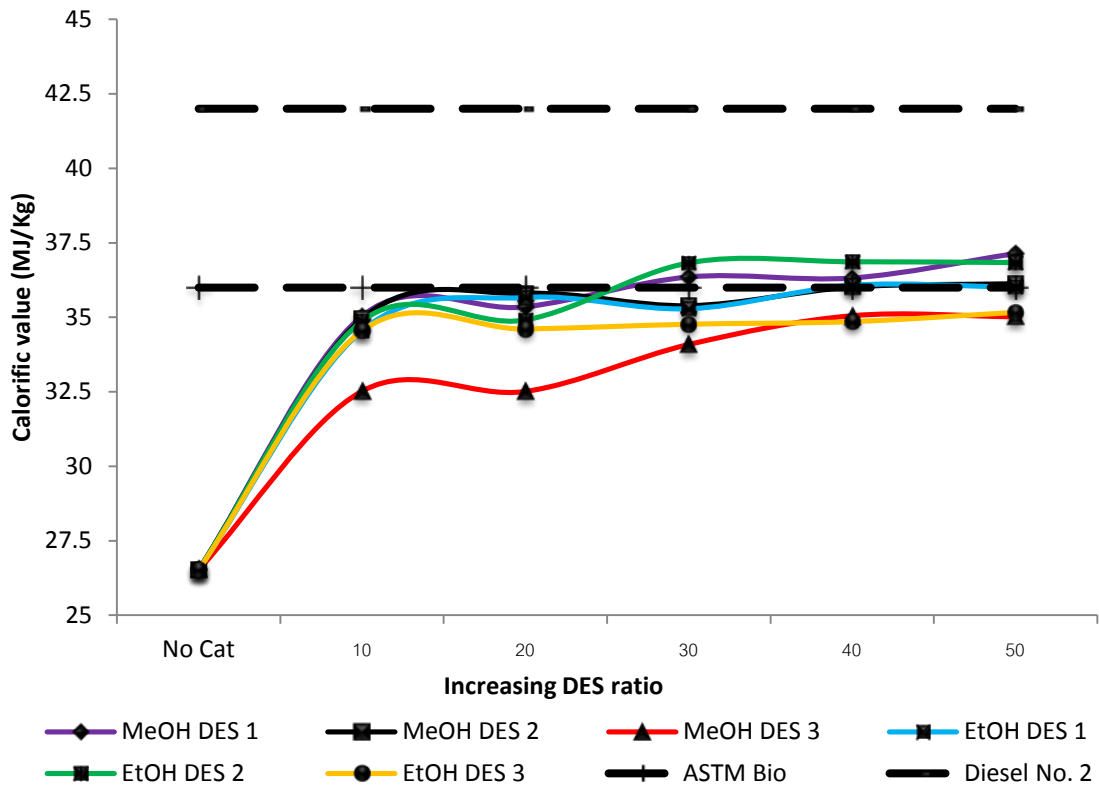


Fig. 8. Effect of alcohol type on supercritical esterification of WTPO on calorific values

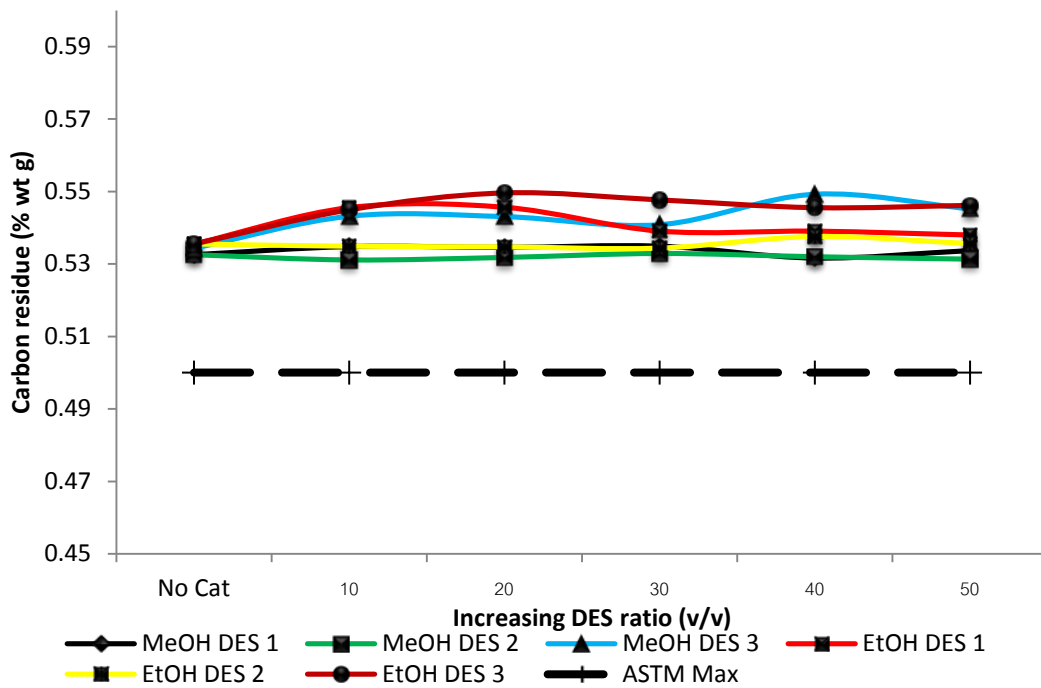


Fig. 9. Effect of alcohol type on supercritical esterification of WTPO on carbon residue