Thermal stability of Sewage Sludge Pyrolysis oil

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Abstract- The stability of the oil phase obtained from intermediate pyrolysis process was used for this investigation. The analysis was based on standard methods of determining kinematic viscosity, gas – chromatography / mass - spectrometry for compositional changes, FT-IR for functional group, Karl Fischer titration for water content and bomb calorimeter for higher heaating values. The methods were used to determine changes that occurred during ageing. The temperatures used for thermal testing were 60 ˚C and 80 ˚C for the periods of 72 and 168 h. Methanol and biodiesel were used as solvents for the analysis. The bio-oil samples contained 10 % methanol, 10 % Biodiesel, 20 % Biodiesel and unstabilised pyrolysis oil. The tests carried out at 80 ˚C showed drastic changes compared to those at 60 ˚C. The bio-oil samples containing 20 % biodiesel proved to be more stable than those with 10 % methanol. The unstabilised pyrolysis oil showed the greatest changes in viscosity, composition change and highest increase in water content. The measurement of kinematic viscosity and gas chromatograph mass spectrometry were found to be more reliable for predicting the ageing process.

Keywords- Stability; Pyrolysis oil; Sewage sludge; Intermediate pyrolysis; Pyroformer.

1. Introduction

Bio-oils contain a range of compounds varying from acids, phenols, aldehydes, ketones, oxygenated compounds and many more depending on the feedstock [1]. The source of instability of bio-oils arises when different compounds react to form other molecules with diverse compositions producing water as a by-product [1]. In addition to this, Czernik and Bridgwater [2] state that the presence of high oxygen content in bio-oils causes instability and it also causes variation in oil properties.

Refrigeration is one of the methods used to delay polymerisation from occurring; however Diebold and Czernik [3] showed that the addition of solvents to pyrolysis oils decreased the aging of the oils. Diebold and Czernik [3] studied six different solvents that included; 10 wt% methanol, 10 wt% ethanol, 10 wt% ethyl acetate, a mixture of 10 wt% acetone and methanol, and a mixture of 10 wt% methyl isobutyl ketone and methanol. They studied the stability at a range of temperatures from 7˚C to 90 ˚C. They found that the addition of 10 % wt of methanol proved to be the most effective amongst the solvents to increase stability by reducing the molecular weight increase and viscosity. Bouchera et al [4] studied the stability of bio-oil obtained from vacuum pyrolysis of wood at 40, 50 and 80 ˚C. They found tests carried out at 80 ˚C showed significant changes compared to other temperatures. They also found that the addition of methanol to the bio-oil slowed the aging process. Hilten and Das [5] studied accelerated stability over 24 h at 80 ˚C for five samples; pure pine, pine stabilised with methanol, pine stabilised with ethanol, pure peanut hull, and peanut pine stabilised with methanol. They used thermal and oxidative tests to determine the stability of the oils. The tests analysed changes in structure, viscosity, solids formation and oxidative onset temperature. It was found that pine stabilised with methanol showed the most stability when viscosity and solids content were measured.

The main aim for this study is to determine the stability of sewage sludge oil derived from intermediate pyrolysis. The oil phase of bio-oil derived from sewage sludge will be used in this study. The oil phase differs from all the other pyrolysis oils as it is miscible with biodiesel without using any emulsification process. The study will investigate the stability of the oil in 10

wt% methanol, 10 wt% biodiesel, 20 wt% biodiesel and pure oil phase without any solvent. The test temperatures used were 60 and 80 ˚C for a time period of 72 and 168 h. These time periods were used as they represent a variation in the test.

2.   Materials and Methods

2.1. Bio-oil production

The sewage sludge pyrolysis oil was obtained from an intermediate pyrolysis process that utilises a reactor called the pyroformer [7]. The reactor is made of carbon steel with 180 cm in length and 20 cm in diameter. The reactor is driven by two screws, the inner and outer screw moving in opposite directions [8]. The reactor was operated at 500 ˚C with gases escaping at the outlet. The gases are then passed through the filters and sent to the condenser cooled by water. The condensable gases are collected as bio-oil while the   non condensable gases are sent through the electrostatic precipitator [8].

2.2. Bio-oil mixtures

The bio-oil obtained from the pyrolysis process comprised of two phases, the oil and aqueous phase. The oil phase was separated from the aqueous phase using a simple separating funnel [8]. To investigate the stability of the oil phase, two solvents are used, methanol and biodiesel. The fractions used are 10 vol% methanol (10%MeOH), 10 vol% biodiesel (10%BD), 20 vol% biodiesel (20%BD) and unstabilised pyrolysis oil (PO).

2.3. Stability tests

The thermal stability of bio-oils was determined using viscosity, composition change, structural changes, heating value, water content and pH. The bio-oil mixtures were placed in 30 ml sealed bottles to prevent loss of volatiles. The mixtures were placed in the oven for 72 and 168 hours at 60 and 80 ˚C. The bottles were weighed before and after the experiments.

2.4. Analysis methods

The kinematic viscosity was measured using three different sized Cannon-Fenske routine viscometers. The viscometer sizes used were 100 that measures ranges of 3 to 15 mm^2/s, 150 for measurements range of 7 to 35 mm^2/s and 200 for measurement range of 20 to 100 mm^2/s. The ASTM D445 was used for the analysis of viscosity. This method involves noting the time taken for a fluid to flow under gravity from a specified point on the glass tube to another.

The gas chromatography-mass spectrometry (GC-MS) was used to determine composition of the bio-oil. The GC-MS used was a Hewlett Packard HP 5890 with an automatic injector and sampler. Helium is used as the carrier gas. The column is a DB 1701, non polar, 60 m length, inner diameter 0.25 mm and film thickness 0.25 μm. Mass spectrometer HP 5972 series is used as the detector. The samples were diluted with chloroform to a ratio of 1:100.

The water content was determined using a Karl Fischer Titrator known as Mettler Toledo v20 volumetric Titrator using ASTM D1744. The titrant used was hydranal composite 5 and solvent dichloromethane.

The higher heating value was measured using an automated bomb calorimeter model Parr 6100. Benzoic acid was used to calibrate the calorimeter.

The pH was measured using a Sartorius Basic Meter PB-11 connected to a glass electrode.

3. Results and Discussion

3.1. Oil characterization

Table 1 shows the compositional analysis based on dry basis (db) obtained for the sewage sludge pyrolysis oil and biodiesel sample. Biodiesel has a high carbon and hydrogen content compared to the sewage sludge pyrolysis oil. However it has lower oxygen, nitrogen and sulphur content compared to pyrolysis oil. The high carbon, hydrogen with lower sulphur makes biodiesel superior to the pyrolysis oil. The same factors make biodiesel a better fuel.

Table 1. Characteristics of the oils [8]

Parameter	Pyrolysis	Biodiesel
C (wt %)	64.69	78.86
H (wt %)	9.71	12.63
N (wt %)	5.84	0.10
O (wt %)	12.76	7.67
S (wt %)	3.26	0.74
HHV	35	46

3.2. Viscosity

The measurement of viscosity is a major parameter to be studied for the investigation of the ageing properties of the bio-oil. Table 2, shows an increase of viscosity from 72 h to 168 h. Fig.1 shows the viscosity trend at 80 ˚C while Fig. 2 shows the trend at 60 ˚C. Significant changes in viscosity occurred at 80 ˚C after 168 h. 10 % MeOH sample shows an interesting trend at 60 and 80˚C. Fig. 2 shows a 1.1 % increase in viscosity for 10 % MeOH after 168 h at 60 ˚C while Fig. 1, shows that the viscosity more than double at 80˚C after 168 h. The 20 % BD sample shows 11.2 % increase in viscosity at 60 ˚C after 168 h while this increases by 39.2 % at 80 ˚C after the same time. The increase of viscosity with time is attributed to polymerisation reactions occurring creating heavier oil fractions [1, 2, 4].

It appears to show that according to the changes in kinematic viscosity, the 20 % BD sample is more thermally stable than the 10 % MeOH. This might be due to the increase in concentration of biodiesel as the 10 % biodiesel is less stable than the 10 % MeOH. The addition of solvents to the pyrolysis oil shows an improvement in the stability of the bio-oils. Authors like Diebold and Czernik [1], Bouchera et al [4] and Hilten and Das [5] found the addition of 10% methanol to bio-oil to be more stable than other unstabilised oils.

3.3. Composition changes

GC-MS analysis was carried out for all samples for the unaged and aged at periods of 72 and 168 h. Major differences are observed in the chromatographs obtained for PO, 10 % MeOH, 10 % BD and 20 % BD. Fig. 3 shows the GC-MS spectra for the unstablised PO [8]. The retention times displayed in Fig. 3 are; 11.08 min – Methyl benzene, 15.38 min – Ethyl benzene, 17.62 min –

Styrene, 30.8 min – Phenol, 35.04 min – 4 Methyl phenol and 46.25 min – 1H-indole. After thermal heating at 80 ˚C after 72 h, there was an increase of compounds that were; 2-Ethyl phenol at 39.38 min, Methyl ester, hexadecanoic acid at 63.04 min, Methyl ester, 9-Octadecenoic acid at 69.51 min and 9,17-Octadecadienal,(z) detected at 69.66 min. The formation of these esters confirms the presence of esterification reactions. After 168 h at 80 ˚C, the esters are not detected but a new compound of 1,3 dimethyl benzene at 15.73 min is seen. There is also an increase in concentration of compounds after 168 h of thermal heating.
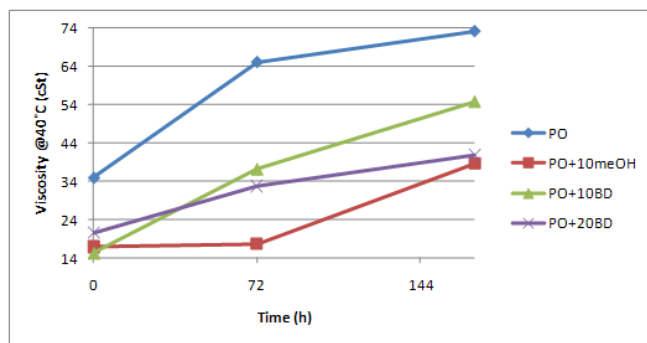
Fig. 4 shows the GC-MS spectra for 10 % MeOH, the major compounds detected are; Methyl benzene at 11.04 mins, Ethyl benzene at 15.35 mins, 1,2 dimethyl benzene at 17.22 mins, 1-Decene at 20.13 mins, Phenol at 30.78 mins, 4 methyl phenol at 35.06 mins, and 1H-indole at 46.24 mins. After thermal heating at 80 ˚C at 168 h, new compounds are detected. These are; 1,4-dimethyl benzene at 15.73 mins, 2-Methyl phenol at 33.31 mins and 2-Ethyl phenol at 39.39 mins. The 10 % MeOH showed the greatest decrease in compounds after thermal heating at 72 h but then increased in composition after 168 h. The 10 % MeOH showed the presence of more isomers than all the other fractions. The isomers are 2-methyl phenol, 4-methyl phenol, 1,4-dimethyl benzene and 1,3-dimethyl benzene. This shows the presence of hydrogenation reactions that occur within the hydrocarbons like methyl benzene that form isomers.

Fig. 5 shows the GC-MS spectra for the 10 % BD. Major compounds detected before aging were; Methyl benzene at 11.08 mins, Methyl ester, hexadecanoic acid at 63.75 mins, Methyl ester, 10-Octadecenoic acid at 69.91 mins, Methyl ester, 10, 13-Octadecadienoic acid at 70.03 and Methyl ester, Octadecanoic acid at 70.24 mins. After aging at 80 ˚C at 168 h, new compounds are detected. These are; Ethyl benzene at 15.34 mins, Phenol at 30.77 mins, 4-Methyl phenol at 35.05 mins, and Methyl ester, 9-Octadecenoic acid at 69.70 mins.

Fig. 6 shows the GC-MS spectra for the 20 % BD. Major compounds detected before ageing are; Methyl benzene at 11.08 mins, Methyl ester, hexadecenoic acid at 63.76 mins, Methyl ester,

Table 2. Viscosities of bio-oil fractions

Samples	Viscosity at 40°C for unaged samples (± 1) (mm²/s)	Viscosity at 40°C for samples aged at 60°C for 72 h (± 1) (mm²/s)	Viscosity at 40°C for samples aged at 60°C for 168 h (± 1) (mm²/s)	Viscosity at 40°C for samples aged at 80°C for 72 h (± 1) (mm²/s)	Viscosity at 40°C for samples aged at 80°C for 168 h (± 1) (mm²/s)
PO	34.83	37.59	45.12	65.04	73.11
PO+10%M	16.84	25.73	25.92	17.69	38.69
PO+10%B	15.21	25.50	39.12	37.14	54.78
PO+20%B	20.51	21.47	23.77	32.74	40.78

Fig. 1. Viscosity against time for bio-oil samples aged at 80°C
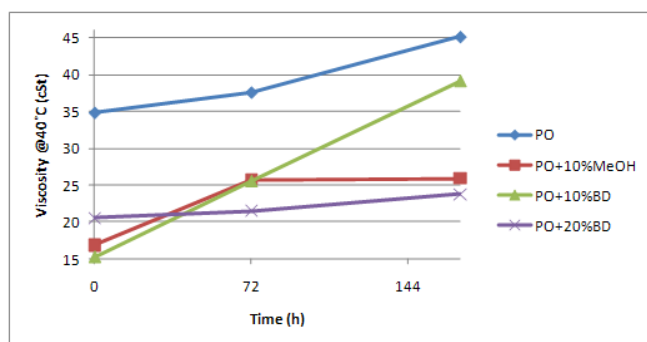
Fig. 2. Viscosity against time for bio-oil aged at 60 °C

9-Octadecenoic acid at 69.98 mins, Methyl ester, 9,12-Octadecadienoic acid at 70.08 mins, Methyl ester, Octadecanoic acid at 70.26 mins and Methyl ester, 9,12, 15-Octadecatrienoic acid at 70.49 mins. Three compounds are detected after 168 h of thermal heating at 80° C. These are; Ethyl benzene at 15.33 mins, Phenol at 30.75 mins and 4-Methyl phenol at 35.03 mins.

Overall, the greatest increase in concentration of the compounds was Methyl benzene and Ethyl benzene observed in PO, 10 % MeOH and 10 % BD. The dominant reactions that seemed to have occurred during thermal aging are hydrogenation and esterification reactions.

3.4. Functional groups

The changes in functional groups of the oils were studied using the FT-IR analysis. The FT-IR spectra in Fig.7 show the results of PO, 10 % MeOH, 10 % BD and 20 % BD at 80 °C with a range from 4000 to 400 cm⁻¹. A summary of the the overall functional groups displayed in bio-oil fractions are shown in Table 3, Table 4, Table 5 and Table 6.

More structural changes were expected in the unstabilised pyrolysis (PO) compared to the rest of the samples. The unstabilised pyrolysis oil showed changes with the formation of an additional amide group with the peak at 1514 cm⁻¹ with a structure of C-N-H bend. The peak at 1378 cm⁻¹ corresponds to the formation of the phenol group with a structure of C-O-H bend. In addition to this, a new peak formation at 1269 cm⁻¹ corresponds to primary aliphatic alcohols similar in structure to the phenol with C-O-H bend. However after 168 h of thermal heating, there is an additional peak formation at 1269 cm⁻¹ that relates to secondary aliphatic alcohols with a C-O-H bend. The structure of the FT-IR spectra for the pyrolysis oil after 72 and 168 h is very similar.

The 10 % MeOH shows different varying peaks at different positions. The peak at 1710 cm⁻¹ indicates the presence of a C=O stretch at 80 °C for 72 h that corresponds to a carboxylic acid. This peak is then lowered at 80 °C after 168 h to 1708 cm⁻¹ with C=O stretch that might be attributed to a ketone. The change in band length might suggest a further reaction that occurs with time possibly an oxidation reaction. After 168 h additional bands at 811 cm⁻¹ and 741 cm⁻¹ are formed. The wavelength at 811 cm⁻¹ indicates the presence of primary aliphatic alcohols with C-O-H bend. The wavelength at 741 cm⁻¹ corresponds to an amide with NH_2 wag.

The 10 % BD solvent samples shows three new peaks after 72 h and an additional two after 168 h

as shown in Fig. 7. After 72 h of aging, there is formation of a peak at 1668 cm^{-1} that indicates an amide with C=O stretch. Another peak at 1457 cm^{-1} that is due tertiary alcohols with C-O-H bend is formed. An additional peak at 752 cm^{-1} that corresponds to an amide is also formed. After 168 h, a peak at 3200 cm^{-1} is observed that corresponds to a hydroxy group. Another peak at 1515 cm^{-1} that may be attributed to the presence of an amide with C-N-H bend is seen. The formations of amides are due to the reactions occurring between carboxylic acid and an amine.

Fig. 7 shows the FT-IR spectra for 20 % BD. Table 6 shows a summary of the spectra from the unaged to the aged samples. A new peak is formed after 72 h at 802 cm^{-1}. This peak corresponds to a primary aliphatic alcohol with C-O-H bend. After 168 h, all peaks detected before ageing emerge with an additional peak at 1670 cm^{-1}. The peak at 1670 cm^{-1} corresponds to an amide with C=O stretch. The formation of these peaks would be a result of hydrolysis and amide formation reactions.

3.4.1. Functional group changes at 60°C

FT-IR analysis was used to observe the changes in functional groups at 60 °C as shown in Fig.8. The PO at 60 °C displays the same peaks as those observed at 80 °C after 72 h except for the formation of a single peak at 1550-1510 cm^{-1} that is due to C-N-H bend. The structures at both temperatures are comparable.

The structural changes for 10 % MeOH at 60 and 80 °C appear to be different. Additional peaks are observed at 60 °C than at 80 °C. After 72 h at 60 °C, peaks at 1261, 966, 909, 812 and 741 cm^{-1} are observed. The peak at 1261 cm^{-1} is due to the presence of a secondary aliphatic alcohol with C-O-H bend. The peaks at 966 and 909 cm^{-1} are due to alkene compounds with a CH$_2$ wag.
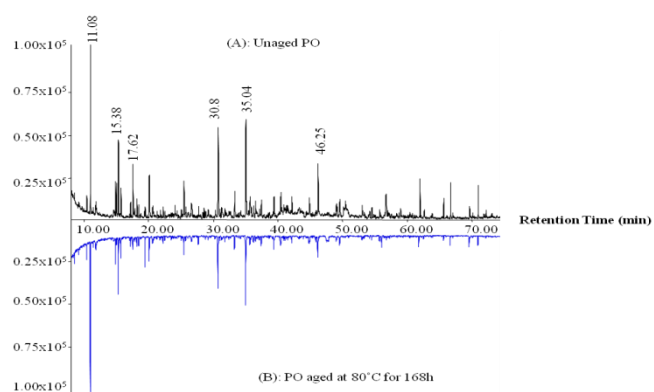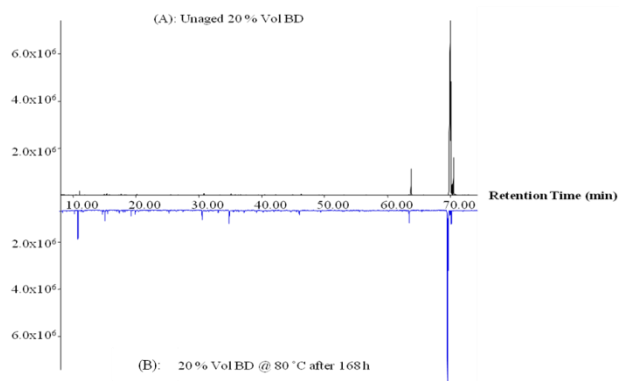

Fig. 3. GC/MS spectra for PO from unaged (A) to thermal heating after 168 h (B).
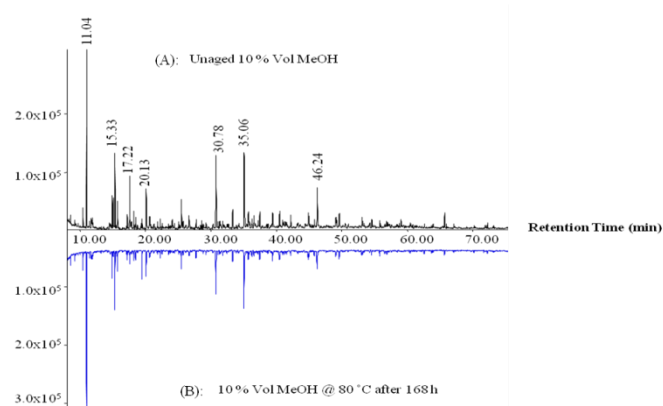
Fig. 4. GC/MS spectra for 10 % MeOH from unaged to changes after thermal heating 168 h.
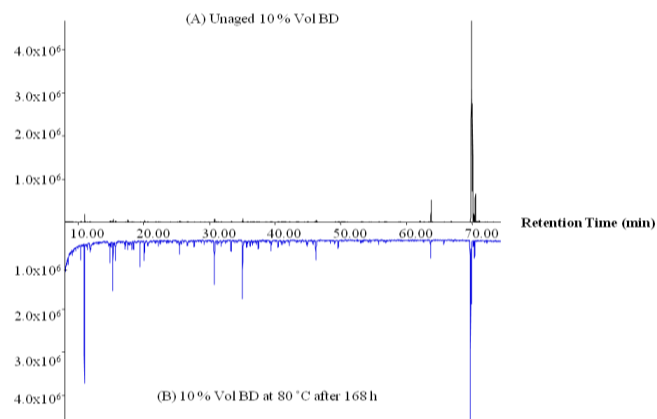
Fig. 5. GC/MS spectra for 10 % BD from unaged to changes after thermal heating after 168 h.

Fig. 6. GC/MS spectra for 20 % BD from unaged to changes after thermal heating after 168 h

The peak at 812 cm^{-1} corresponds to primary aliphatic alcohols with C-O-H bend. The peak between 720-600 cm^{-1} might be attributed to an amide with NH_2 wag. The 10 % MeOH also displays two additional peaks after 168 h compared to the peaks after the same time at 80 ˚C. The two peaks are 1261 and 811 cm^{-1} that has already been identified after 72 h at 60 ˚C.

The 10 % BD fractions displays a different structural print at 60 ˚C to that obtained at 80 ˚C. Two additional peaks are identified after 72 and 168 h at 60 ˚C. These peaks occur at 1740 and 1170 cm^{-1}. The peak at 1740 cm^{-1} corresponds to carboxylic acid with C=O stretch while the peak at 1170 cm^{-1} corresponds to tertiary aliphatic alcohols with C-C-O stretch. The peak at 3200 cm^{-1} that appears at 80 ˚C after 168 h is not detected at 60 ˚C after the same time. This might be due a certain reaction occurring at higher temperature.

The 20 % BD at 60 ˚C shows a similar finger print to the one displayed at 80 ˚C. However there are additional peaks displayed at 60 ˚C after 72 h. These peaks have been identified to be 3194 cm^{-1} that corresponds to carboxylic acid with O-H stretch. The peak at 1673 cm^{-1} corresponds to amides with C=O stretch. The peak at 1515 cm^{-1} also corresponds to amide with C-N-H bend. The peaks at 1197 and 1170 cm^{-1} corresponds to tertiary aliphatic alcohols with C-C-O stretch. The peak at 1515 cm^{-1} also corresponds to an amide with C-N-H bend. The peak at 1197 and 1170 cm^{-1} corresponds to tertiary aliphatic alcohols with C-C-O stretch. The peak at 1515 cm^{-1} also corresponds to amide with C-N-H bend. The peak at 724 cm^{-1} corresponds to amide with C-N stretch.

After 168 h at 60 ˚C, two peaks identified at 80˚C after the same time disappear at 60 ˚C. These are; 3201 cm^{-1} that is attributed to O-H stretch and 1515 cm^{-1} that is due to an amide with C-N-H bend.
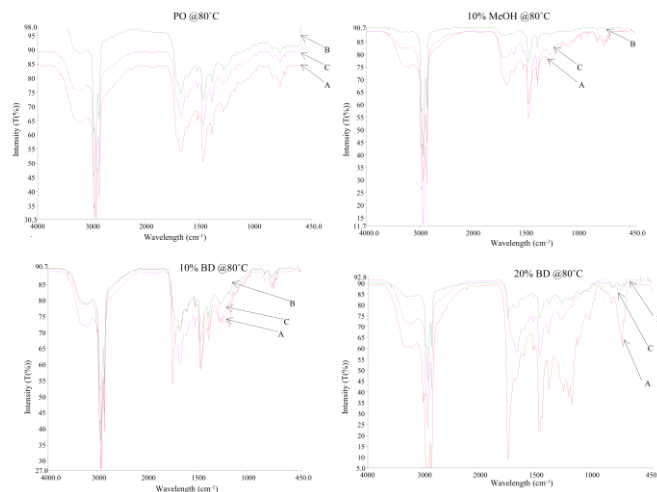
Fig. 7. FT-IR spectra of bio-oil fractions aged at 80˚C. (A) is for unaged sample, (B) for aged sample after 72h, (C) for aged sample after 168h.

Table 3. Summary of major functional groups in the Pyrolysis oil (PO)

Wavele	Type of	Unaged(P	Aged at	Aged at
2950-	Alkyl, C-	√	√	√
1700-	C=C	-	√	√
1690-	Amide,	√	√	√
1490-	Amide,	√	-	-
1430-	Secondar	√	√	√
1410-	Tertiary,	√	√	√
800-750	Tertiary,	√	√	√

Table 4. Summary of major functional groups contained in 10 % Vol MeOH

Wavelen	Type of	Unaged(1	Aged at	Aged at
2950-	C-H	√	√	√
1690-	Amide,	√	-	-
1780-	COOH	-	√	-
1750-	Ketone,	-	-	√
1490-	C-N-H	√	√	√
1430-	Tertiary,	√	√	-
1410-	Secondar	-	-	√
900-800	Primary,	-	-	√
800-750	C-C-O	√	-	-
720-600	Amide,	-	-	√

Table 5. Summary of major functional groups contained in 10%Vol Biodiesel

Wavelen	Type of	Unaged(1	Aged at	Aged at
3400-	O-H	-	-	√
2950-	Alkyl, C-	√	√	-
1780-	COOH	√	-	-
1690-	Amide,	-	√	√
1550-	Amide,	-	-	√
1490-	Amide,	√	√	√
1430-	Secondar	-	√	-
720-600	Amide,	-	√	√

Table 6. Summary of major functional groups contained in 20%Vol Biodiesel

| Wavelen	Type of	Unaged(2	Aged at	Aged at
3400-	O-H	√	-	√
2950-	Alkyl, C-	√	√	√
1690-	Amide,	-	-	√
1550-	Amide,	√	-	√
1490-	Amide,	√	√	√
1210-	Tertiary,	√	-	√
900-800	Primary,	-	√	√
750-700	Amide,	√	-	-

3.5. Higher heating values

The higher heating value is the amount of heat given out by a substance during combustion. The heating values of the bio-oil fractions were measured to investigate changes that might have occurred. Fig. 9 shows a plot of heating value against aging time of the bio-oil fractions. The 10 % MeOH showed the greatest decrease in heating value after 72 h and then increased dramatically with 7.5 % rise. The PO showed a similar trend to that of 10 % MeOH. The fractions of 10 % BD and 20 % BD show a decrease of heating value as the aging time increases. This might be due to the production of water arising from esterification reactions that occur within the the samples causing a decrease in heating value. The fluctuating heating values do not show a clear trend of how the ageing process affects the heating values.
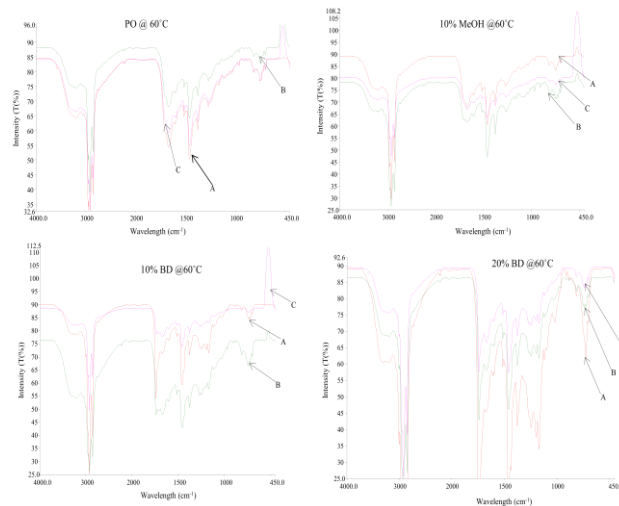

Fig. 8. FT-IR spectra of bio-oil fractions aged at 60˚C. (A) is for unaged sample, (B) for aged sample after 72hrs, (C) for aged sample after 168hrs.

3.6. Water content

The percentage of water in bio-oil presents different attributes to its properties. A higher percentage of water content causes a decrease in the higher heating value but increases the flow of the bio-oil. Figure 10 shows the water content measurements of the bio-oil. The pure PO showed the greatest increase in water content with a 53 % rise. This increase arouse due to esterification reactions occurring producing water as a by-product. This is supported by the GC-MS results that displayed an increase of compounds after 72 of ageing at 80 ˚C, Czernik et al [6] also found similar results. The 10 vol % MeOH did not show any increase after 72 h but then increased the water content by 22 % after 168 h of ageing. The presence of 10 vol % MeOH caused dissolution of some compounds present in the bio-oil causing a delay in polymerisation reactions. The 10 % BD showed a percentage decrease after 72 h and then increased after 168 h. The 20 % BD showed a different trend, the water content decreased with increasing heating time. There is no clear explanation of the differences in the water content for the two concentrations of the biodiesel. The results obtained are contrary to those obtained for higher heating values. Further investigations might be needed.
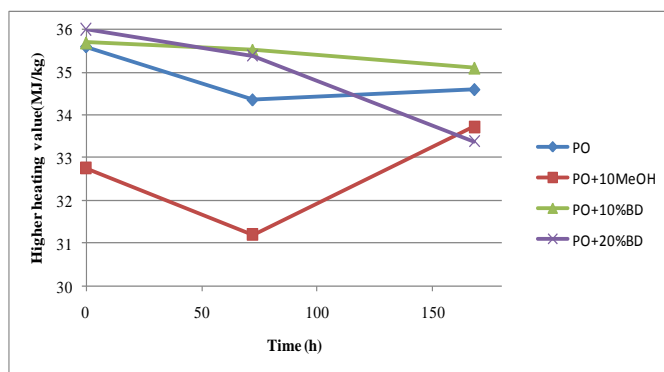
Fig. 9. Heating values of bio-oil from the unaged to aged at 80°
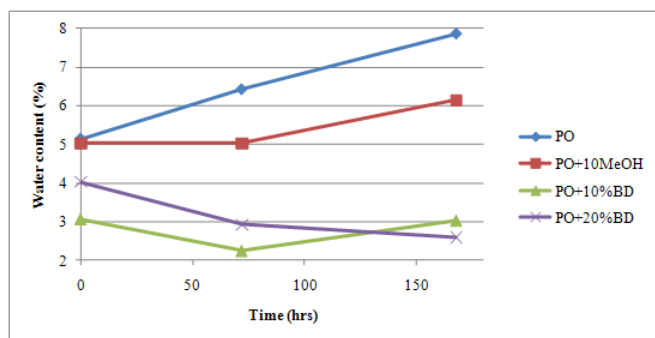
Fig. 10. Water content measurement against ageing time for bio-oil samples aged at 80°C
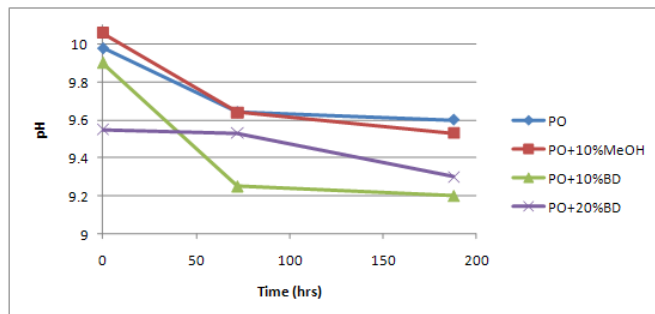
Fig. 11. pH measurements of bio-oil samples aged at 80°C

3.7. pH

The pH of the bio-oils ranges from 9 to 10 as shown in Fig. 11. This indicates that all the bio-oils fractions are alkaline although the 10 % MeOH is slightly more alkaline than rest of the samples. In general, Fig. 11 shows a slight decrease in pH as as the heating time increases from the unaged samples to 168 h. The changes in pH are not significant as bio-oil retains their alkalinity state with an overall pH of 9.

4. Conclusion

The most effective temperature for testing thermal stability was at 80 °C as this showed the most drastic changes compared to 60 °C, Bouchera et al [4], Hilten and Das [5], also found this. The most reliable measurement of checking thermal stability seems to be observing the change in viscosity and composition compared to higher heating value, water content and pH. The 20 % Biodiesel showed the least change in viscosity compared to other bio-oil fractions. The 20 % Biodiesel proved to be more thermally stable than

10 % MeOH when using viscosity as the parameter for determining stability. The increase in concentration of the biodiesel from 10 % to 20 % greatly affected the stability of the bio-oil fractions.

The results from the GC-MS show that the unstabilised pyrolysis oil (PO) showed the highest change in compounds and concentration after aging. This was expected as the PO contained no solvent so reactions like esterification were expected. The increase in percentage of water for the aged samples of the unstabilised pyrolysis oil shown in Fig. 10, confirms the existence of esterification reactions. As these form water as a by-product.

The 20 % Biodiesel showed the least change in concentration and compounds after aging compared to other oil fractions.

The GC/MS results showed an overall increase in concentration of aromatic hydrocarbons like Methyl benzene and Ethyl benzene in PO, 10 % MeOH and 10 % Biodiesel. According to the change in composition of compounds, hydrogenation and esterification reactions might have occurred.

The changes in functional groups analysed by the FT-IR was unexpected. The unstabilised pyrolysis oil only showed a single change at 1514 cm^{-1} that corresponded to C-N-H bend compound that could be a methyl amine. More functional groups were expected for the unstabilised oil.

The 20 % BD on the other hand showed the greatest increase in functional groups. The peak at 3194 cm^{-1} corresponded to carboxylic acid with O-H stretch. This peak could represent Hexadecanoic

acid or Octadecanoic acid that is central to biodiesel. The peak at 1673 cm^{-1} corresponded to amides with C=O stretch. The amide formation is a result of the reaction between the carboxylic acid like Octadecanoic acid and an amine that could be present in the pyrolysis oil. The peaks at 1197 cm^{-1} and 1170 cm^{-1} corresponds to tertiary aliphatic alcohols with C-C-O stretch. The aliphatic would have resulted from the reaction between an alkyl and hydroxyl compound found in the biodiesel to form these peaks.

The use of FT-IR to detect change in functional groups is not a reliable method of assessing the stability of the bio-oil as the information obtained is limited.

Acknowledgements

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